Thermal Phenomena 1

THERMODYNAMICS

zeroth& first laws, heat transfer & applications

THERMO=Related to Heat

DYNAMICS = The study of motion

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Thermodynamics:

- Is the study of the relationship between **heat** and **motion**.
- Is a **macroscopic** description of the properties of a system using **state variables**

Thermodynamics:

- Study of energy transfers (engines)
- Changes of state (solid, liquid, gas...)

Heat:

- Transfer of microscopic thermal energy

Thermal Equilibrium:

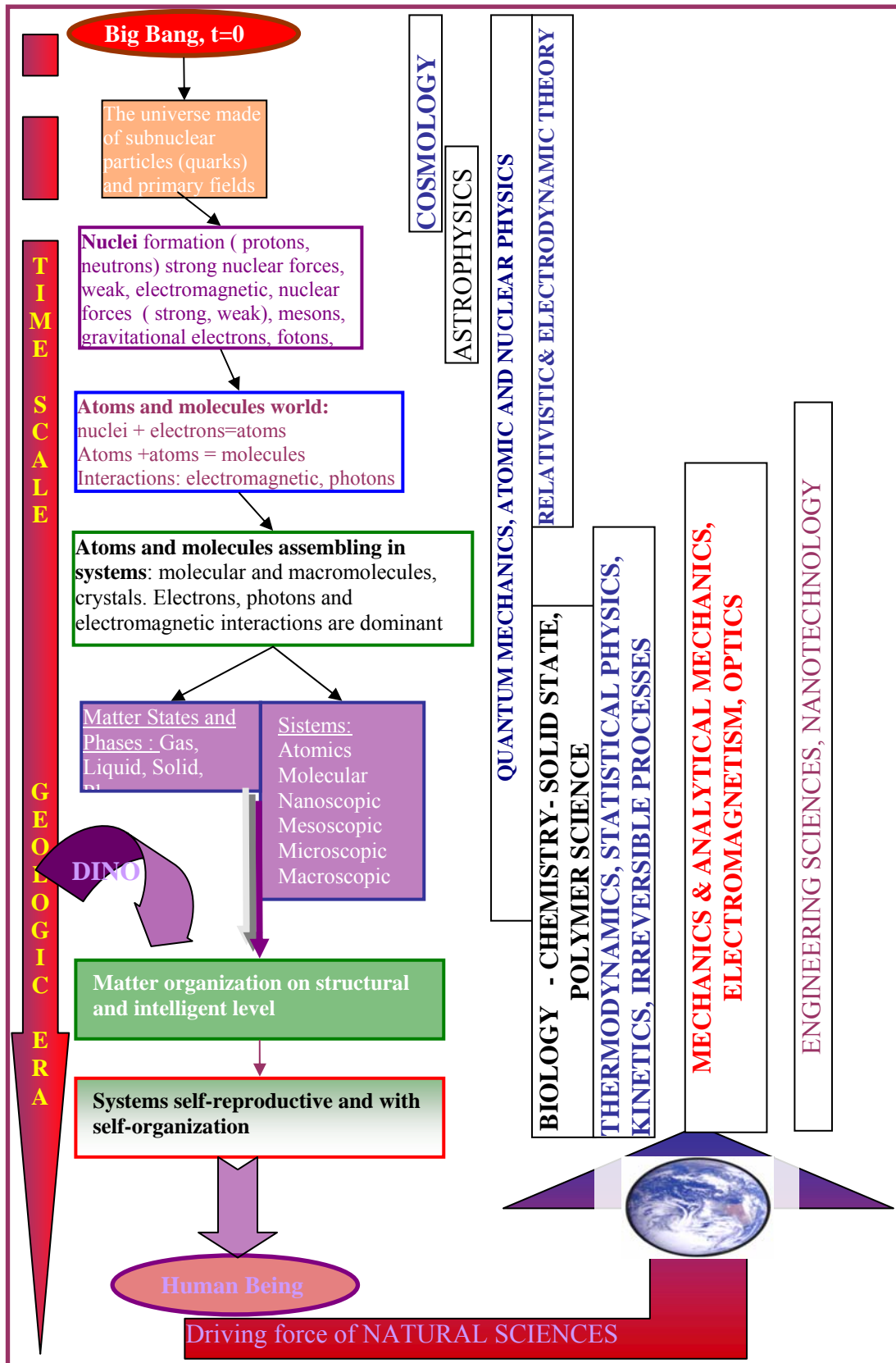- Conditions after two objects are in thermal contact and finish exchanging heat.

Nanothermodynamics:

- A generic approach to material properties and thermal phenomena at nanoscale.

If our small minds, for some convenience, divide this...Universe into parts - physics, biology, chemistry, geology, astronomy, and so on – remember that nature does not know it!
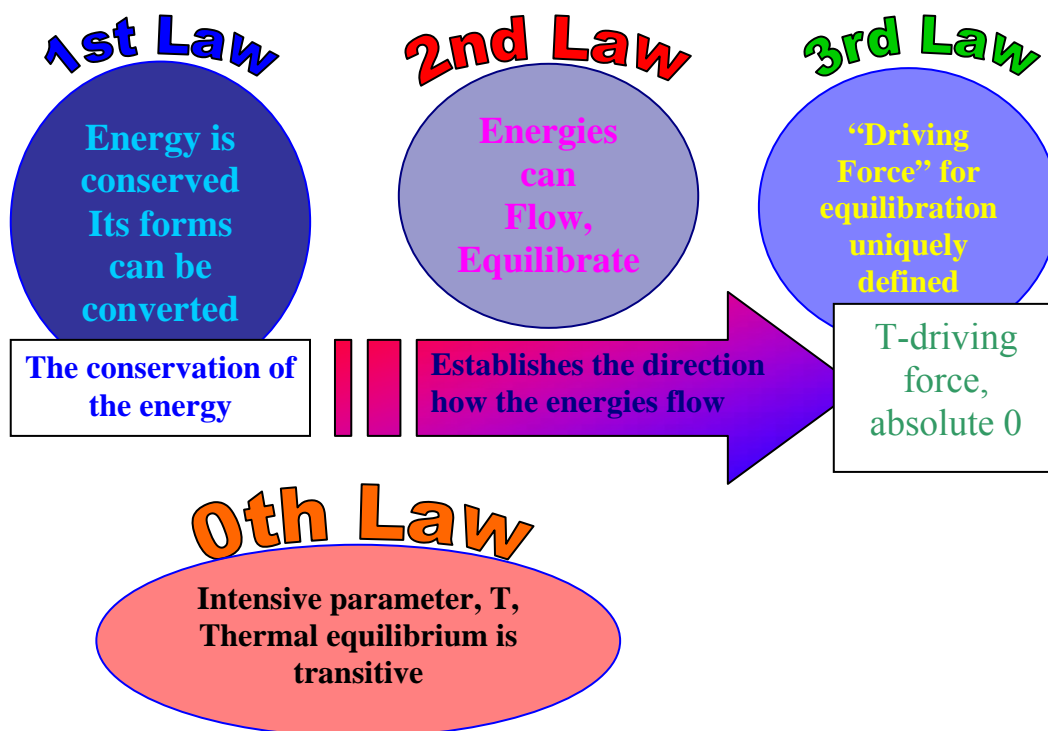
Richard P. Feynman, 1963

http://www.zyvex.com/nanotech/feynman.html

Big Bang, t=0

The universe made of subnuclear particles (quarks) and primary fields

Nuclei formation (protons, neutrons) strong nuclear forces, weak, electromagnetic, nuclear forces (strong, weak), mesons, gravitational electrons, fotons,

Atoms and molecules world:
nuclei + electrons=atoms
Atoms +atoms = molecules
Interactions: electromagnetic, photons

Atoms and molecules assembling in systems: molecular and macromolecules, crystals. Electrons, photons and electromagnetic interactions are dominant

Matter States and Phases : Gas, Liquid, Solid,

Sistems:
Atomics
Molecular
Nanoscopic
Mesoscopic
Microscopic
Macroscopic

DINO

Matter organization on structural and intelligent level

Systems self-reproductive and with self-organization

Human Being

Driving force of NATURAL SCIENCES

T I M E   S C A L E

G E O L O G I C   E R A

COSMOLOGY

ASTROPHYSICS

QUANTUM MECHANICS, ATOMIC AND NUCLEAR PHYSICS

RELATIVISTIC& ELECTRODYNAMIC THEORY

BIOLOGY - CHEMISTRY- SOLID STATE, POLYMER SCIENCE

THERMODYNAMICS, STATISTICAL PHYSICS, KINETICS, IRREVERSIBLE PROCESSES

MECHANICS & ANALYTICAL MECHANICS, ELECTROMAGNETISM, OPTICS

ENGINEERING SCIENCES, NANOTECHNOLOGY

III

Thermodynamics laws Overview

1st Law

Energy is conserved Its forms can be converted

The conservation of the energy

2nd Law

Energies can Flow, Equilibrate

Establishes the direction how the energies flow

3rd Law

"Driving Force" for equilibration uniquely defined

T-driving force, absolute 0

0th Law

Intensive parameter, T, Thermal equilibrium is transitive

1st Law: The total energy of the universe is conserved (?!).

2nd Law: The total entropy of the universe is increasing (!). The second law tells us the direction of energy conservation.

3rd Law: Establishes an important reference state to define absolute zero and entropy.

Three Laws (restated)

The British scientist and author C.P. Snow had an excellent way of remembering the three laws:

1. *You cannot win (that is, you cannot get something for nothing, because matter and energy are conserved).*

2. *You cannot break even (you cannot return to the same energy state, because there is always an increase in disorder; entropy always increases).*

3. *You cannot get out of the game (because absolute zero is un-attainable).*

Table of Content

Chapter 1

The physics of the thermal phenomena learning

1.1 Problem base learning thermal phenomena

A thermodynamics course for a first year has had for long time a large experience with simple point of view: a specific thermodynamics for engineers, one for chemistry (chemical thermodynamics), one for biology and one for students at physics. For century that is truth when the interdisciplinary sciences still were not born. Departments from Faculty of Physics, University of Bucharest, have developed in the last decade large interdisciplinary fields such as Medical- Physics, Biophysics, and Environment Physics, Computational Physics and not the last Engineering and Material sciences. In each field a large thermal phenomena are involved. The new European learning system with 3 years base learning, 2 years Master and 3 years PhD studies need a new Problem Based Learning (PBL) environment for a first course in thermodynamics. The students should be challenged through a strong emphasis on design projects that expand the boundary of their thermodynamics knowledge through the integration of fluid mechanics and heat transfer fundamentals, many examples from chemistry, biology, environment and engines engineering.

Actual development of the nanoscience and nanotechnology bring the thermal phenomena at nanoscale level where the thermodynamics laws still do not loose in their consistency and value. The computational aspects involved by modeling, programming languages generate a virtual science where the simulation methods produced useful information in understanding of the materials world, particularly thermal phenomena and kinetics physics.

In this context, a Problem Based Learning (PBL) environment for a first course should be paid attention to the thermal phenomena with a deeply understanding of the classical thermodynamics and kinetics physics laws and their applications with design projects.

At present, the thread that spans over 2 hours course and 3 hours laboratory (with 1 hour practice) defines first year course for undergraduate students at Faculty of Physics.

A thread is defined as a sequence of courses with an identifiable set of objectives and outcomes, tying a number of courses to each other and is consistent with the program's educational objectives.

The course belonging to the Physics & Engineering Physics System Thread (PEPST) targeting basics for 3 years and needs for master program should gradually encompass the thermal phenomena for all master sections. In addition should give a basic experience in theoretical aspects combined with first design project in research.

Systems Thread are thermodynamics and heat transfer, kinetics physics along with applications in interdisciplinary fields and computational methods (in biology, environment, chemistry engineering, renewable energies, material science with weight to synthesis methods and thermal properties related to dimensional aspects).

This system thread should be defined as The Physics of the thermal phenomena (PTP)

As an integral course of the PEPST, and therefore the course designer must not only revisit what and how information is conveyed but also what students are learning (really getting out of the course).

The mission of the PEPST is to provide undergraduate physicist students at University the knowledge and the tools required for the analysis of thermal phenomena related problems and the design of vary applications covering energy conversion devices and machines, biological-chemical processes, environment analysis, material synthesis, material design with extremely thermal properties.

Having identified the mission of the thread, one needs to write related educational objectives. The following are the educational objectives of the PTP:

1. Get knowledge with vary thermodynamics systems, methods and processes to build such systems.
2. As much as possible relate one systems with a specific field of research and its advances. That will give general idea about thermodynamics systems, and state parameters.
3. Introducing the fundamental parameters: pressure and temperature, and actual methods of measurements (covering classics methods and gauges, sensors). Thus zeroth law get practical aspects.
4. The energetic aspect where deal with the first law complemented with many applications to get importance of the heat and work, engine efficiency, heat pumps, enthalpy and Hess law, energy in crystals through Haber-Born cycle and macromolecular systems, bond energy, dissociation, etc.
5. Fluids and thermal transport explaining different mechanisms are integrated to open a basic idea with Mathematical Equations for Physics
6. The second law and third law, developed in Part II, are introduced in different ways surprising aspects which make experimental basis to statistical physics and thermodynamics. A series of applications such as phase diagrams, osmosis related to dialyses, nucleation and growth where give an idea about size dependent properties, etc.

That is in agreement with the following the educational objectives of the PTP for junior students who should get in two semesters a large experimental basis in:

1. apply the fundamental principles of thermodynamics, fluid mechanics and heat transfer,combined with other engineering, mathematics and science principles, to accurately predict the behavior of energy systems and properly design required energy systems.
2. identify, analyze, and experiment with energy systems through *integrated* hands-on laboratory experiences in thermal sciences
3. utilize modern numerical and experimental techniques for the analysis and design of energy systems
4. develop a systematic problem solving methodology and needed skills to address open ended design issues, function in teams properly, and report technical information effectively.

5. identify the thermodynamic state of any substance and demonstrate the successful retrieval of thermodynamic properties, given thermodynamic property tables;
6. identify, formulate, and solve problems in classical thermodynamics;
7. demonstrate the development of a systematic approach to problem solving;
8. apply fundamental principles to the analysis of thermodynamic power and cycles; phase diagrams, heat transport chemical reactions, etc
9. apply fundamental principles to the design of thermodynamic systems;
10. integrate the use of computer tools in the analysis and performance of thermodynamic systems.

And get as outcomes:
1. knowledgeable in the management and use of modern problem solving and design methodologies.
2. understand the implications of design decisions in a research activity or in the global engineering marketplace to appropriate physical phenomena in vary stuff through material science
3. are able to formulate and analyze problems, think creatively, communicate effectively, synthesize information, and work collaboratively.
4. have an appreciation and an enthusiasm for life-long learning.
5. actively engage in the science of improvement through quality driven processes.
6. practice in the field of Physics Science professionally and ethically.
7. are prepared for positions of leadership in research, business and in industry.

Particularly for PTP course the student outcomes are expected to have:
1. an ability to apply knowledge of mathematics, science, and engineering; related to thermal phenomena
2. an ability to design and conduct experiments, as well as to analyze and interpret data;
3. an ability to design a system, component, or process to meet desired needs;
4. an ability to function on multi-disciplinary teams;
5. an ability to identify, formulate and solve problems with practical applications to engineering
6. an understanding of professional and ethical responsibility;
7. an ability to communicate effectively;
8. the broad education necessary to understand the impact of physics and engineering solutions in a global and societal context;
9. a recognition of the need for, and ability to engage in life-long learning;
10. a knowledge of contemporary issues;
11. an ability to use the techniques, skills, and modern engineering tools necessary for research and engineering practice.

The objectives and outcomes for PTP are in agreement with Bloom's Taxonomy of Learning [14]. This taxonomy of learning ensures consistency between the teaching approach/focus (how and what professors provide their students) and assessment methods and features six levels of increasing difficulty for students.

A traditional thermodynamics course concentrates on the first three levels. The design driven, problem-based PTP course engages students in higher order cognitive

skills and allows for creativity and technical maturity. Bloom's taxonomy of learning levels are as follows:

1. Knowledge: (List, Recite)
2. Comprehension (Explain, Paraphrase)
3. Application (Calculate, Solve)
4. Analysis (Classify, Predict, Model, Derive, Interpret)
5. Synthesis (Propose, Create, Design, Improve)
6. Evaluation (Judge, Select, Justify, Recommend, Optimize).

1.2 A new role for old science (a point of view)

Having an experience of 24 years divided equal three parts, research, industry, and teaching I find myself reflecting on the changes I have seen related to thermal phenomena and other advanced fields. Although some of the changes have been painful, I am encouraged to see traditional areas of materials science and classical phenomena of physics reinvent themselves and find new roles. What gives a real buzz at the moment is seeing the emergence of 'structural materials underpinning functional materials', building from bottom-up, self-assembling, heat transport and micro/nanofluidics in MEMS/NEMS, nanomaterials synthesis covering nanochemistry/nanoelectrochemistry, Physical Vapour deposition, Molecular beam epitaxy (MBE), etc.

I have seen multinational companies move away from their traditional materials base and refocus on higher-added-value markets, which are not subject to cyclical changes. This has been a common theme throughout the industry and research. The research either in academia or in industry binds teaching system to what we need as stuff, goods, commodities and useful to find a job. This driven force oriented teaching system from a large knowledge to a specific oriented knowledge with good background in natural sciences. The research spend in industry and academia has mirrored this trend and the focus of cutting-edge research has shifted elsewhere. At the same time, the spend on 'functional' materials has increased. This feels right as research funding should provide support where industry needs to be in the future, rather than where it has been in the past.

Why "old" now is "new" science.

Let us takes an example. Over time in industry, researchers presented their early work on new families of materials, such as conjugated polymers, dendritic structures, and biomaterials. We can now see some of these areas begin to form embryonic industries. One area in which is a good example of where traditional materials can find a fresh role, is the electronics and display industry based on conjugated polymers. There is a revolution taking place, with a range of new start-up companies, such as Cambridge Display Technology, E Ink, Gyricon, Infineon Technologies, Plastic Logic, PolyIC, Polymer Vision, and Universal Display Corporation, challenging the Si-based world and the plasma and liquid-crystal display market. The flat-panel display business is huge and growing rapidly. However, large displays are still made by expensive photolithography techniques. A new manufacturing approach is needed to lower costs and open up new design opportunities. Flexible displays offer substantial rewards by being thin, light, robust, conformable, and can be rolled away when not in use. In addition, plastic-based substrates, coupled with recent developments in the deposition and printing of organic light-emitting polymers and active matrix thin-film transistor arrays, open up the possibility of cost-effective, roll-to-roll processing in high volumes.

To replace glass, a plastic substrate needs to be able to offer the same properties, i.e. clarity, dimensional and **thermal stability, solvent resistance, a low coefficient of thermal expansion, and a smooth surface**. No plastic film offers all of these properties, so any candidate substrate will almost certainly be a multilayer composite structure. To illustrate this, let's look at the films that are currently being proposed as replacements for glass. These consist of first a base film; this will likely have good transparency, excellent dimensional stability, a thermal expansion coefficient as low as possible, and a smooth surface. The next layer may be a hard coat to prevent scratching during processing and provide solvent resistance. On top of this goes the barrier coating. The required barrier properties are several orders of magnitude better than can currently be achieved by a plastic film, as displays based on organic light-emitting diodes are extremely sensitive to oxygen and moisture. One approach, which has been pioneered by start-up company Vitex Systems, is to lay down a stack of alternating organic and inorganic coatings. The organic coatings planarize out surface defects that lead to pinholes, while the inorganic layers make the diffusion path for water and oxygen more tortuous. Finally, a conductive layer is deposited on top – at present this is likely to be inorganic but one day may be organic. At this stage, the process gets really complicated as circuitry is laid down. The display is built on top of this structure. Clearly, the final structure is complex. In addition to choosing the right materials, one now has a new set of issues associated with the properties of multilayer structures. What will happen when the structure is flexed or dropped? Can it withstand thermal shock or exposure to the environment? Will it still retain the required barrier and conductive properties after this type of treatment? How do you turn the above steps into a roll-to-roll process? What you now start to see is a new area of materials science – structural materials underpinning functional materials. Some of the science required to address these issues is already in place, but much further research will be needed.

We saw an example that apparently is not connected with thermal phenomena but need in design of new multifunctional materials of lot of things already developed in "old" thermodynamics and kinetic physics. This presents a new role for those of us coming from a traditional materials background. To fully engage, however, we need to recognize that the world of materials has changed. We need to focus on the exciting new challenges that the emerging functional materials industries will present to us.

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Chapter 2

Thermodynamic Systems: Definitions

Systems, surroundings, boundaries

- ➡ **Systems**: A system is a collection of matter within defined boundaries
- ➡ **Surroundings**: Everything outside a system is surroundings.
- ➡ **Boundary**: The boundary or wall separates a system from its surroundings.
- ➡ **Wall**: boundary
- ➡ **Adiabatic**: Walls, thermal isolated.
- ➡ **Diabatic or non-adiabatic walls**: Thermal conducting walls.

The system and surroundings change heat, work and substance through boundary.

This is established by a continuous interaction. The nature of interaction defines the system nature.

2.1 Dimensional characteristics of the systems

- ➡ **Macroscopic**: composed of number of constituents comparable with Avogadro's number (its dimension is enormous by comparison with atoms and molecules)
- ➡ **Microscopic**: the dimension is at microscopic scale but still high than molecules dimension
- ➡ **Mesoscopic /nanoscopic system:** the properties depends of dimension

If macro and microscopic systems are intuitive, understandable the mesoscopic and nanoscopic systems need a special attention. The mesoscopic systems are actually a well –established field in condensed-matter physics (mesoscopic physics).

Mesoscopic physics focuses on the properties of solids in a size range intermediate between bulk matter and individual atoms or molecules. The size scale of interest is determined by the appearance of novel physical phenomena absent in bulk solids and has no rigid definition; however, the systems studied are normally in the range of 100 nanometres (10^{-7} meter, the size of a typical virus) to 1000 nm (the size of a typical bacterium). Other branches of science, such as chemistry and molecular biology, also deal with objects in this size range, but mesoscopic physics has dealt primarily with artificial structures of metal or semiconducting material, which have been fabricated by the techniques employed for producing microelectronic circuits.

Thus, it has a close connection to the fields of nanofabrication and nanotechnology. The boundaries of this field are not sharp; nonetheless, its emergence as a distinct area of investigation was stimulated by the discovery of three categories of new phenomena in such systems: interference effects, quantum size effects, and charging effects as outputs from artificially layered structures, nanostructure, quantized electronic structure (QUEST); Semiconductor heterostructures.

When the matter on size scale is under 100 nm we usually define the nanoscopic systems where the dimensional effects are much more dependents of surface to volume ratio. In this size scale range, we have nanoparticles less in size as a virus and lot of phe-

nomena should be reconsidered. Anyway the fundamentals laws of the physics and chemistry are not changed, they give us a new perspective to understand the matter.

The thermal physics phenomena are deeply involved in nanometer scale such as: processor heating, micro and nano heat pump and engines where working fluid is transported through micro capillary systems; thermal sensors, pressure sensors, infrared techniques in detection; chemical reactions in microreactors, thermodynamics of the superelastic systems for artificial muscle, electrophoresis and ELISA test,etc. There are few examples where thermal phenomena are successfully applied. In material synthesis field all chemical and physical vapour deposition (CVD and PVD) need transport phenomena and heat exchange, the molecules manipulation using laser beams (tweezers), sol-gel processes, sintering, nanotubes and fullerene synthesis, quantum dots, etc, are also fields which deal with thermal phenomena. Human body is a excellent example where thermodynamics is applying (why we need 37^0C?). In medicine, the direct and inverse osmosis is successfully applied in dialysis techniques. The examples can continue

2.2 Thermodynamics Systems

➡ **Isolated**: no heat, work and mass flow change with surroundings takes place;
➡ **Closed**: no mass flow change, heat and work can be changed with surrounding;
➡ **Adiabatic:** only work can be changed;
➡ **Open:** everything can be changed with surrounding;

If we define the rate of heat and mass flow as:

$$\left.\begin{array}{l} \dot{Q} = \dfrac{dQ}{d\tau} \rightarrow \text{heat flow rate} \\[2mm] \dot{m} = \dfrac{dm}{d\tau} \rightarrow \text{mass flow rate} \end{array}\right\} \tau = \text{time} \qquad\qquad 2.1$$

We can represent the interactions at macroscopic scale as follows:

2.2.1 Isolated system

In figure 2.1 is represented what means for chemists (left) and for physicists an isolated system.

Figure 2.1 Isolated system. Heat, work and mass are not changed from and to system. No flow in and out of system.
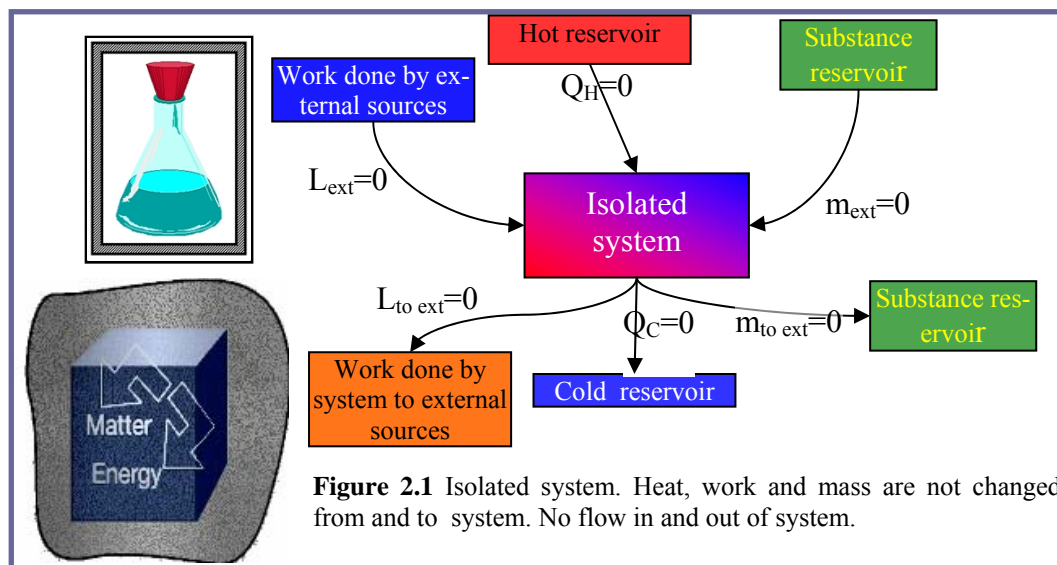
2.2.2 Closed System

In closed systems, nothing leaves the system boundaries. As an example, consider the fluid in the cylinder of a reciprocating engine during the expansion stroke. The system boundaries are the cylinder walls and the piston crown. Notice that the boundaries move as the piston moves (figure 2.2). The **adiabatic** system is a particular case where heat flow is zero from and to system.

Figure 2.2   Closed system, can change energy in both forms but no mass flow exists. a- chemist representation, b-physicists and engineers representation. Up&Left- general representation,
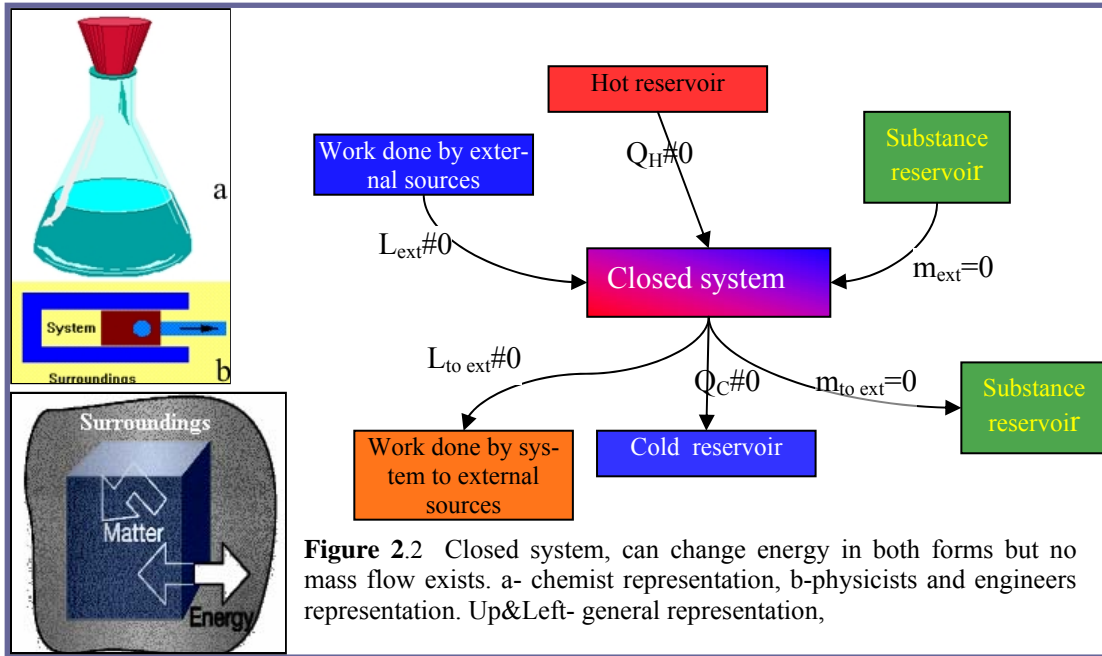
2.2.3 Open System

In open systems (figure 2.3), there is a mass transfer across the system's boundaries; for instance, the steam flow through a steam turbine at any instant may be defined as an open system with fixed boundaries.

Figure 2.3 Open systems, a- an open glass b- turbine Up- general representation
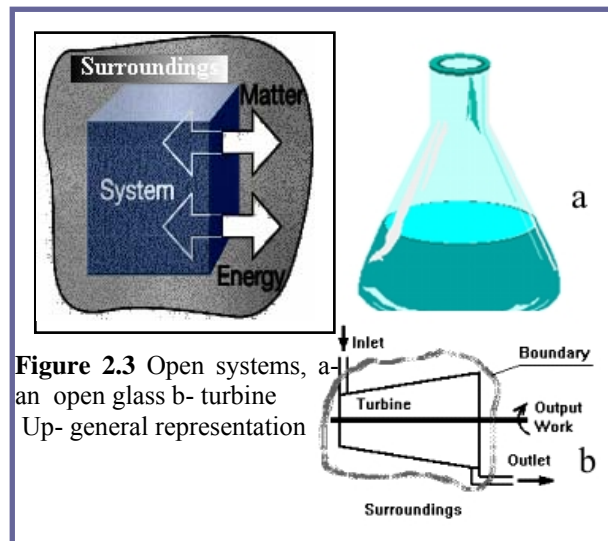
2.3 Systems: homogeneous, heterogeneous

Homogeneous: the properties are identical in any point in system (ex: water in a glass, liquid oxygen in a Dewar vessel. An apple is not a homogeneous system). Often a homogeneous system is associated like a unique *phase* with the same poperties in whole volume closed by its boundary. A mixture water- alcohool is a homogeneous system with two components- in every point concentration, density, temperature, pressure, etc, have identical values.

Heterogeneous: oposite of the homogeneous system. It contains many phases. Examples are everywhere in nature (gased water, ice-water, any sponge, etc). In environment, all systems are open and heterogeneous.

2.4 System constitution: Atoms, Molecules, Substance, Chemical element

Whole world is made of macroscopic objects, large by comparison with their composition atoms and molecules, often known as chemical elements and substances

Atoms: are the "building blocks" of any kind of matter or substance

In his famous lessons, Feynman dedicates the first to the matter structure giving a simple description which can be summarized: *" all objects are made of atoms, small particles in continuous movement an reciprocal interaction generating a dynamic equilibrium"*

His lesson reveals, for anyone who gets basics in science that:

➢ The Matter is made of stable and compact – atoms;
➢ The existence of the perpetual, randomized movements of the atoms and the concept of the thermal agitation;
➢ Gives a general idea on the interaction forces: attraction & repulsion, dynamic equilibrium state;
➢ The modern concept on the discontinous nature of the matter.

The atoms are the key in the matter organization on the different levels. Mendeleev has initiated a systematic organization of the atoms function of their periodical properties. Today everyone knows the periodic table of the elements where chemistry, atomic and nuclear physics, quantum mechanics in their long history characterized each atom using, A-atomic mass, Z- atomic number, number of electrons in shells (orbitals), number of valence electrons, electron affinity, ionization potential.

The periodic table, figure 2.4, sketch what we know about atoms.

Molecule: assemble of atoms covalent bonded**.**

A molecule keeps the composition identical with the considered substance. Each substance is made of one or many molecular species. By extrapolation the molecule with a single element is identifying with the atom.

The number of atomic species is relative small (known 105 atoms extended to exotic atoms we count 113) but the manifold in combination to produce molecules, macromoleculs, molecular and supramolecular assemblies give the diversity in the nature world from dead object to living life.

Figure 2.4 Periodic table, invented by Mendeleev, and characterized by Q-mechanics

How many molecules can exist ???? (2^n, or.....). It can be counted?.

The molecule with the same number of atoms corespond to the simple substance for which the physicist and chemist accomplish compositional analysis (such as mass spectroscopy)

Chemical Elements - Elements are substances that are made up of only one type of atom. At this time, there are 113 known elements, most of which are metals. The symbols shown on the periodic table represent the known elements. Even atoms are made up of smaller particles, but they are not broken down by ordinary chemical means.

A clear distinction between the chemical element and atom should be considered.

The atom is the invariant, which conserves in any transformation and chemical reactions. The chemical element disappears or transform by nuclear reactions. The element is characterized by characteristics in emission/ absorption spectra (atomic, X-ray and nuclear).

Substance-A material with a constant composition. This means that the substance is the same no matter where it is found. NaCl, H_2O, Ne, CO_2, and O_2 are all substances, because their composition will be the same no matter where you find them. All elements and all compounds are defined as substances.

There is an enormous variety of substances due to the large variety of molecular species (over 2 millions of species are known) and their combinations

The physical and chemical properties are defined by molecules's properties.

The pure substances made of a single molecular species still can differ by its isotopic composition

2.5 The properties of a system

Are those characteristics that are used to identify or describe it. When we say that water is "wet", or that silver is "shiny", we are describing materials in terms of their properties. Properties are dividing into the categories of physical properties and chemical properties. Physical properties are readily observable, like; colour, size, lustre, or smell.

Chemical properties are only observable during a chemical reaction. For example, we might not know if sulphur is combustible unless you tried to burn it.

Another way of separating kinds of properties is to think about whether or not the size of a sample would affect a particular property. No matter how much pure copper you have, it always has the same distinctive colour. No matter how much water you have, it always freezes at zero degrees Celsius under standard atmospheric conditions. Methane gas is combustible, no matter the size of the sample.

> Properties, which do not depend on the size of the sample involved, like those described above, are called intensive properties.

Some of the most common intensive properties are; density, freezing point, color, melting point, reactivity, luster, malleability, and conductivity. The temperature and pressure will be the same for each subsystem.
- If we subdivide a system into small subsystems, parameters, called *intensive parameters*, such as the temperature will be the same for each subsystem.
- These parameters are identical for each subsystem into which we might subdivide our system.

> Extensive properties are those that do depend on the size of the sample involved.

- A large sample of carbon would take up a bigger area than a small sample of carbon, so volume is an extensive property. Some of the most common types of extensive properties are; length, volume, mass and weight. *Extensive parameters*, such as the volume, are the sum of the values of each subsystem.
- Parameters of which values for the composite system are the sum of the values for each of the subsystems.
- These parameters are non-local in the sense that they refer to the entire system.

2.6 Physical and Chemical changes

Pieces of matter undergo various changes all of the time. Some changes, like an increase in temperature, are relatively minor. Other changes, like the combustion of a piece of wood, are drastic. These changes are divided into the categories. The main factor that distinguishes one category form the other is whether or not a particular change results in the production of a new substance.

2.6.1 Physical changes

Are those changes that do not result in the production of a new substance. If you melt a block of ice, you still have H_2O at the end of the change. If you break a bottle, you still have glass. Painting a piece of wood will not make it stop being wood. Some common examples of physical changes are; melting, freezing, condensing, breaking, crushing, cutting, and bending. Special types of physical changes where any object changes

state, such as when water freezes or evaporates, are sometimes called change of state operations.

2.6.2 Chemical changes

The chemical reactions, are changes that result in the production of another substance. When you burn a log in a fireplace, you are carrying out a chemical reaction that releases carbon. When you light your Bunsen burner in lab, you are carrying out a chemical reaction that produces water and carbon dioxide. Common examples of chemical changes that you may be somewhat familiar with are digestion, respiration, photosynthesis, burning, and decomposition.

2.7 Thermodynamic system- state variables, thermodynamic coordinates, state equations

- ➡ When a system is in a given state, certain properties have *values only defined by the state of the systems*. Such properties are state variables. There are two basic kinds of such variables or parameters: **Intensive** parameters and **extensive** parameters

- ➡ It has been discovered empirically that even simple *systems require three thermodynamics coordinates*, one of which is the temperature. The other two are called mechanical pair and are different for every system.

- ➡ These thermodynamic coordinates not are each other independent. For every system exists a relation between the thermodynamics coordinates, usually empirically found. Such a relation is called *equations of state*.

For simple, idealized systems, the equation of state can be written down analytically. However, for more system that is complicated the equation of state often has to be determined experimentally.

> The thermodynamics does not supply any instrument to establish the number of the state variables, need and enough.

Chapter 3

Classification of Matter

3.1 States of Matter

- Anything that has mass and volume is matter.
- Matter is also defines as anything with the property of inertia.
- All of the solids, liquids and gases would be classify as some type of matter.
- The scientists classify matter that makes up everything similar with the taxonomy of living things from Biology.

Millions of K → **Fully ionised plasma**

Tens of thousands of K → **Plasma phase**: atoms loose electrons, they move freely among positive charged ions

Thousands of K → **Atoms and molecules dissociation, ionization**: molecules dissociate in component atoms, atoms loose electrons

→ **Gas phase**: atoms or molecules move without constraining

Hundreds of K → **Liquid phase**: atoms or molecules are relatively bonded, they can move relatively freely

Cold → **Solid phase**: atoms and molecules are tightly bonded in a regular structure

Figure 3.1– The states of matter on temperature scale

States of matter, sometimes called phases can be generally classified in gases, liquids, solids and plasma. They are the aggregation states. On a temperature scale, the four states are distributed as in figure 3.1. In table 3.1 there is another classification with point of view mixing.

3.2 Compounds

Compounds are substnces that are made up of more than one type of atom. Water, for example, is made up of hydrogen and oxygen atoms. Carbon dioxide is made up of carbon and oxygen atoms. The salt is made up of sodium and chlorine.

Compounds differ from mixtures in that they are chemically combined. Unlike elements, compounds can be decomposed, or broken down by simple chemical reactions.

Table 3.1 - *Classification of Matter: Elements, Compounds, Mixtures*			
Matter: Anything with mass and volume			
Substance: Matter with constant composition		**Mixture**: Matter with variable composition	
Element: substance made up of only one type of atom, molecule	**Compound**: Two or more elements that are chemically combined	**Heterogeneous Mixtures:** Mixtures that are made up of more than one phase	**Homogeneous Mixtures:** solutions. Mixtures that are made up of only one phase.
Examples gold, silver, carbon, oxygen and hydrogen	**Examples** - water, carbon dioxide, sodium bicarbonate, carbon monoxide	**Examples**: Sand, soil, chicken soup, pizza, chocolate, chip, cookies. Colloidal solutions, seltzer water, etc	**Examples** - Salt, water, pure air, metal alloys,.

3.3 Phase

A phase is any region of a material that has its own set of properties. In a chocolate chip cookie, the dough and the chips have different properties. Therefore, they represent separate phases. Pure gold, which is an element, would only contain one phase. Italian dressing would clearly represent several phases, while a solution of salt water may only contain one phase.

3.4 Homogeneous Materials

Any material that contains only one phase would be considered homogeneous. Elements like hydrogen, compounds like sugar, and solutions like salt water, are all considered homogeneous because they are uniform. Each region of a sample is identical to all other regions of the same sample. It is similar with homogeneous systems.

3.5 Mixtures

Mixtures are made up of two or more substances that are physically combined. The specific composition will vary from sample to sample. Some mixtures are so well blended that they are considered *homogeneous,* being made up of only one phase. Other mixtures, containing more than one phase, are called *heterogeneous*.

3.6 Solutions

Solutions are a special type of homogeneous material, because unlike compounds, the parts of a solution are physically and not chemically, combined. When you mix a glass of salt water, the salt does not chemically react with the water. The two parts just mix so well that the resultant solution is said to be uniform. Ice tea, coffee, metal alloys, and the air we breathe are some examples of solutions. Solutions are made up of two parts: The solute, which is dissolved, and the solvent, which does the dissolving. In the case of salt water, salt is the solute and water is the solvent.

3.7 Heterogeneous mixtures

Heterogeneous mixtures are made up of more than one phase and they can be separated physically. Afore mentioned chocolate chip cookie, a tossed salad, sand, and a bowl of raisin bran cereal are all examples of obvious heterogeneous mixtures.

3.8 Phase diagrams

All states of the matter are congruently organized in a phase diagram. If two state variables are considered independent, such as Temperature and Pressure, then we

have a representation as in figure 3.2. Each phase is a homogeneous system and delimited by boundaries called melting line, sublimation line, etc. Summarizing:

➢ **Phase Diagram:** Plot of Pressure versus Temperature
➢ **Triple Point:** A point on the phase diagram at which all three phases exist (solid, liquid and gas). Other triple points exist in the phase diagram of a substance that possesses two or more crystalline modifications, but the one depicted in the figure is the only triple point for the coexistence of the vapour, liquid, and solid.
➢ **Critical Point:** The point in the phase diagram where are the same, the densities for liquid and vapour (phases). See details in section applications with 1st law

Figure 3.2 Phase diagram for one component system
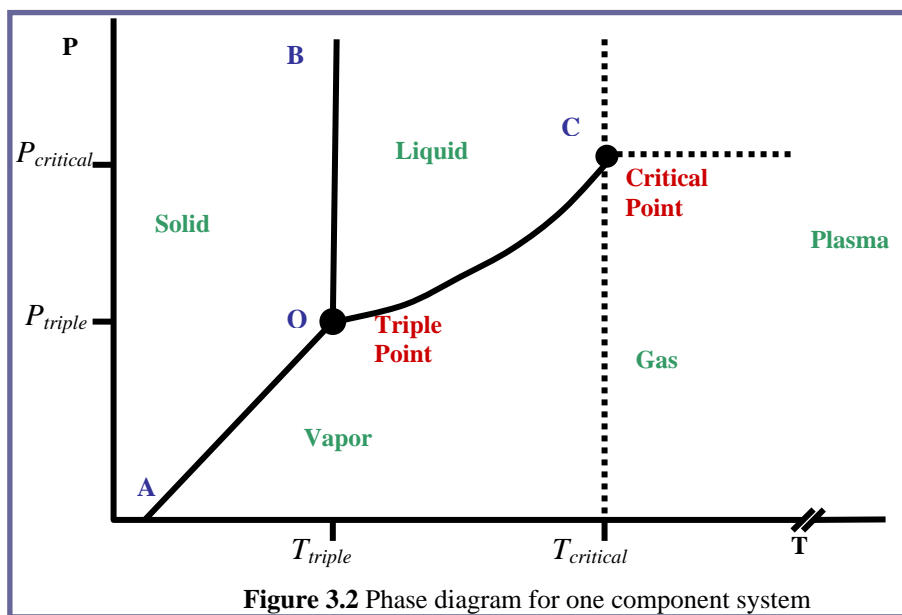
That is, a phase diagram for one-component system. In case of multicomponent systems, we deal with Gibbs rules and we extend these discussions elsewhere. The areas denoted by "Liquid", "Solid" and "Vapour" similarly indicate those pressures and temperatures for which only liquid, solid or vapour phase may exist. The separation lines are usually termed phase boundary or phase coexistence lines. Line OA has its origin at the absolute zero of temperature and OB, the melting line, has no upper limit. The liquid-vapour pressure line OC is different from OB, however, in that it terminates at a precisely reproducible point C, called the critical point. Above the critical temperature, no pressure, however large, will liquefy a gas. Along any of the coexistence curves the relationship between pressure and temperature is given by the Clausius-Clapeyron equation (see chapter Phase transformation), the corresponding phases (gas-liquid, gas-solid, or liquid-solid). By means of this equation, the change in the melting point of the solid or the boiling point of the liquid as a function of pressure may be calculated. When a liquid in equilibrium with its vapor is heated in a closed vessel, its vapor pressure and temperature increase along the line OC. ΔH (enthalpy) and ΔV both decrease and become zero at the critical point, where all distinction between the two phases vanishes. See Phase equilibrium discussions.

Chapter 4

Gases

- ➡ A phase of matter characterized by relatively low density, high fluidity, and lack of rigidity.
- ➡ A gas expands readily to fill any containing vessel. Usually a small change of pressure or temperature produces a large change in the volume of the gas.
- ➡ **The equation of state** describes the relation between the pressure, volume, and temperature of the gas. In contrast to a crystal, the molecules in a gas have no long-range order. For a gases mixture the equation of state takes in account the concentration.

Ideal Gases - In a gas, the size of the sample has very little to do with the size of the actual atoms that make up the gas itself. Even in relatively dense gas samples, the space in between the molecules will be much larger than the molecules themselves. When we do math problems involving gases, we treat the particles as point masses, or particle with mass but no volume. Ideal gases differ from real gases in another important way.

In **real gases**, there will be an attraction between the particles involved. These attractions are often minor and we ignore them when we do math problems involving gases. It is important to remember the differences between real gases and ideal gases. It is also interesting to note that real gases will act most like ideal gases at low pressure and high temperature, when the gas sample is less dense.

4.1 Ideal Gases, Experimental Laws

An ideal gas is one in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces. One can visualize as a collection of perfectly hard spheres, which collide but which otherwise, do not interact with each other. In such a gas, all the **internal energy** is in the form of kinetic energy and any change in internal energy is accompanied by a change in temperature.

An ideal gas is characterizing by three **state variables**: absolute pressure (P), volume (V), and absolute temperature (T). The relationship between them may be deduced from **kinetic theory** and experimental from the Boyle-Marriotte, Guy-Lussac, Charles, Mole proportionality (Avogadro) Laws.

4.1.1 Boyle-Marriotte's Law

Boyle's experiment

Some of the earliest quantitative measurements were performed on gases. Robert Boyle conducted the first of these studies in 1662.

Robert Boyle employed a J-shaped piece of glass tubing sealed on one end. A gas (air) has been trapped in the sealed end of the tube and varying amounts of mercury added to the J-shaped tube to vary the pressure of the system. Boyle systematically varied the pressure and measured the volume of the gas.

The measurements were performed using a fixed amount of gas and a constant temperature. In such way, Boyle was able to examine the pressure-volume relationship without complications from other factors such as changes in temperature or amount of gas.

Data Analysis

Once the volume-pressure data obtained, the next challenge is to determine the mathematical relationship between the two properties. Although an enormous number of relationships are possible, one likely possibility is that the volume will be directly related to the pressure raised to some power:

$T = \text{const} \quad n = \text{const}$

$\dfrac{P_2}{P_1} = \dfrac{V_1}{V_2}$ **Boyle-Mariotte**

$$V = C_{BL} P^a$$

The exponent a is expected to be independent of the mass of gas and temperature; the goal is to determine the value of a from the "experimental" data. The constant C_{BL} is expected to vary with the mass of gas and the temperature; at this point, this constant is not of interest. A simple way to determine the value of a is to prepare a plot of ln V vs ln P. If the proposed relationship is valid (and it might not be valid), this plot should yield a straight line of slope a. Thus the linearity of the plot serves as a test of our original hypothesis (that the volume-pressure relation may be described by the equation shown above) where $a=1$

Calculations using Boyle's Law

Boyle's Law states that the product of the pressure and volume for a gas is a constant for a fixed amount of gas at a fixed temperature. Written in mathematical terms, this law is: $PV = const$

A common use of this law is to predict how a change in pressure will alter the volume of the gas or vice versa. Such problems can be regarded as a two state problem, the initial state (represented by subscript i) and the final state (represented by subscript f). If a sample of gas initially at pressure P_i and volume V_i is subjected to a change that does not change the amount of gas or the temperature, the final pressure P_f and volume V_f are related to the initial values by the equation: $P_i V_i = P_f V_f$. The law of the isotherm compressibility for gases at low and moderate pressures were studied by R. Boyle (1627-1691) and E. Mariotte(1620-1684). Boyle, 1664, was first who stated the law of the isotherm compressibility and later on Mariotte (1676), shows that PV=const for a gas with mass and temperature constant. Resuming the global and differential form for Boyle-Marriotte' Law is shown in figure 4.1.

$$P_0 V_0 = P_1 V_1 = ... = const; \quad d(PV)_T = 0; \quad PdV + VdP = 0$$
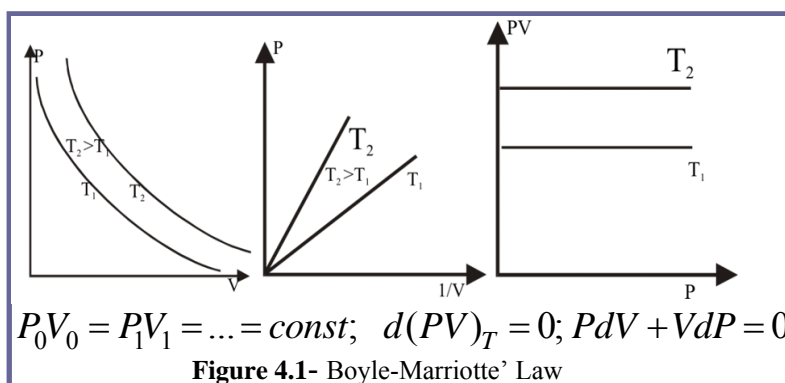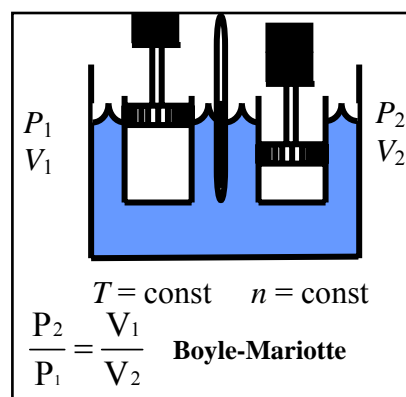
Figure 4.1- Boyle-Marriotte' Law

4.1.2 Charles' Law, Guy –Lussac' law

The next significant advance in the study of gases came in the early 1800's in France. Hot air balloons were extremely popular at that time and scientists were eager to improve the performance of their balloons. Two of the prominent french scientists, Jacques Charles and Joseph-Louis Gay-Lussac, made detailed measurements on how the volume of a gas was affected by the temperature of the gas. Given the interest in hot air balloon at that time, it is easy to understand why these men should be interested in the temperature-volume and pressure-temperature relationship for a gas.

Just as Robert Boyle made efforts to keep all properties of the gas constant except for the pressure and volume, so Jacques Charles took care to keep all properties of the gas constant except for temperature and volume.

The equipment used by Jacques Charles was very similar to that employed by Robert Boyle. A quantity of gas was trapped in a J-shaped glass tube that was sealed at one end. This tube immersed in a water bath, by changing the temperature of the water, Charles was able to change the temperature of the gas. The pressure held constant by adjusting the height of mercury so that the two columns of mercury had equal height, and thus the pressure was always equal to the atmospheric pressure.

Intuitively, is expecting that the volume of the gas will increase as the temperature increases. Is this relationship linear? A plot of V vs T can use to test this hypothesis. If a decrease in temperature results in a decrease in volume, what happens if the temperature is lowered to a point where the volume drops to zero?

A negative volume is obviously impossible, so the temperature at which the volume drops to zero must, in some sense, be the lowest temperature that can be achieved.

This temperature is called absolute zero.

Guy-Lussac describes his experiment in same way keeping volume constant. Plot P vs. T shown same linearity. which has been historically called **Guy- Lussac (1802);** α, the coefficient of dilatation.

If the **volume is constant**, then the ideal gas law takes the form proposed by **Charles.**

$$V = \text{const} \quad n = \text{const}$$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1}$$

Charles's Law

$$P = \text{const} \quad n = \text{const}$$

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$
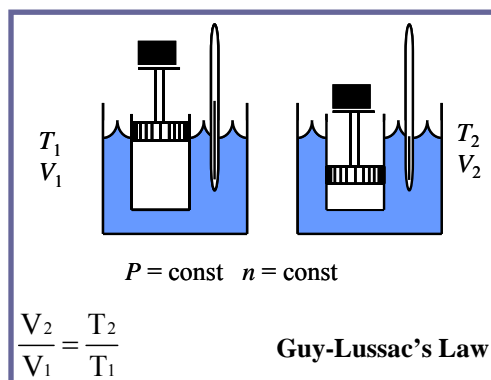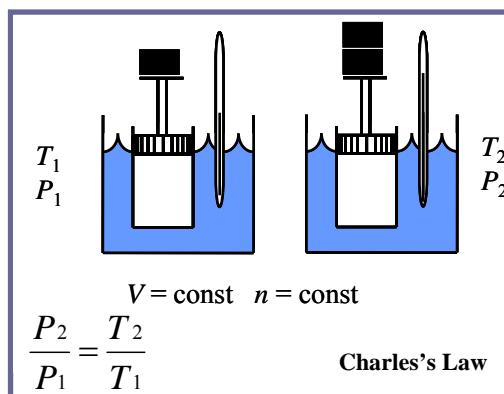
Guy-Lussac's Law

Charles' Law $P_t = P_0(1+\beta t)$; $\dfrac{P_t}{P_0} = \dfrac{\dfrac{1}{\beta}+t}{\dfrac{1}{\beta}} = \dfrac{T}{T_0}$ $\Leftrightarrow \dfrac{P_2}{P_1} = \dfrac{T_2}{T_1}$

Guy-Lussac' law $V_f = V_i(1+\alpha \Delta t)$; $\dfrac{V_f}{V_i} = \dfrac{\dfrac{1}{\alpha}+\Delta t}{\dfrac{1}{\alpha}} \Leftrightarrow \dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$

with $\Delta t = t-t_0$, $t_0 = 0^0 C$

Both laws are applicable in a limited range of pressures. Charles' law is using to build the thermometer with gas as reference in calibration other thermometers.

Experimental data (Guy-Lussac, 1802) shown that α and β are pressure and temperature independents being identical for all gases.

The most accurate measurements give for α and β:

$\alpha = \beta = \dfrac{1}{273.15} = 0.0036609$ (K^{-1})

A P-V-T diagram defines all the possible states of an ideal gas. It is appropriate for experiments performed in the presence of a constant atmospheric pressure. All the possible states of an ideal gas represented by a **P-V-T** surface as illustrated below (figure 4.2). The behaviour when any one of the three state variables kept constant is also shown.
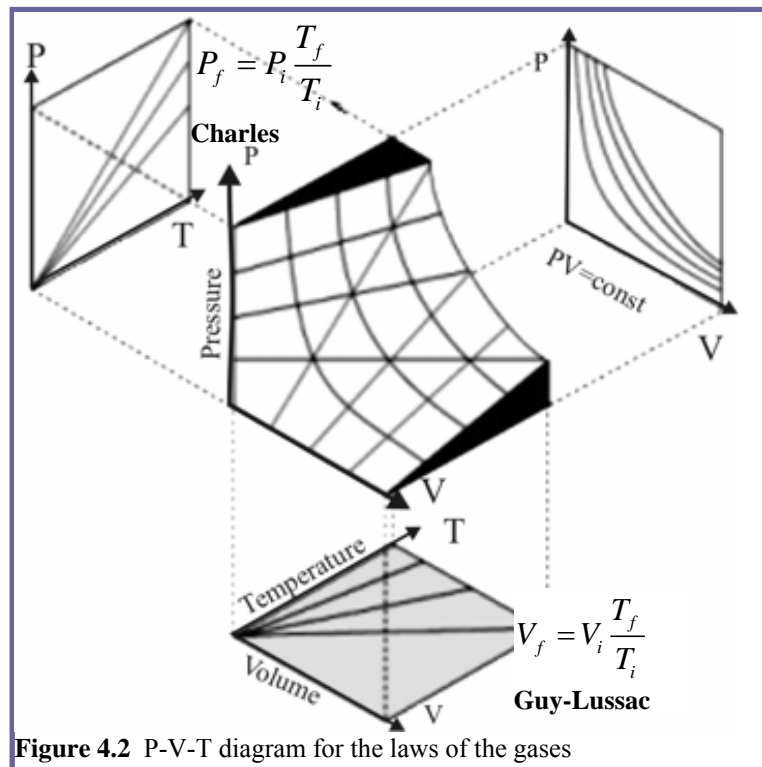
Figure 4.2 P-V-T diagram for the laws of the gases

4.1.3 Mole Proportionality Law, Avogadro's law

In the previous experiments, we have examined three important gas laws. Boyle's Law states that the product of the pressure and volume of a gas is a constant for a constant amount of gas and temperature. Charles's Law and the Gay-Lussac' Law state that the volume or the pressure of a gas is directly proportional to the temperature of the gas, provided the amount of gas.

In this experiment, we will examine a fourth important gas law: Avogadro's Law.

During the first half of the nineteenth century, Lorenzo Romano Amedeo Carlo Avogadro, count of Quaregna and Cerreto, made major contributions towards elucidating reaction stoichiometry and explaining why compounds reacted in certain well-defined integer ratios. These studies led Avogadro to address the question of how the amount of gas affect the volume of the gas and how best to think about the amount of a gas. Experimentally, the easiest way to quantify the amount of gas is as a mass. Avogadro played an important role in establishing the atoms existence. The number of molecules in a mole is named after him.

$$T = \text{const} \qquad P = \text{const}$$

$$\frac{V_2}{V_1} = \frac{n_2}{n_1} \qquad \textbf{Avogadro's Law}$$
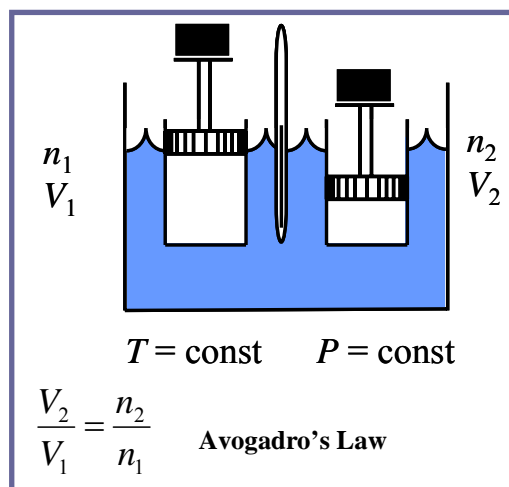
The mole

➡ A mole (abbreviated mol) of a pure substance is a mass of the material in grams that is numerically equal to the molecular mass in atomic mass units (amu).

➡ A mole of any material will contain Avogadro's number of molecules. For example, carbon has an atomic mass of exactly 12.0 atomic mass units - a mole of carbon is therefore 12 grams.

➡ For an isotope of a pure element, the **mass number A** is approximately equal to the mass in amu. The accurate masses of pure elements with their normal isotopic concentrations can be obtained from the **periodic table**.

➡ One mole of an ideal gas will occupy a volume of 22.4 liters at STP (Standard Temperature and Pressure, 0°C and one atmosphere pressure).

➡ Avogadro's number

$$N_A = 6.0221367 \times 10^{23} /mol$$

One mole of an ideal gas at STP occupies 22.4 liters.

STP

STP is used widely as a standard reference point for expression of the properties and processes of ideal gases.

The standard temperature is the freezing point of water and the standard pressure is one standard atmosphere.

These are quantifying as follows:

➡ Standard temperature: 0°C = 273.15 K

➡ Standard pressure = 1 atmosphere = 760 mmHg = 101.3 kPa

➡ Standard volume of 1 mole of an ideal gas at STP: 22.4 liters

4.1.4 Ideal Gas Law and the Gas Constant

At this point, we have experimentally explored four gas laws. To find the ideal gas law we need only three of them.

Boyle's Law	Charles's Law	Avogadro's Law
For a constant amount of gas at a constant temperature, the product of the pressure and volume of the gas is a constant. $PV = \text{const}_{BL}$	For a constant amount of gas at a constant pressure, the volume of the gas is directly proportional to the absolute temperature. $V = \text{constant}_{CL}\, T$	At a given temperature and pressure, equal volumes of gas contain equal numbers of moles. $V = \text{constant}_{AL}\, n$

Intuitively, one expects that each of these laws is a special case of a more general law. That general law,
Ideal Gas Law: $P\,V = n\,R\,T$
The constant R is called the gas constant.

In each of these laws, the identity of the gas is unimportant

➡ n = number of moles
➡ R = universal gas constant = 8.3145 J/mol K
➡ N = number of molecules
➡ k = Boltzmann constant = 1.38066×10^{-23} J/K = 8.617385×10^{-5} eV/K
➡ $k = R/N_A$
➡ N_A = Avogadro's number = 6.0221×10^{23}

Using the other three gas laws, we arise to another well-known equation:

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

The ideal gas law can be viewed as arising from **the kinetic pressure** of gas molecules colliding with the walls of a container in accordance with Newton's laws. But there is also a statistical element in the determination of the average kinetic energy of those molecules. The temperature is taken to be proportional to this average kinetic energy; this invokes the idea there is a direct connection between temperature defined in thermodynamics by zeroth and second law with average kinetic energy.

4.1.5 Dalton's Law

One of the important predictions made by Avogadro is that the identity of a gas is unimportant in determining the P-V-T properties of the gas. This behaviour means that a gas mixture behaves in exactly the same fashion as a pure gas. (Indeed, early scientists such as Robert Boyle studying the properties of gases performed their experiments using gas mixtures, most notably air, rather than pure gases.)

The ideal gas law predicts how the pressure, volume, and temperature of a gas depend upon the number of moles of the gas.

Air, for example, is composed primarily of nitrogen and oxygen. In a given sample of air, the total number of moles is:

$$n = n_{nitrogen} + n_{oxygen}$$

This expression for n can be substituted into the ideal gas law to yield:

$$P \, V = (\, n_{nitrogen} + n_{oxygen} \,) \, R \, T$$

All molecules in the gas have access to the entire volume of the system, thus V is the same for both nitrogen and oxygen. Similarly, both compounds experience the same temperature. One can therefore split this expression of the ideal gas law into two terms, one for nitrogen and one for oxygen:

$$P = n_{nitrogen} \, R \, T/V + n_{oxygen} \, R \, T/V$$

$$P = P_{nitrogen} + P_{oxygen}$$

The above equation is called Dalton's Law of Partial Pressure, and it states that the pressure of a gas mixture is the sum of the partial pressures of the individual components of the gas mixture. $P_{nitrogen}$ is the partial pressure of the nitrogen and P_{oxygen} is the partial pressure of oxygen.

$$N_{nitrogen} = n_{nitrogen} \, R \, T/V$$
$$P_{oxygen} = n_{oxygen} \, R \, T/V$$

We will notice that the equations for the partial pressures are really just the ideal gas law, but the moles of the individual component (nitrogen or oxygen) are used instead of the total moles. Conceptually $P_{nitrogen}$ is the contribution nitrogen molecules make to the pressure and P_{oxygen} is the contribution oxygen molecules make.

4.2 Gases at moderate and high pressure

The best representation for gases at pressures over the atmospheric pressure is that proposed by Amagat: PV=f(P), figure 4.3.

In figure 4.3, it observes that not all real gases have an ideal behaviour.
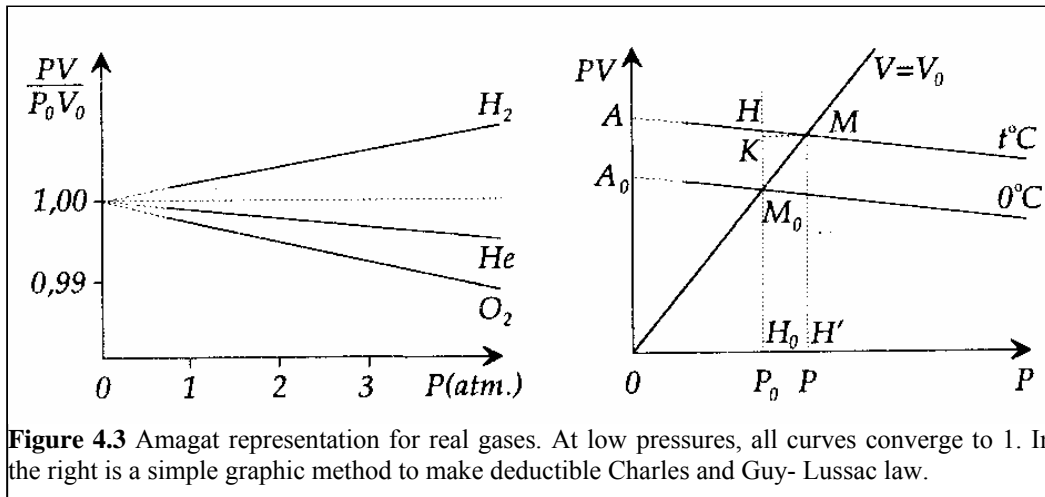
Figure 4.3 Amagat representation for real gases. At low pressures, all curves converge to 1. In the right is a simple graphic method to make deductible Charles and Guy- Lussac law.

Each gas has a proper way in behaviour with pressure. However, all gases at low pressure have same behaviour like an ideal gas: PV/P_0V_0 goes to unity. In consequence, the law Boyle-Mariotte is a limit case of the isotherm compressibility for real gases.

For a given mass of gas, PV has a limit value, constant for all gases, independent of their nature when pressure reach a very low value.

$$\lim_{P \to 0}(PV) = const.; \quad (\text{T and m } = const)$$

The table 4.1 shows several values of the PV for representative gases. All values are represented in Amagat' units (e.g reported to PV at P=1atm)

To have an idea with the real gases behaviour figure 4.4 shows in Amagat coordinates several examples. The diagrams describe:

a. The gases, easy liquefiable (CO_2, C_2H_4, SO_2, NH_3) are more compressible, the gases (H_2, He, Ne) are less compressible and liquefiable.

b. At high pressures (~ 1000 atm) the gases have PV values close to twice than Boyle- Mariotte value;

c. In range 1-10 atm are observable deviations from the ideal law up to 10%;

d. The curves PV_{rel}-P are temperature dependent (figure 4.4 right);

e. Boyle temperature,T_B: is the temperature where the isotherm has tangent the line PV_{rel}=1 at P>0. In that point the isotherm has a minimum with

$$\left(\frac{\partial (PV)}{\partial P} \right)_{T_B} = 0$$

and is coincident with the coordinate PV. At Boyle temperature in the low pressure range the gases have an ideal behaviour e.g $(PV)_{TB}$=const (CO_2: t_B= 400^{0}C; N_2- t_B =52^{0}C; H_2 - t_B= -165^{0}C; He, has -240^{0}C).

f. The gases less liquefiable (at very low temperatures), H_2, He, N_2, O_2, CO, have a behaviour close to pV=const, in the error experimental limit, at pressures lower than 0.1 atm and usual temperatures.

Table 4.1: The relative product for three gases at 0^{0}C; and CO_2,(tc=+31^{0}C);PV_{rel}= $PV/(P_0V_0)_{P=1atm}$)			
Pressure (atm)	H_2 (0^{0}C)	N_2 (0^{0}C)	CO_2 (40^{0}C)
1	1,0000	1,0000	1,0000
50	1,0330	0,9846	0,7413
100	1,0639	0,9846	0,2695
400	1,2775	1,2557	0,7178
1000	1,7107	2,0641	1,5525
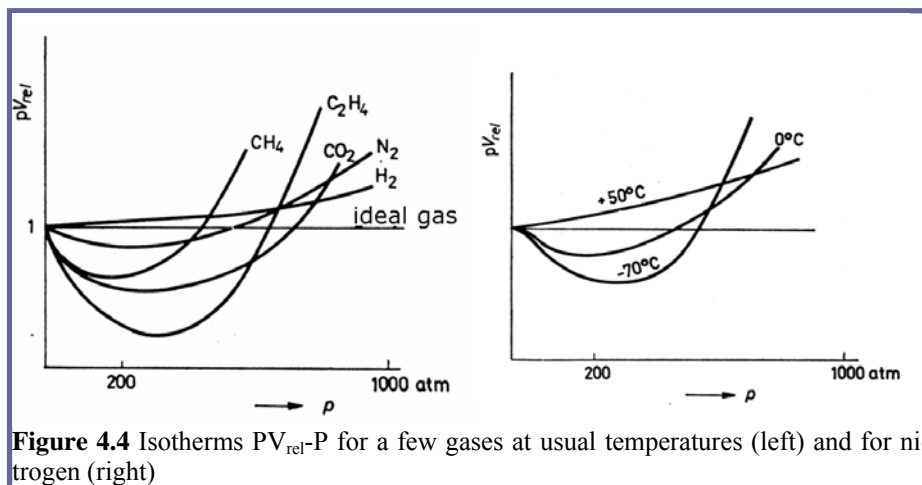
Figure 4.4 Isotherms PV_{rel}-P for a few gases at usual temperatures (left) and for nitrogen (right)

4.3 Real Gases

At lower temperatures and higher pressures, the equation of state of a real gas deviates from that of a perfect gas (figure 4.4).

Various empirical relations have been proposed to explain the behaviour of real gases.

The equations:

- J. van der Waals (1899),

$$\left(P+\frac{a}{\overline{V}^2}\right)\left(\overline{V}-b\right)=RT$$

- P. E. M. Berthelot (1907),

$$\left(P+\frac{a}{T\overline{V}^2}\right)\left(\overline{V}-b\right)=RT$$

- F. Dieterici (1899),

$$Pe^{\frac{a}{\overline{V}^2RT}}\left(\overline{V}-b\right)=RT$$

are frequently used. The molar volume $\overline{V}$ is the molecular weight divided by the gas density; a and b are constants characteristic of the particular substance under considerations.

In a qualitative sense, b is the excluded volume due to the finite size of the molecules and roughly equal to four times the volume of 1 mole of molecules.

The constant, a, represents the effect of the forces of attraction/repulsion between the molecules. In particular, the internal energy of a Van der Waals gas is $-a/\overline{V}$.

None of these relations gives a good representation of the compressibility of real gases over a wide range of temperature and pressure. However, they reproduce qualitatively the leading features of experimental pressure-volume-temperature surfaces.

Schematic isotherms of a real gas, the pressure as a function of the volume for fixed values of the temperature, are shown in figure 4.5. Here T_1 is a very high temperature and its isotherm deviates only slightly from that of a perfect gas; T_2 is a somewhat lower temperature where the deviations from the perfect gas equation are quite large; and T_c is the critical temperature. *The critical temperature is the highest temperature at which a liquid can exist*. That is, at temperatures equal to or greater than the critical temperature, the gas phase is the only phase that can exist (at equilibrium)
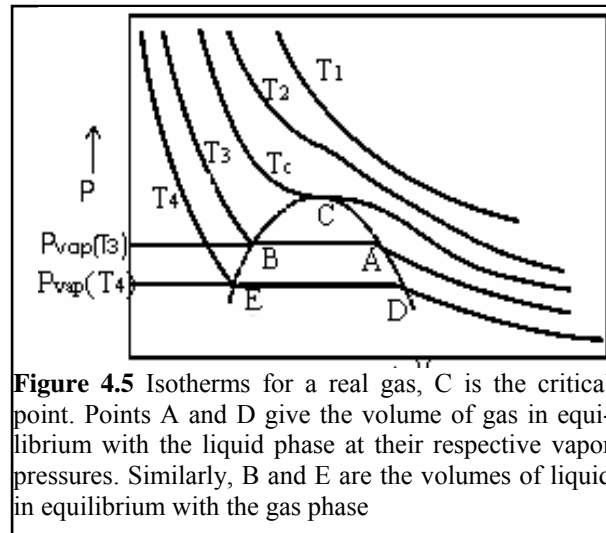
Figure 4.5 Isotherms for a real gas, C is the critical point. Points A and D give the volume of gas in equilibrium with the liquid phase at their respective vapor pressures. Similarly, B and E are the volumes of liquid in equilibrium with the gas phase

regardless of the pressure. Along the isotherm for T_c lies the critical point, C, which is characterized by zero first and second partial derivatives of the pressure with respect to the volume.

This is expressed as equation: (see details in applications with 1st law)

$$\left(\frac{\partial P}{\partial \overline{V}}\right)_c = \left(\frac{\partial^2 P}{\partial \overline{V}^2}\right)_c = 0$$

Note: The critical phenomena are a special chapter in thermodynamics and statistical mechanics. Evidenced in gases this phenomenon is present in any phase transition solid-solid (such as graphite-diamond). Moreover, if we replace the coordinates with the others such as government outputs and population expectations for a macroeconomic system we can find interesting results for a new interdisciplinary field, Econophysics.

Chapter 5

Liquids

➡ Macroscopically, liquids are distinguished from crystalline solids in their capacity to flow under the action of extremely small shear stresses and to conform to the shape of a confining vessel.

➡ Liquids differ from gases in possessing a free surface and in lacking the capacity to expand without limit.

➡ On the scale of molecular dimensions, liquids lack the long-range order that characterizes the crystalline state,

➡ They possess a degree of structural regularity that extends over distances of a few molecular diameters. In this respect, liquids are wholly unlike gases, whose molecular organization is completely random.

The **liquid state** of a material has a definite volume, but it does not have a definite shape and takes the shape of the container, unlike that of the solid state. Unlike the gas state, a liquid does not occupy the entire volume of the container if its volume is larger than the volume of the liquid. At the molecular level, the arrangement of the molecules is **random**, unlike that of the solid state in which the molecules are regular and periodic. The molecules in the liquid state have translational motions as those in a gas state. There is short order intermolecular ordering or structure, however.

The most familiar liquid states at room temperature are water, alcohol, benzene, carbon tetrachloride, corn oil, Castor oil, and gasoline.

Glasses, although solids, are often called **frozen liquids**, because the arrangements of molecules in glasses are very similar to those in liquid states

Its phase diagram, shown schematically in the figure 3.2, describes the thermodynamic conditions under which a substance may exist indefinitely in the liquid state.

The area designated by "Liquid" depicts those pressures and temperatures for which the liquid state is energetically the lowest and therefore the stable state.

5.1 Liquid Crystals

There is no actually advanced technology in fields such as displays, laptops, thermometers, sensors without liquid crystals. The liquid crystals are well known by its opto-electrical properties large exploited in displays technology. However, many of those properties are dependent of thermodynamic conditions and phase transformations that appear to exploit an opto-electrical property. Therefore, we pay some extension with liquid crystals to present a few properties and astonished applications:

➡ Liquid crystals are a state of matter that mixes the properties of both the liquid and solid states.

➡ Liquid crystals may be described as condensed fluid states with spontaneous anisotropy.

The liquid crystals are categorizing in two ways:

➡ **Thermotropic** liquid crystals, prepared by heating the substance. Liquid crystals are a state of matter that combines a kind of long-range order (in the sense of a solid) with the ability to form droplets and to pour (in the sense of

waterlike liquids). They also exhibit properties of their own such as the ability to form monocrystals with the application of a normal magnetic or electric field; an optical activity of a magnitude without parallel in either solids or liquids; and a temperature sensitivity that results in a color change in certain liquid crystals. Thermotropic liquid crystals are either nematic or smectic.

➡ **Lyotropic** liquid crystals, prepared by mixing two or more components, one of which has polar character (for example, water).

> Thermotropic liquid crystals are divided, according to structural characteristics, into two classes: nematic and smectic.

> Nematics are subdivided into ordinary and cholesteric or chiral.

When the solid that forms a liquid crystal is heated, it undergoes transformation into a turbid system that is both fluid and bi-refringent.

The consistency of the fluid varies with different compounds from a paste to a free-flowing liquid.

When the turbid system is heated, it is converted into an isotropic liquid (optical properties are the same regardless of the direction of the measurement).

These changes in phases can be represented schematically:

$$\text{SOLID} \underset{\text{COOLING}}{\overset{\text{HEATING}}{\rightleftarrows}} \text{LIQUID CRYSTAL} \underset{\text{COOLING}}{\overset{\text{HEATING}}{\rightleftarrows}} \text{LIQUID}$$

5.1.1 Lyotropic liquid crystals

They have an amphiphilic components, a compound with a polar head attached to a long hydrophobic tail. Sodium stearate and lecithin (a phospholipid) are typical examples of amphiphiles.

Starting with a solid amphiphile and adding water, the lamellar structure (molecular packing in layers) is formed. By step-wise addition of water, the molecular packing may take a cubic structure, then hexagonal, then micellar (see micelle system and colloids), followed by true solution.

The process is reversible when water is withdrawn. Thousands of compounds will form liquid crystals on heating, and still more will do so if two or more components are mixed.

5.1.2 Nematic structure

Nematic liquid crystals are subdivided into the ordinary nematic and the chiral-nematic. The molecules in the ordinary *nematic* structure maintain a parallel or nearly parallel arrangement to each other along the long molecular axes (Fig 5.1). They are mobile in three directions and can rotate about one axis. This structure is one-dimensional.

When the nematic structure is heated, it generally transforms into the isotropic liquid where the completely disordered motions of the molecules produce a phase in which all directions are equivalents. The nematic structure is the highest-temperature mesophase in thermotropic liquid crystals. The energy required to deform a nematic liquid crystal is so small that even the slightest perturbation caused by a dust particle can distort the structure considerably.

Nematic liquid crystal- nematic structure maintain a parallel or nearly parallel arrangement to each other along the long molecular axes

Chiral-nematic structure, all parallel molecules are cooperative twist along of helix axis

Figure 5.1- *Nematic Liquid Crystal*
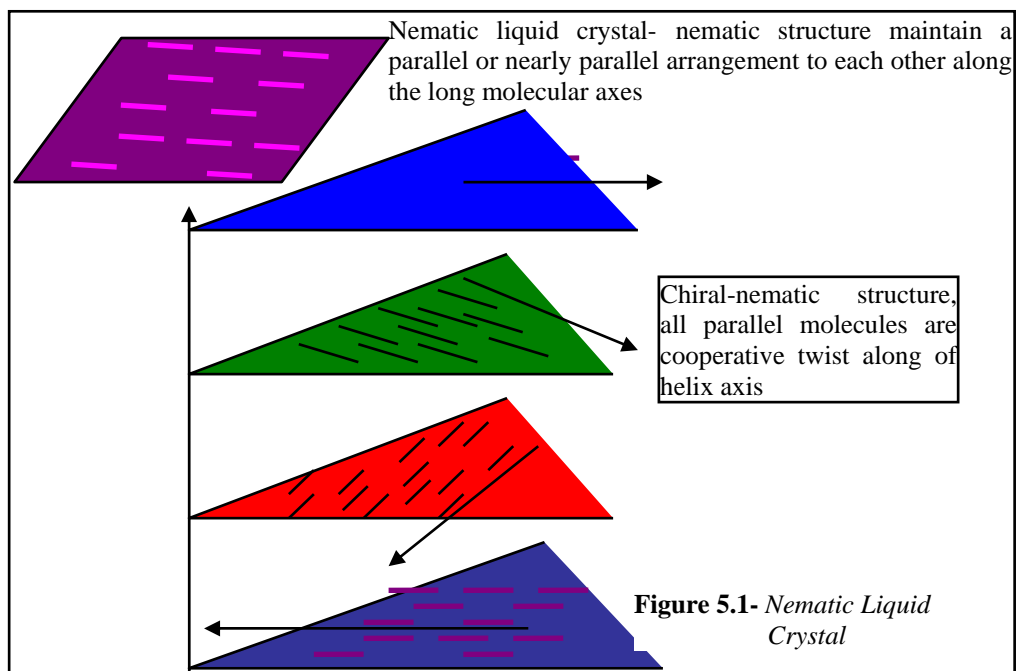
In the *chiral-nematic* structure (Fig.5.1), the direction of the long axis of the molecule in a given layer is slightly displaced from the direction of the molecular axes of the molecules in an adjacent layer. If a twist is applied to this molecular packing, a helical structure is formed. The helix has a temperature-sensitive pitch. The helical structure serves as a diffraction grating for visible light. Chiral compounds show the cholesteric-nematic structure (twisted nematic), for example, the cholesteric esters.

5. 1.3 Smectic structure

The term smectic includes all thermotropic liquid crystals that are not nematics.
In the smectic phase:

➡ A small amount of orientational order of nematic liquid crystals present, there is also a small amount of positional order.

➡ In most smectic structures, the molecules are free to bounce around randomly; they tend to point along a specific direction and arrange themselves in layers, either in neat rows or randomly distributed. The molecules can move in two directions in the plane and rotate about one axis.

➡ Smectic liquid crystals may have structured or unstructured strata. Structured smectic liquid crystals have long-range order in the arrangement of molecules in layers to form a regular two-dimensional lattice.

➡ The most common of the structured liquid crystals is smectic B. Molecular layers are in well-defined order, and the arrangement of the molecules within the strata is also well ordered. The long axes of the molecules lie perpendicular to the plane of the layers.

➡ In the smectic A (Fig. 5.2) structure, molecules are also packed in strata, but the molecules in a stratum are randomly arranged. The long axes of the molecules in the smectic A structure lie perpendicular to the plane of the layers.

■ Molecular packing in a smectic C (Fig. 5.2) is the same as that in smectic A, except the molecules in the stratum are tilted at an angle to the plane of the stratum.

When a liquid crystal possesses a chiral nematic phase, its smectic phases, if present, are either smectic A or smectic C. In some cases, the tendency of the molecules to form a twisted phase is large enough that a smectic phase with a twist exists. Over 20 different smectic liquid-crystal phases have been identified, each appearing quite different under a microscope.

Smectic A

Smectic C

Figure 5.2, *Liquid Crystal Smectics*

Smectic C*
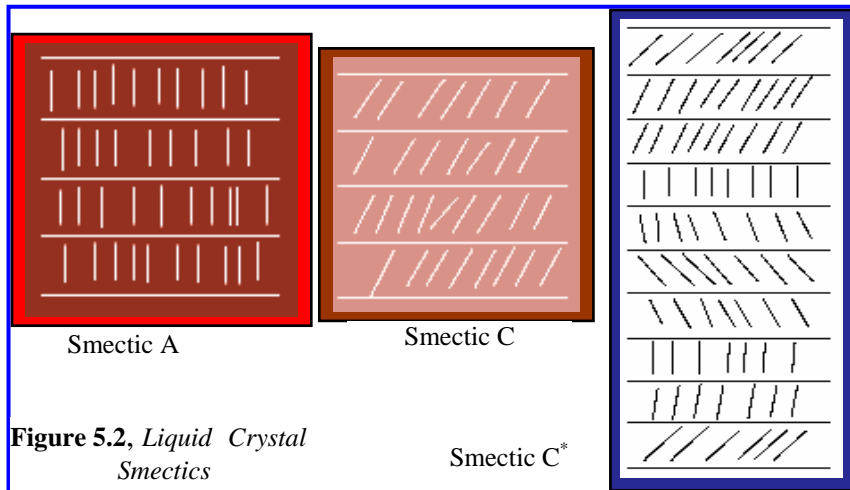
Chapter 6

Solids and solid phases

The solid phase is the most representative in the materials' world spanning from ideal crystalline to nanostructures and polymers, composites and gels, ceramics and glasses. In each field of material science the thermal phenomena are involved either in methods of synthesis or in thermal properties where need materials characterization.

New advances in material science and characterization using tools of nanotechnology evidenced many aspects in size dependent physical-chemical properties. This is the rationale for larger introspection in solid phase, related to possible case study for thermal physics.

6.1 Structure of Solids

➡ **Crystalline solid**: atoms show short and long range order
➡ **Amorphous solid** (non-crystalline): atoms show short-range order only. A rigid material whose structure lacks crystalline periodicity. The pattern of its constituent atoms or molecules does not repeat periodically in three dimensions. **Terminology**: amorphous and noncrystalline are synonymous.

A solid is distinguishes from its other amorphous counterparts (liquids and gases) by its viscosity: a material is considered solid (rigid) if its shear viscosity exceeds 10^{14} Poise (10^{13} Pascal · second).

6.2 Crystalline Solids

6.2.1 Ideal Crystal structure

The ideal crystalline structures were studied by crystallography, a science branch who studied first the beautiful gems existing and "manufactured" by nature. Further with X-Ray diffraction method was established the periodicity of the atom arrangement in crystals. A large effort at the beginning of the last century has been consumed to classify crystals in lattice and find their symmetry properties. The most important curiosity with the atom arrangement in crystals is that they reproduce the most perfect geometrical polyhedron existing in the Euclidean Geometry. That is, it can result from the electrical field symmetry produced by atoms as electrical charges. In systemized scheme are presented few of crystal properties related to atom arrangement in lattices.

The crystals have two parts:
➡ **lattice** - regular periodic array of points in space;
➡ **basis** - a group of atoms located at each point in the lattice

Lattices: in three dimensions there are only 14 unique lattices (Bravais lattices) found. They are represented in table 6.1. (NOTE: the spheres are just points in space - NOT atoms!) . In figure 6.1 is shown the coordinate system which is not Euclidean. For particular systems (cubic and triclinic) the coordinate
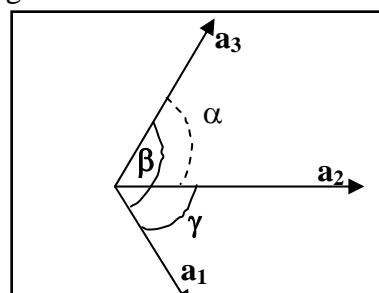
Figure 6.1- The coordinate system for lattice representation in affine Euclidean space.

axis are coincident with the edges of the geometrical figures (cube or parallelepiped) and the angles' axis are all 90^0. This representation is the most appropriate with the symmetry properties of each crystal. Particularly the translation symmetry conserves the equivalence of lattice and basis for any arbitrary displacement.

Notice that a lattice is not a crystal; even so the two words are often used synonymously in colloquial language, especially in the case of elemental crystals where the base consists of one atom only.

All possible lattices can be described by a set of three linearly independent vectors which for any integers the position vector $\vec{R}$ for an arbitrary position in lattice is:

$$\vec{a_1}, \ \vec{a_2}, \ \vec{a_3}; \ \left|\vec{a_1}\right| = a_1, \ \left|\vec{a_2}\right| = a_2, \ \left|\vec{a_3}\right| = a_3$$

$$\vec{R} = n_1 \vec{a_1} + n_2 \ \vec{a_2} + n_3 \vec{a_3}$$

with n1, n2, n3, integers translation operation. Any translation operation gives all equivalent points in lattice:

$$\vec{R}_{n+m} = \vec{R}_n + \vec{R}_m = \left(n_1 + m_1\right)\vec{a_1} + \left(n_2 + m_2\right)\vec{a}_2 + \left(n_3 + m_3\right)\vec{a}_3$$

The lattice parameters are length of the primitive vectors: $\vec{a}_1, \vec{a}_2, \vec{a}_3$. For a cubic lattice, $\left|\vec{a}_1\right| = \left|\vec{a}_2\right| = \left|\vec{a}_3\right| = a_0$, the lattice parameter.

Examples: Cr, bcc lattice, one Cr atom basis, $a_o = 2.88$ Angstroms; Cu, fcc lattice, one Cu atom basis, $a_o = 3.615$ Angstroms; Si, fcc lattice, two Si atom basis, one Si atom at (0,0,0), other Si atom at (1/4, 1/4, 1/4)a, $a_o = 5.43$ Angstroms

6.2.2 Planes in a crystal

The procedure to identify the planes in crystals has been described by Miller and sketched in table 6.2. In figure 6.2 are shown the atoms packing in plane. It must take in account the atoms are considered rigid sphere in contact each other. How are distribute atoms in plane? Note how open some surfaces are packed and how dense others are packed. Different surfaces have different arrangements of atoms => different properties.

Other, close packed planes:

Two surfaces produce the maximum possible density for packing spheres. The surface layers and second layers of atoms are identical, but the positions of atoms in the third planes are different. If the planes are denoted with A – first layer, B-second layer, C-third layer we have few examples with most closed packing planes in hexagonal and fcc lattices. fcc (111) = diagonal cut through the face centered cubic structure (shown above) ABCABCABC repeat pattern; hcp (0001) = base plane of the hexagonal close packed structure ABABAB repeat pattern.
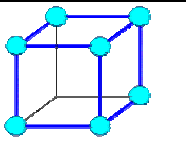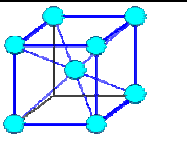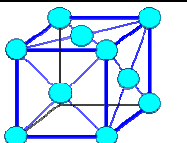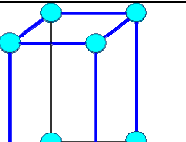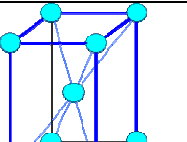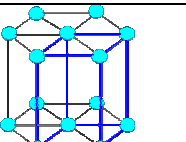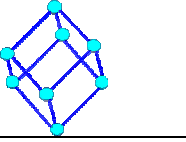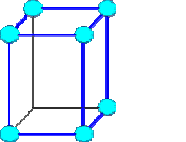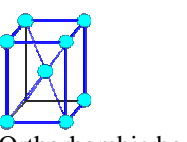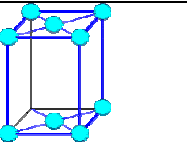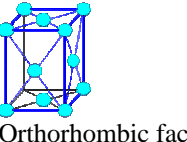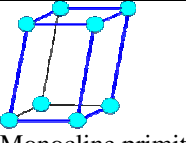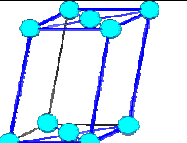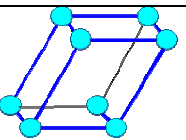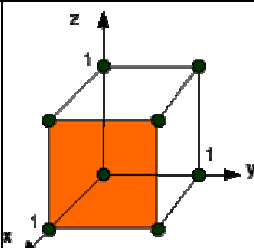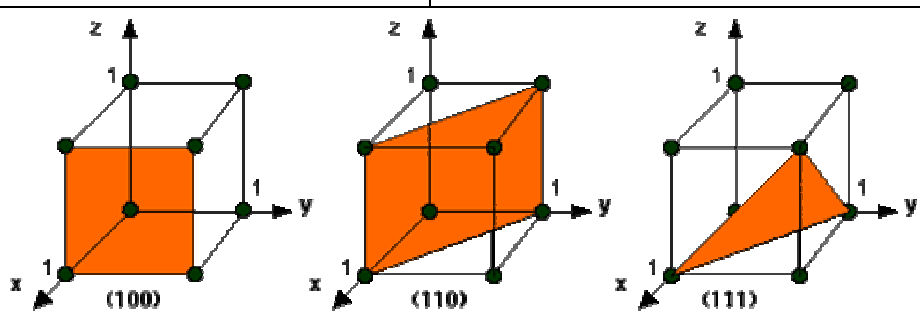
Crystal system Length of Base vectors	Angles between axes	Table 6.1- 14 Bravais lattices organized in 7 systems		
		Bravais Lattices		
Cubic $a_1 = a_2 = a_3$	$\alpha = \beta = \gamma = 90^0$	cs-cubic primitive	bcc-cubic body centered	fcc-cubic face centered
Tetragonal $a_1 = a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^0$	Tetragonal primitive	Tetragonal body centered	
Hexagonal $a_1 = a_2 \neq a_3$	$\alpha = \beta = 90^0$, $\gamma = 120^0$			
Rhombohedral $a_1 = a_2 = a_3$	$\alpha = \beta = \gamma \neq 90^0$			
Orthorhombic $a_1 \neq a_2 \neq a_3$	$\alpha = \beta = \gamma = 90^0$	Orthorhombic primitive	Orthorhombic body centered	Orthorhombic base face centered Orthorhombic face centered
Monoclinic $a_1 \neq a_2 \neq a_3$	$\alpha = \beta = 90^0$, $\gamma \neq 90^0$	Monocline primitive		Monocline base face centered
Triclinic $a_1 \neq a_2 \neq a_3$	$\alpha \neq \beta \neq \gamma \neq 90^0$			

Table 6.2 – Planes in crystals, This is procedure that describe planes by **Miller indices**	
General procedure	**Specific example**
1. Cut crystal along some plane. cut along a face of a cube	
2. Determine x, y, z, intercepts (x_o, y_o, z_o)	(1, infinity, infinity)
3. Take reciprocals and reduce to smallest integer. $\left(\dfrac{1}{x_0}, \dfrac{1}{y_0}, \dfrac{1}{z_0} \right)$	(100) plane [if we had used the (200) plane, reduce to (100)]
  Other cubic surfaces	

Figure 6.2- The packing of the atoms in crystalline planes for two examples of lattices. More dense packing is realized in fcc lattice than in cubic.

34
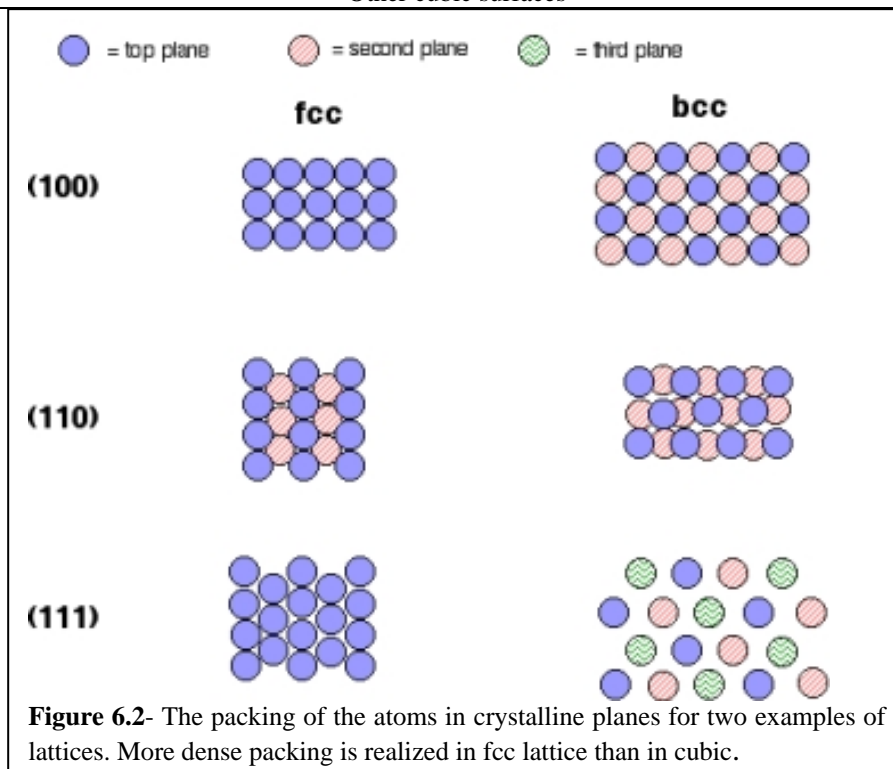
6.2.3 Directions in Crystal

Define a vector [h k l] between two lattice points. When the direction is negative, instead of a minus sign, use a bar over the number,

The angle (α) between any two vectors [h_1 k_1 l_1] and [h_2 k_2 l_2]

$$\cos\alpha = \frac{h_1 k_1 + h_2 k_2 + h_3 k_3}{\sqrt{h_1^2 + k_1^2 + l_1^2}\sqrt{h_2^2 + k_2^2 + l_2^2}}$$

for **cubic** lattices: [h k l] is normal vector to (h k l) plane spacing (d) between (hkl) planes is given by:

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$$

where a_o is the length of one side of the cube face

Example: spacing between (100) planes in a simple cubic lattice:
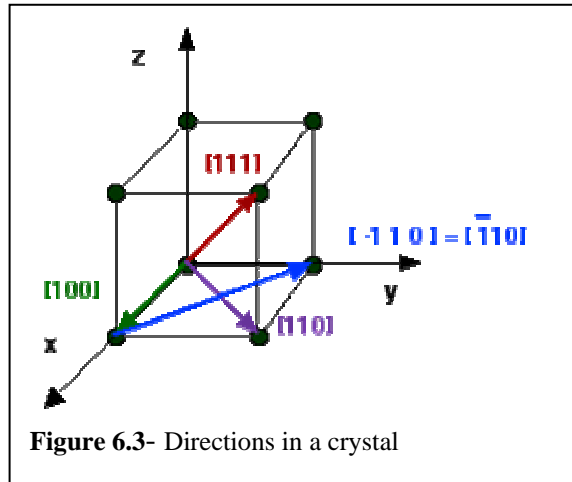
Figure 6.3- Directions in a crystal

$$d = \frac{a_0}{\sqrt{1^2 + 0^2 + 0^2}} = a_0$$

6.3 Thin films

- ➡ thin = less than about one micron (10,000 Angstroms, 1000 nm)
- ➡ film = layer of material on a substrate (if no substrate, it is a "foil")

Applications:
- ➡ Microelectronics - electrical conductors, electrical barriers, diffusion barriers, etc
- ➡ Magnetic sensors - sense I, B or changes in them
- ➡ Gas sensors, SAW (surface acoustic waves) devices
- ➡ Tailored materials - layer very thin films to develop materials with new properties
- ➡ Optics - anti-reflection coatings
- ➡ Corrosion protection
- ➡ Wear resistance, etc.

Special Properties of Thin Films:

They are different from bulk materials. Thin films may be: not fully dense, under stress, different defect structures from bulk, quasi - two dimensional (very thin films), strongly influenced by surface and interface effects This will change electrical, magnetic, optical, thermal, and mechanical properties

Typical steps in making thin films:
1. emission of particles from source (heat, high voltage)
2. transport of particles to substrate (free vs. directed)
3. condensation of particles on substrate (how do they condense ?)

Simple model: Figure 6.4

Figure 6.4- A simple model for thin film deposition
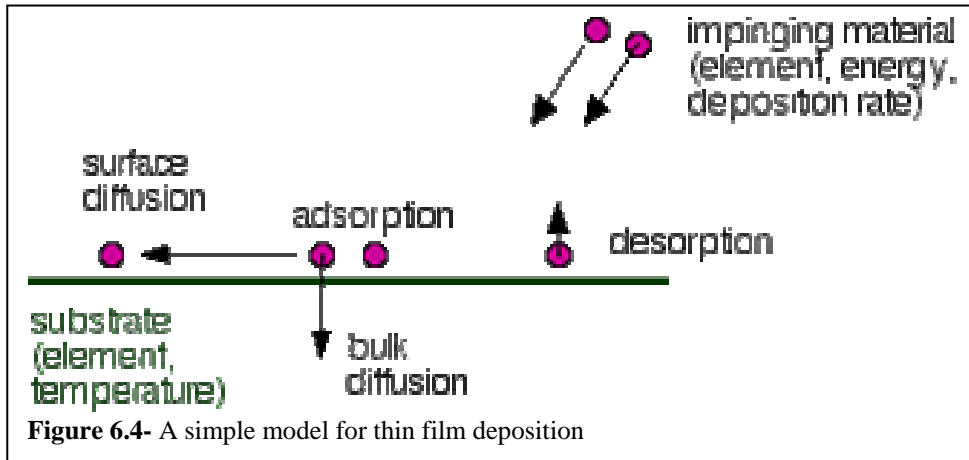
The physics involved in thin films
1. Thermodynamics and kinetics : phase transition - gas condenses to solid , nucleation , growth kinetics , activated processes (desorption, diffusion, allowed processes and allowed phases)
2. Solid state physics; crystallography, defects, bonding
3. Electricity and magnetism: optics, conductivity – resistivity, magnetic properties
4. Mechanics : stresses in films, friction and wear

6.4 Non-crystalline (amorphous) solids

6. 4. 1 Amorphous solids: preparation

Techniques commonly used to prepare amorphous solids include vapor deposition, electrodeposition, anodization, evaporation of a solvent (gel, glue), and chemical reaction (often oxidation) of a crystalline solid. None of these techniques involves the liquid state of the material.

Types of amorphous solids: oxides, glasses, generally the silicates, are the most familiar amorphous solids. However, as a state of matter, amorphous solids are much more widespread than just the oxide glasses. There are both organic (for example, polymers) and inorganic (for example, the silicates) amorphous solids.

6.4.2 Glasses

- Not stable state for most pure metals
- Can be formed in metals by very rapid cooling (10^6 K/sec)
- Readily formed from many metal alloys, semiconductors, oxides - especially at low temperatures
- Generally less dense than crystalline materials
- No crystalline defects since no crystal structure

The glasses are a special solid phase, particularly an amorphous state. A distinctive class of amorphous solids consists of glasses, which are defining as amorphous solids obtained by cooling of the melt. Upon continued cooling below the crystalline melting point, a liquid either crystallizes with a discontinuous change in volume, viscosity, entropy, and internal energy, or (if the crystallization kinetics are slow enough and the

quenching rate is fast enough) forms a glass with a continuous change in these properties. The glass transition temperature is defined as the temperature at which the fluid becomes solid (that is, the viscosity $> 10^{14}$ poise) and is generally marked by a change in the thermal expansion coefficient and heat capacity. [Silicon dioxide (SiO2) and germanium dioxide (GeO2) are exceptions.]

It is intuitively appealing to consider a glass to be both structurally and thermodynamically related to its liquid; such a connection is more tenuous for amorphous solids prepared by the other techniques

Examples of glass formers exist for each of the bonding types: covalent [As2S3], ionic [KNO3-Ca(NO3)2], metallic [Pd4Si], van der Waals [o-terphenyl], and hydrogen [KHSO4]. Glasses can be prepared which span a broad range of physical properties. Dielectrics (for example, SiO2) have very low electrical conductivity and are optically transparent, hard, and brittle. Semiconductors (for example, As2SeTe2) have intermediate electrical conductivities and are optically opaque and brittle. Metallic glasses (for example, Pd4Si) have high electrical and thermal conductivities, have metallic luster, and are ductile and strong.

6.4.2.1 Glasses for glassware

Glasses for glassware are usually prepared by mixing at solid state the different oxides precursors (Carbonates, nitrates, sulfates, oxides..) and then melt at relatively high temperature (1300-2000°C) the mixture to obtain a liquid.

When a liquid is cooling at a high rate, to prevent crystallization then an amorphous glassy solid is obtained. The fast cooling rate over the solidification point prevents the sample to have sufficient time to reach true equilibrium at each temperature appropriate to the temperature of solidification.

Since the crystal is invariably the thermodynamically stable low-temperature phase, the glass transition corresponds to a transition from a high-temperature liquid into a nonequilibrium metastable low-temperature solid. This transition occurs at a temperature Tg where the shear viscosity becomes large, greater than 1000 Pascal-seconds.

Changes in the heat capacity and coefficient of thermal expansion are also generally observed near Tg.

Materials having this ability to cool without crystallizing are relatively rare, silica (SiO2) being the most common example. Although glasses can be made without silica, most commercially important glasses are based on it. Silica has melting point over

Atomic and molecular structure for a hypothetical oxide B_2O_3 transformed in bi-dimensional structure as crystalline state for low cooling rate (a) and in glass-like state for high cooling rate (b). In (a) long and short range order coexists, in (b) only short range order is persistent.
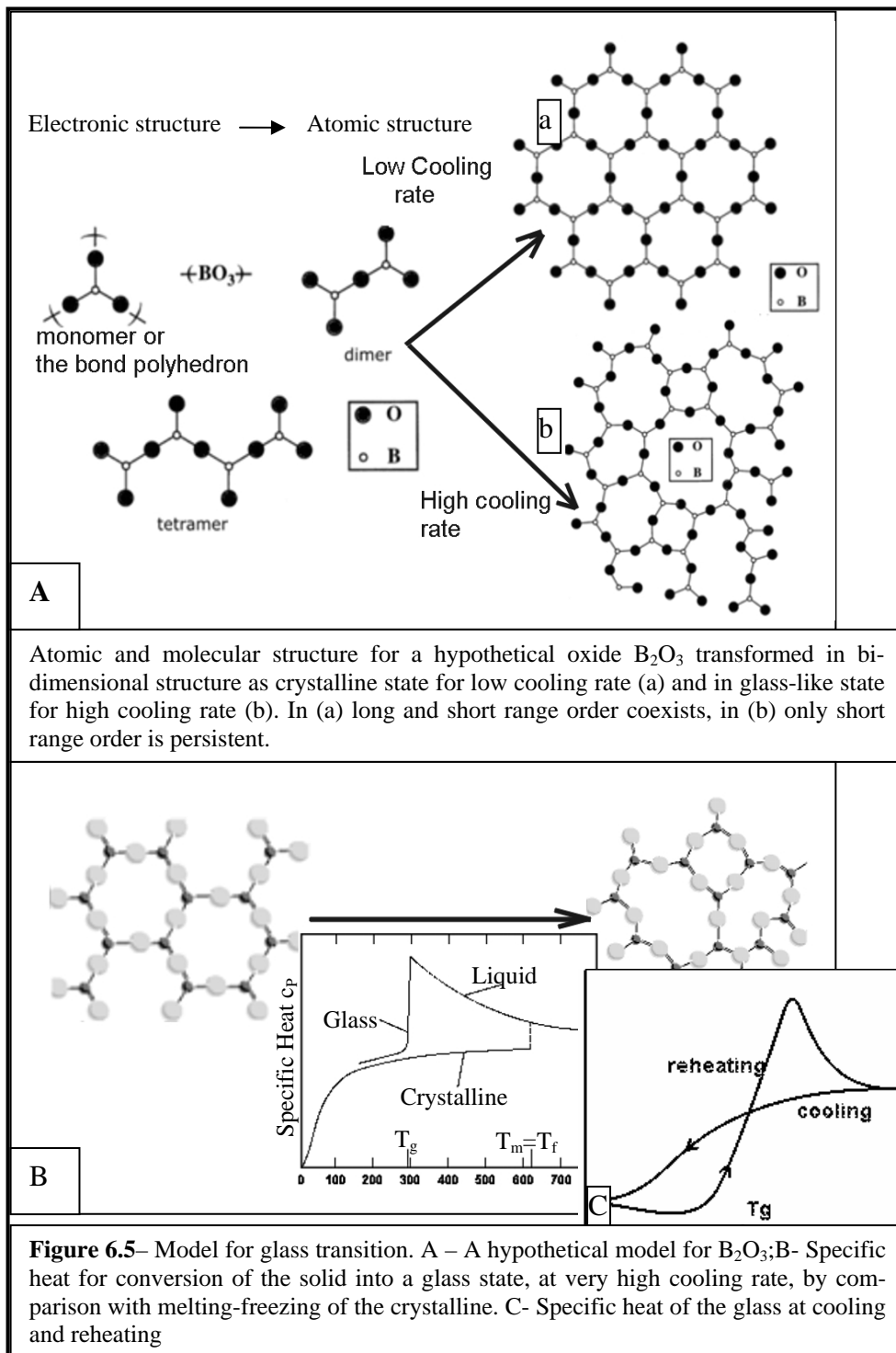
Figure 6.5– Model for glass transition. A – A hypothetical model for B_2O_3;B- Specific heat for conversion of the solid into a glass state, at very high cooling rate, by comparison with melting-freezing of the crystalline. C- Specific heat of the glass at cooling and reheating

1700^0 C and in liquid state has high viscosity being difficult to work. To decrease the melting point other oxides are added (such as: 1. Na_2O in carbonate form. Sodium oxide make silica to melt at very low temperature becoming a liquid state, well-known "the water glass" 2. Adding CaO in carbonate form at a composition silica-sodium oxide is obtaining regular glasses for glassware. 3. Special kinds of glass have other oxides as major ingredients. For example, boron oxide (B_2O_3) added to silicate glass make a

low-thermal-expansion glass for chemical glassware that must withstand rapid temperature changes, for example, Pyrex glass. This type of glass is known as a borosilicate. Also, lead oxide (PbO) is used in optical glass and lead crystal because it gives a high index of refraction.

6.4.2.2 Glass from Gels

Glass researchers in the late 70's start investigating intensively low temperature processing routes for oxides glass manufacturing. The high temperature structure of the liquid is characterized by an amorphous state (no order at long distance) which is preserved by cooling the melt rapidly at room temperature. The resulted solid is structurally amorphous and presents, when heated, the characteristic glass transition temperature.

Network randomness is what we try to create and preserve in order to obtain the glass. And by doing that we consume a lot of energy to destroy the order initially present on the various crystalline precursors. Creating this random network by using liquid precursors, in the same way macromolecular chemist do to elaborate polymers, is what glass scientists dreamed and achieved 25 years ago. They reconstruct the glass amorphous state using a "bottom-up" approach. No need any more to go at the melting temperature since the network structure is already elaborated at relatively low temperatures (20-80°C).

This chemical approach of making a material starting with molecular precursors and elementary building blocks (here SiO_2 tetrahedra) pass beyond the initial restricted field of glass and ceramics science intimate circle of researchers. Is widely used today for tailoring structures at the molecular level to create new materials with enhanced performances, less energy consumption, better homogeneity (mixing at molecular level) high purity. Liquids successive can be purified by distillation at ppb or even lower levels, whereas such purity is much difficult to achieve in the solid state extend composition range.

However making a glass from a gel is useless unless the technique offers significant advantages over the traditional melting technique. Homogeneity, purity and low temperature synthesis are the main attributes which can favorably compete if the cost is not prohibitively high. Therefore the first attempt to synthesize glass from gels was focused on silica (a simple from fundamental point of view system but extremely difficult to melt oxide).

That was the beginning of an extraordinary research effort started in the late 70s' known today as sol-gel process: a physico-chemical route for obtaining glassy and ceramic materials at relatively low temperatures starting from liquids.

Although the sol-gel technique has drastically evolved since, and is now used for a variety of materials in any imaginable form (thin and thick films, fibers, membranes, nanopowders, bulk porous or dense ceramics), composition and structure (Inorganic, organic-inorganic hybrids, semiconductors, nano-textured materials, etc.), it is worthwhile to recall the basics of the initial challenges the researchers were facing in the starting of this exciting technological field.

6.4.3 Ceramics

The word *ceramic* is derived from Greek, and in its strictest sense refers to clay in all its forms. However, modern usage of the term broadens the meaning to include all inorganic non-metallic materials. Up until the 1950s or so, the most important of these were the traditional clays, made into pottery, bricks, tiles and the like, along with cements and glass. The traditional crafts are described in the article on pottery. Histori-

cally, ceramic products have been hard, porous and brittle. The study of ceramics consists to a large extent of methods to mitigate these problems, and accentuate the strengths of the materials, as well as to offer up unusual uses for these materials.

Examples of Ceramic Materials

- Silicon nitride (Si_3N_4), which is used as an abrasive powder.
- Boron carbide (B_4C), which is used in some helicopter and tank armor.
- Silicon carbide (SiC), which is used as a succeptor in microwave furnaces, a commonly used abrasive, and as a refractory material.
- Magnesium diboride (MgB_2), which is an Unconventional superconductor
- Zinc oxide (ZnO), which is a semiconductor, and used in the construction of varistors
- Ferrite (Fe_3O_4), which is ferrimagnetic and is used in the core of electrical transformers and magnetic core memory.
- Steatite is used as an electrical insulator (alumino-magnesian compound sintered
- Bricks (mostly aluminium silicates), used for construction.
- Uranium oxide (UO_2), used as fuel in nuclear reactors.
- Yttrium barium copper oxide ($YBa_2Cu_3O_{7-x}$), a high temperature superconductor.

6.4.3.1 Properties of Ceramics

Mechanical properties

Ceramic materials are usually ionic or glassy materials. Both of these almost always fracture before any *plastic deformation* takes place, which results in poor *toughness* in these materials. Additionally, because these materials tend to be porous, the pores and other microscopic imperfections act as stress concentrators, decreasing the toughness further, and reducing the tensile strength. These combine to give catastrophic failures, as opposed to the normally much more gentle failure modes of metals.

These materials do show plastic deformation. However, due to the rigid structure of the crystalline materials, there are very few available slip systems for dislocations to move, and so they deform very slowly. With the non-crystalline (glassy) materials, viscous flow is the dominant source of plastic deformation, and is also very slow. It is therefore neglected in many applications of ceramic materials.

These materials have great strength under compression, and are capable of operating at elevated temperatures. Their high hardness makes them widely used as abrasives, and as cutting tips in tools.

Refractory behaviour

Some ceramic materials can withstand extremely high temperatures without losing their strength. These are called refractory materials. They generally have low thermal conductivities, and thus are used as thermal insulators. For example, the belly of the *Space Shuttles* is made of ceramic tiles which protect the spacecraft from the high temperatures caused during reentry.

The most important requirements for a good refractory material are that it not soften or melt, and that it remains unreactive at the desired temperature. The latter re-

quirement pertains to both self-decomposition and reaction with other compounds that might be present, either of which would be detrimental.

Porosity takes on additional relevance with refractories. As the porosity is reduced, the strength, load-bearing ability, and environmental resistance increases as the material gets more dense. However, as the density increases the resistance to thermal shock (cracking as a result of rapid temperature change) and insulation characteristics are reduced. Many materials are used in a very porous state, and it is not uncommon to find two materials used: a porous layer, with very good insulating properties, with a thin coat of a more dense material to provide strength.

It is perhaps surprising that these materials can be used at temperatures where they are partially liquefied. For example, silica firebricks used to line steel-making furnaces are used at temperatures up to 1650°C, where some of the brick will be liquid. Designing for such a situation unsurprisingly requires a substantial degree of control over all aspects of construction and use.

Electrical behaviour

One of the largest areas of progress with ceramics was their application to electrical situations, where they can display a bewildering array of different properties.

Electrical insulation and dielectric behaviour

The majority of ceramic materials have no mobile charge carriers, and thus do not conduct electricity. When combined with strength, this leads to uses in power generation and transmission. Power lines are often supported from the pylons by porcelain discs, which are sufficiently insulating to cope with lightning strikes, and have the mechanical strength to hold the cables.

A sub-category of their insulating behaviour is that of the dielectrics. A good dielectric will maintain the electric field across it, without inducting power loss. This is very important in the construction of capacitors. Ceramic dielectrics are used in two main areas. The first is the low-loss high-frequency dielectrics, used in applications like microwave and radio transmitters. The other is the materials with high dielectric constants (the ferroelectrics). Whilst the ceramic dielectrics are inferior to other options for most purposes, they fill these two niches very well.

Ferroelectric, piezoelectric and pyroelectric

A ferroelectric material is one that can spontaneously generate a polarization in the absence of an electric field. These materials exhibit a permanent electric field, and this is the source of their extremely high dielectric constants.

A piezoelectric material is one where an electric field can be changed or generated by applying a stress to the material. These find a range of uses, principally as transducers - to convert a motion into an electric signal, or vice versa. These appear in devices such as microphones, ultrasound generators, and strain gauges.

A pyroelectric material develops an electrical field when heated. Some ceramic pyroelectrics are so sensitive that they can detect the temperature change caused by a person entering a room (approximately 40 microkelvin). Unfortunately, such devices lack accuracy, so they tend to be used in matched pairs - one covered, the other not - and only the difference between the two used.

Semiconductivity

There are a number of ceramics that are semiconductors. Most of these are transition metal oxides that are II-VI semiconductors, such as zinc oxide. Whilst there is talk of making blue LEDs from zinc oxide, ceramicists are most interested in the electrical properties that show grain boundary effects. One of the most widely used of these is the varistor. These are devices that exhibit the unusual property of negative resistance. Once the voltage across the device reaches a certain threshold, there is a breakdown of the electrical structure in the vicinity of the grain boundaries, which results in its electrical resistance dropping from several mega-ohms down to a few hundred. The major advantage of these is that they can dissipate a lot of energy, and they self reset - after the voltage across the device drops below the threshold, its resistance returns to being high.

This makes them ideal for surge-protection applications. As there is control over the threshold voltage and energy tolerance, they find use in all sorts of applications. The best demonstration of their ability can be found in electricity sub stations, where they are employed to protect the infrastructure from lightning strikes. They have rapid response, are low maintenance, and do not appreciably degrade from use, making them virtually ideal devices for this application.

Semiconducting ceramics are also employed as gas sensors. Various gases when pass over a polycrystalline ceramic its electrical resistance changes. With tuning to the possible gas mixtures, very inexpensive devices can be produced.

Superconductivity

Under some conditions, such as extremely low temperature, some ceramics exhibit *superconductivity* (a phenomenon related with the electrical resistance deacreasing to zero value when the temperature goes to low value). The exact reason for this is not known, but there are two major families of superconducting ceramics.

The complex copper oxides are exemplified by Yttrium barium copper oxide, often abbreviated to YBCO, or 123 (after the ratio of metals in its stoichiometric formula [[$YBa_2Cu_3O_{7-x}$]]). It is particularly well known because it is quite easy to make, its manufacture does not require any particularly dangerous materials, and it has a superconducting transition temperature of 90K (which is above the temperature of liquid nitrogen (77K)). The x in the formula refers to the fact that fully stoichiometric YBCO is not a superconductor, so it must be slightly oxygen-deficient, with x typically around 0.3.

The other major family of superconducting ceramics is magnesium diboride. It is currently in a family of its own. Its properties are not particularly remarkable, but it is chemically very different from all other superconductors in that it is neither a complex copper oxide nor a metal. Because of this difference, it is hoped that the study of this material will lead to fundamental insights into the phenomenon of superconductivity.

6.4.3.2 Processing of Ceramic Materials

Non-crystalline ceramics, being glasses, tend to be formed from melts. The glass is shaped when either fully molten, by casting, or when in a state of toffee-like viscosity, by methods such as blowing to a mould.

Crystalline ceramic materials are not amenable to a great range of processing. Methods for dealing with them tend to fall into one of two categories - either make the ceramic in the desired shape, by reaction in situ, or by forming powders into the desired

shape, and then sintering to form a solid body. A few methods use a hybrid between the two approaches.

In situ manufacturing

The most common use of this type method is in the production of cement and concrete. Here, the dehydrated powders are mixed with water. This starts hydration reactions, which result in long, interlocking crystals forming around the aggregates. Over time, these result in a solid ceramic.

The biggest problem with this method is that most reactions are so fast that good mixing is not possible, which tends to prevent large-scale construction. However, small-scale systems can be made by deposition techniques, where the various materials are introduced above a substrate, and react and form the ceramic on the substrate. This borrows techniques from the semiconductor industry, such as chemical vapour deposition and is very useful for coatings. These tend to produce very dense ceramics, but do so slowly.

Sintering-based methods

Definition: The bonding of adjacent surfaces of particles in a mass of powder or a compact by heating. Sintering strengthens a powder mass and normally produces densification and, in powdered metals, recrystallization.

The principle of sintering-based methods is simple. Once a roughly held together object (called a "green body") is made, it is baked in a kiln, where diffusion processes cause the green body to shrink. The pores in the object close up, resulting in a denser, stronger product. The firing is done at a temperature below the melting point of the ceramic. There is virtually always some porosity left, but the real advantage of this method is that the green body can be produced in any way imaginable, and still be sintered. This makes it a very versatile route.

There are thousands of possible refinements of this process. Some of the most common involve pressing the green body to give the densification a head start and reduce the sintering time needed. Sometimes organic binders are added to hold the green body together; these burn out during the firing. Sometimes organic lubricants are added during pressing to increase densification. It is not uncommon to combine these, and add binders and lubricants to a powder, then press. (The formulation of these organic chemical additives is an art in itself. This is particularly important in the manufacture of high performance ceramics such as those used by the billions for electronics, in capacitors, inductors, sensors, etc. The specialized formulations most commonly used in electronics are detailed in various books.

A slurry can be used in place of a powder, and then cast into a desired shape, dried and then sintered. Indeed, traditional pottery is done with this type of method, using a plastic mixture worked with the hands.

If a mixture of different materials is used together in a ceramic, the sintering temperature is sometimes above the melting point of one minor component - a liquid phase sintering. This results in shorter sintering times compared to solid state sintering.

6.4.3.3 Other applications of ceramics

A couple of decades ago, Toyota researched production of a ceramic engine which can run at a temperature of over (3300°C). Ceramic engines do not require a cooling system and hence allow a major weight reduction and therefore greater fuel efficiency.

Fuel efficiency of the engine is also higher at high temperature. In a conventional metallic engine, much of the energy released from the fuel must be dissipated as waste heat in order to prevent a meltdown of the metallic parts.

Despite all of these desirable properties, such engines are not in production because the manufacturing of ceramic parts is difficult. Imperfection in the ceramic leads to cracks. Such engines are possible in laboratory research, but current difficulties in manufacturing prevent them from being mass-produced.

6.5 Sol-Gel Processing

Definition: A method for the preparation of ceramic composites in which the reinforcement in the form of whiskers, fibers, weaves and particulates can be infiltrated with a low-viscosity sol—with or without the application of pressure. After gelation there exists an intimate interface between the phases.

Sol-Gel processing is used extensively in creating polymer ceramic composites and new generation of glasses. A combination of chemical reactions turns a homogeneous solution of reactants into an infinite molecular weight oxide polymer as seen in the following. Today's sol-gel processing is a form of nanostructure processing. It begins with a nanometer sized unit and undergoes reactions on the nanometer scale, resulting in a material with nanometer features.

Figure 6.6- An example to produce sols of silica of organic silicon compounds (Example of a general sol-gel reaction)
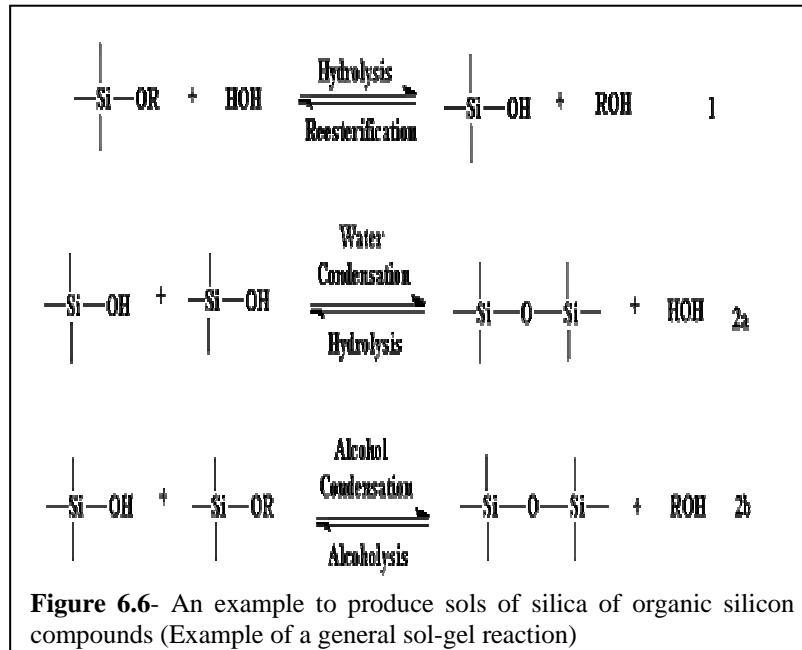
Sol-gel processing results in highly pure, uniform nanostructures. Sol-Gel Processing Steps (These are general steps, regardless of the starting materials): Mixing ; Gelling - defined empirically as the time when the solution shows no flow ; Shape Forming - can form three different shapes; thin film, fiber, bulk ; Drying ; Densification: in general thermal treatment, pyrolysis, sintering. **Advantages of the sol-gel process:** Simplicity, Flexibility, Low temperatures, Small capital investment.

Chapter 7

Polymers

➡ A substance made of many repeating chemical units or molecules. The term polymer is often used in place of plastic, rubber or elastomer.

➡ Also is a high molecular weight substance, natural or synthetic, which can be represented as a repeated small unit (monomer). A copolymer contains more than one type of monomeric unit.

➡ A molecule with a large molecular weight formed by the linking of 30 to 100,000 (or more) repeating units

➡ A high-molecular-weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit, the monomer (e.g., polyethylene, rubber, cellulose). Synthetic polymers are formed by addition or condensation polymerization of monomer. If two or more different monomers are involved, a copolymer is obtaining. Some polymers are elastomers, some plastics and other we call them thermosetting.

The aim of the chapter is to introduce to the main concepts and modern developments in polymer science and to bring the students to a basic level in this field related to thermal physics phenomena for polymeric systems.

In strict term, a *polymer* is a *substance* composed of molecules which have long sequences of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent, bonds.

Macromolecules are building by linking together monomer molecules through chemical reactions, the process by which this is achieved being known as *polymerization.*

Although the words *polymer* and *macromolecule* are usually interchangeably, the latter strictly defines the molecules of which the former is composed.

General definitions and basic terms encountered in polymer science: monomer, polymer, oligomer, macromolecule, monomeric unit, constitutitutive repeating unit (CRU), degree of polymerization; Molecular weights (molar masses) and weight distribution functions; Number-average molar mass and weight-average molar mass; most probable distribution; Polydisperse and monodisperse polymers. All are sketched in figure 7.1.

The large dimensions, chain structure and high flexibility of the macromolecules determine the main properties of polymers.

Conformations of the macromolecules: one set of configurations taken by CRU and the pendant groups in the macromolecular chain corresponding to minimum energy.

Configuration and configurationally isomerism: Local isomers and trans-cis-isomers; regular and irregular macromolecules; stereoregular polymers; tacticity and different types of tactic macromolecules; atactic, isotactic and sindiotactic polymers.

Possible states of polymer materials: high-elastic (rubbery), viscoelastic, glassy and crystalline states, liquid state.

There are major differences between low-molar-mass compounds and macromolecular compounds.

Figure- 7.1- Polymer definition
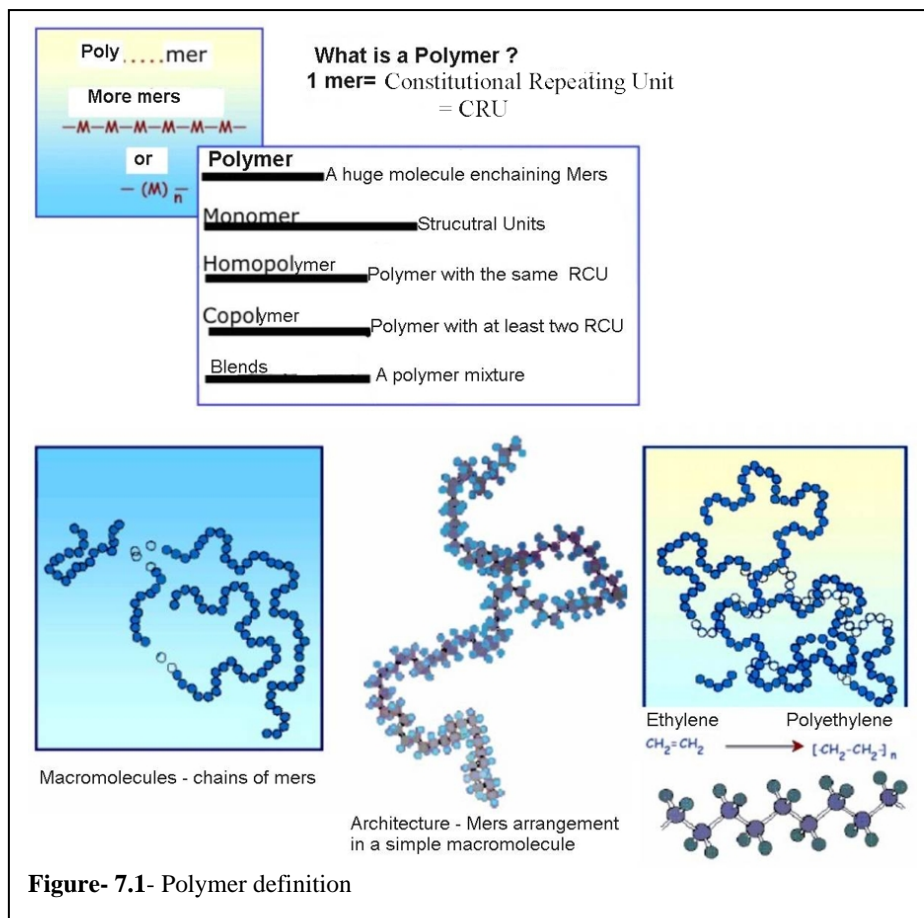
The polymers as industrial materials are finding as plastics, fibres, films, rubbers, resins, coatings, photoresists, displays in electronic industry.

Polymer science study all subjects related to synthesis and characterization of the polymer systems, the relationship with other fundamental disciplines.

7.1 Polymer Classification

There are different types of polymer classification: Single-strand and double strand (ladder and spiro) macromolecules and polymers; Linear, branched, ladder, comb-shaped, star-like and cross-linked polymers; Natural and synthetic polymers; Organic and inorganic polymers; homopolymers, copolymers, block- and graft-copolymers. Homo- and hetero-chain polymers; polyelectrolytes and ionogenic polymers (ionomers); Plastic, thermosetting, elastomers etc.

Figure 7.2-Polymer Classification – skeletal structures

Figure 7.3- Polymer Classification 1
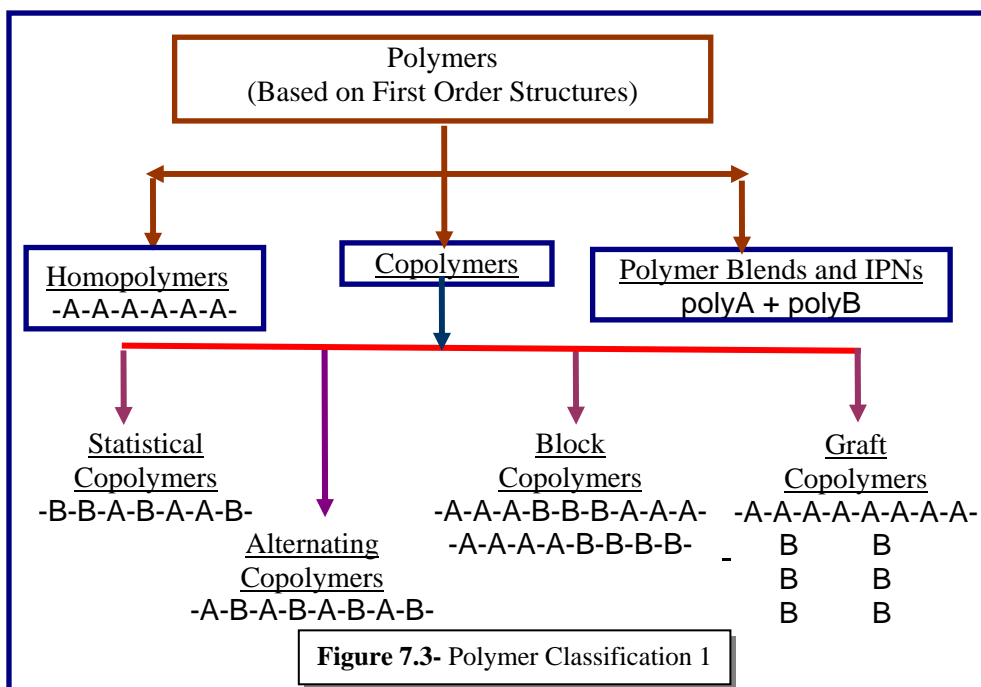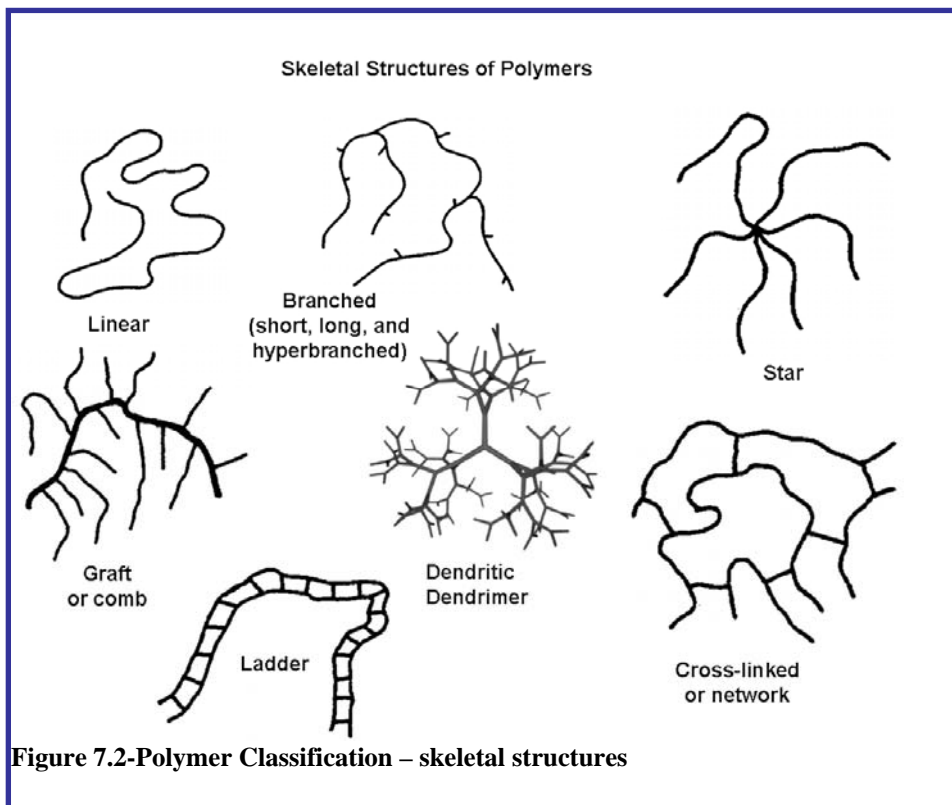
Homopolymer: Formal definition: a polymer derived from one species of monomer. Structure-based definition: a polymer whose structure can be represented by multiple repetition of single type of repeat unit which may contain one or more species of monomer units (structural units).

Copolymer: Formal definition: a polymer derived from more than one species of monomer. Structure-based definition: a polymer whose molecule contains two or more different types of repeat unit (polymers nine and ten in Table 7.5 usually are considered as homopolymers.)

Polymer Blends and IPNs: Linked together through secondary (physical) forces. IPNs: interpenetration polymer networks.

Thermoplastic: Heat moldable or processible, *e.g.*, plastics, fibers - linear or branched polymers.

Thermoset: Heat non-processible, *e.g.*, highly crosslinked polymers.

Elastomer: Polymers that can be stretched to high extensions and rapidly recover their original dimensions when the stress is released, *e.g.*, lightly crosslinked (chemically – vulcanized, physically – thermoplastic) polymers

Homochain polymers: Carbon-chain and silicon-chain polymers. Polyalkylenes (polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyacrylates etc.). Polyalkenylenes (polybutadiene, polyisoprene, their copolymers with alkylenes). Polyalkylenes (polyacetylene). Polyarylenes, polycycloalkenylenes. Polysilanes.

Heterochain polymers: (Oxygen, carbon) chain-polymers - polyethers (polyethylenoxide), polyesters (polyethylene thereftalate), polycarbonates. (Nitrogen, carbon)-chain polymers - polyamines, polyimines, polyamides, polyurethanes, polypyridinedyls. (Sulfur, carbon)-chain polymers - polythioethers, polysulfones.

Biopolymer: Polypeptides and proteins, DNA and RNA , polysaccharides etc.

Organic and inorganic polymers - polysiloxanes, polyorganophosphasenes.

Figure 7.4 -Polymer Classification 2

Monomer	Polymer	Nomenclature
(1) Ethylene $CH_2 = CH_2$	Polyethylene (PE) $+CH_2-CH_2+_n$	**I- Homopolymers**
(2) Propylene $CH_2=CH$ $\vert$ CH_3	Polypropylene (PP) $+CH_2-CH+_n$ $\vert$ CH_3	
(3) Tetrafluoroethylene $CF_2=CF_2$	Polytetrafluoroethylene (PTFE) $+CF_2-CF_2+_n$	**Teflon**
(4) Styrene $CH_2=CH$ $\vert$ (phenyl)	Polystyrene (PS) $+CH_2-CH+_n$ $\vert$ (phenyl)	
(5) Methyl methacrylate CH_3 $\vert$ $CH_2=C$ $\vert$ $C=O$ $\vert$ OCH_3	Poly(methyl methacrylate) (PMMA) CH_3 $\vert$ $+CH_2-C+_n$ $\vert$ $C=O$ $\vert$ OCH_3	**II**
(6) Vinyl chloride $CH_2=CH$ $\vert$ Cl	Poly(vinyl chloride) (PVC) $+CH_2-CH+_n$ $\vert$ Cl	
(7) Vinyl acetate $CH_2=CH$ $\vert$ O $\vert$ $C=O$ $\vert$ CH_3	Poly(vinyl acetate) (PVA) $+CH_2-CH+_n$ $\vert$ O $\vert$ $C=O$ $\vert$ CH_3	
(8) Ethylene glycol $HO-CH_2-CH_2-OH$ Ethylene oxide ⟶ △	Poly(ethylene glycol) (PEG) $HO+CH_2-CH_2-O+H$ $+CH_2-CH_2-O+$ Poly(ethylene oxide)	**III** **Carbowax**
(9) Ethylene glycol $HO-CH_2-CH_2-OH$ and terephthalic acid O O $\Vert$ $\Vert$ $HO-C-$(phenyl)$-C-OH$	Poly(ethylene terephthalate) (PET)* O O $\Vert$ $\Vert$ $+O-CH_2-CH_2-O-C-$(phenyl)$-C+_n$	**Mylar, Dacron**
(10) Hexamethylene diamine $H_2N-(CH_2)_6-NH_2$ and sebacic acid O O $\Vert$ $\Vert$ $HO-C(CH_2)_8-C-OH$	Poly(hexamethylene sebacate) (nylon 6.10)* H H $\vert$ $\vert$ $+N+(CH_2)_6N-C+(CH_2)_8C+_n$ $\Vert$ $\Vert$ O O 6 carbons 10 carbons	**Ultramid**

Figure 7.5 Polymers- Nomenclature, Some trademark are specified

7.2 Physical states

At a given temperature, and following a given processing route, polymeric materials can be found in a variety of physical states (figure 7.6)

Liquid. Polymer melts and solutions are liquids, but they often are very viscous and show marked viscoelastic properties.

Glass. Because of the difficulty of crystallizing polymers, polymer glass are very common. Familiar examples include polystyrene and PMMA (organic glass)

Crystalline. Polymers can sometimes crystallise, but crystallisation is usually not complete, owing to kinetic limitations and the presence of quenching disorder. In such semi-crystalline materials very small crystals exist in a matrix of amorphous material, which can be in either a liquid-like or glassy state. Semicrystalline polymers examples: Polyethylene, many synthetic polymers, also biopolymers such starch.

Liquid Crystalline. Some polymers are built rather of rigid macomolecules, which can line up to form liquid crystalline phases. These can form the basis of very strong engineering materials like aramides (Kevlar).

Figure 7 6- Some of physical states in polymers
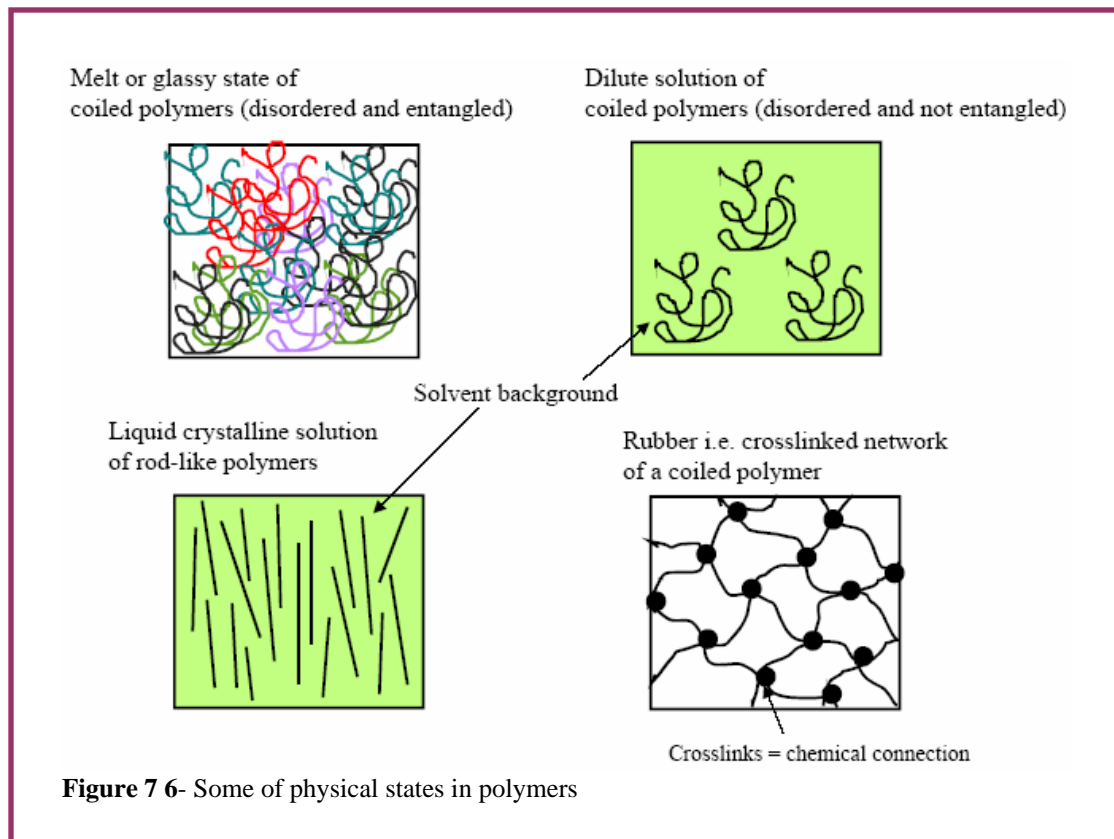
7.3 Synthesis and Transformations in Polymers

Synthesis of Polymers. Two terms are used for synthesis: Polymerization and polycondensation with subchapters-Thermodynamics of polymerization and kinetics (chemical, photochemical initiation, chain propagation, termination and chain transfer).

Thermodynamics defines conditions if a polymerization takes place. Molar masses and molar-mass-distribution of polymer obtained by polymerization are dependent of the reaction mechanisms and of the surroundings.

Other subjects encountered (just counted):

- Reactivity of monomers and radicals. Radical polymerization Radical copolymerization. Equation copolymer composition. Relative reactivities of monomers and radicals.
- Polymerization in bulk, solution, emulsion and suspension.
- Cationic polymerization. Monomers and catalysts. Elemental stages of polymer synthesis by cationic polymerization. Role of the solvents.
- Anionic polymerization. Monomers and catalists. "Living" polymers.
- Ionic and coordination polymerization. Homogenous and heterogenous catalysts. Ziegler-Natta catalysts. Stereoregularity and its control. Optically active polymers.
- Polycondensation. Types of polycondensation reactions. Main difference between polymerization and polycondensation. Thermodynamic polycondensation.
- Melt, solution and interfacial polycondensation
- Degradation of polymers. Mechanism of chain and random degradation, depolymerization.
- Thermal, oxidative, thermo-oxidative and photochemical degradation.
- Crosslinking of polymers. Aging of polymers. Durability.
- Principles of polymer stabilization. Stabilizers. Modification of polymers using block- and graft copolymerization.

7.4 Thermodynamics related to polymers

7.4.1 Single polymer chain

- Flexibility of a polymer chain. Flexibility mechanisms: rotational-isomeric, persistent, freely-jointed. Persistent length of a polymer chain, Kuhn segment length. Stiff and flexible chains
- Ideal polymer coil. Gaussian distribution for the end-to-end vector. Radius of gyration of ideal polymer coil. Polymer density distribution inside the coil. Polymer coils in dilute solutions.
- Helical macromolecules. Helix-coil transition
- Ring macromolecules.Topological restrictions, topological properties of polymer chains. Scaling methods in polymer science.

7.4.2 Polymer solutions

- Collapse of macromolecules in poor solvents (coil-globule transition).
- Volume interactions. Concept of θ-temperature.
- Excluded volume problem. Properties of coils with excluded volume. Scale invariance of properties and concept of universality
- Dilute, semi-dilute and concentrated polymer solutions. Flory theory. Diagram of states for polymer solutions.
- Thermodynamics of polymer behaviour in the solution. Constitutive equation. Phase diagram for polymer-solvent systems. Dependence of solubility on the chain length. Method of fractional precipitation. Chromatography of polymers.
- Osmotic pressure of polymer solutions. Determination of the number - average molar mass from the osmometry data.
- Hydrodynamics of macromolecules in solution. Viscosity of dilute polymer solutions.Hydrodynamic interactions. Models of permeable and impermeable

polymer coils. Connection of characteristic viscosity with molar mass and average dimensions of macromolecules.

➢ Elastic light scattering by dilute polymer solutions. Determination of molecular masses and coil dimesions by elastic light scattering. Zimm diagrams. Dynamic light scattering, determination of diffusion coefficient of coils.

➢ Ion-containing macromolecules (polyacids, polybases and their salts). Quantitative characteristics of the strength of polyacids and polybases. Polyelectrolytes in aqueous solutions. Debye-Huckel screening of electroelastic interactions. Counterion condensation and binding. Notion of electrostatic persistent length. Polyampholytes. Ionomers.

➢ Concentrated polymer solutions. Association of macromolecules and structure formation in concentrated solutions. Liquid-crystalline solutions of stiff-chain macromolecules

7.5 Structure and Physical Properties of Solid Polymers

The peculiarities of molecular structure of polymers give the basic principles of molecular packing, which is different than in crystals. There are amorphous and crystalline polymers but their description is not similar with regular solids. Two-phase model. The crystallization of polymers, Melting point, and glass transition are dependent of molecular and supramolecular structure, molar mass. Some of characteristics are sketched in next sections

7.5.1 Tacticity

Tacticity is simply the way pendant groups are arranged along the backbone chain of a polymer.

To illustrate tacticity, we are going to use one of those vinyl polymers, particularly polystyrene.

In fig.7.7 polystyrene is drawn as flat picture and real picture where carbon chain has zig-zag connections as required for chemical bonding. The pendant groups (phenyls and hydrogen) tend to be point away from the chain. In that picture, all the phenyl groups are located on the same side of the polymer chain, but they do not have to be this way. The pendant phenyl groups can be on either the right or left side of the chain. If all of the phenyl groups are on the same side of the chain, we say the polymer is *isotactic*.

If the phenyl groups come on alternating sides of the chain, the polymer is said to be *syndiotactic*. If the phenyl groups are on both sides and right and left follow in no particular order, in a random fashion, than we say the polymer is *atactic*.

Note: Isotactic polystyrene isn't produced commercially. We're just using it as a hypothetical example. Other polymers can be isotactic, though.

When polymers have a regular arrangement of their atoms, like in the isotactic and syndiotactic polystyrene, it is very easy for them to pack together into crystals and fibres. But if there is no order, as is the case with the atactic polystyrene, packing can't occur. This is because molecules pack best with other molecules of the same shape.
(Try packing a box full of identical objects, and different objects, and we'll get the idea.)

This can be a big problem in some polymers. Tacticity makes a big difference in polystyrene. Free radical vinyl polymerization normally can only produce atactic poly-
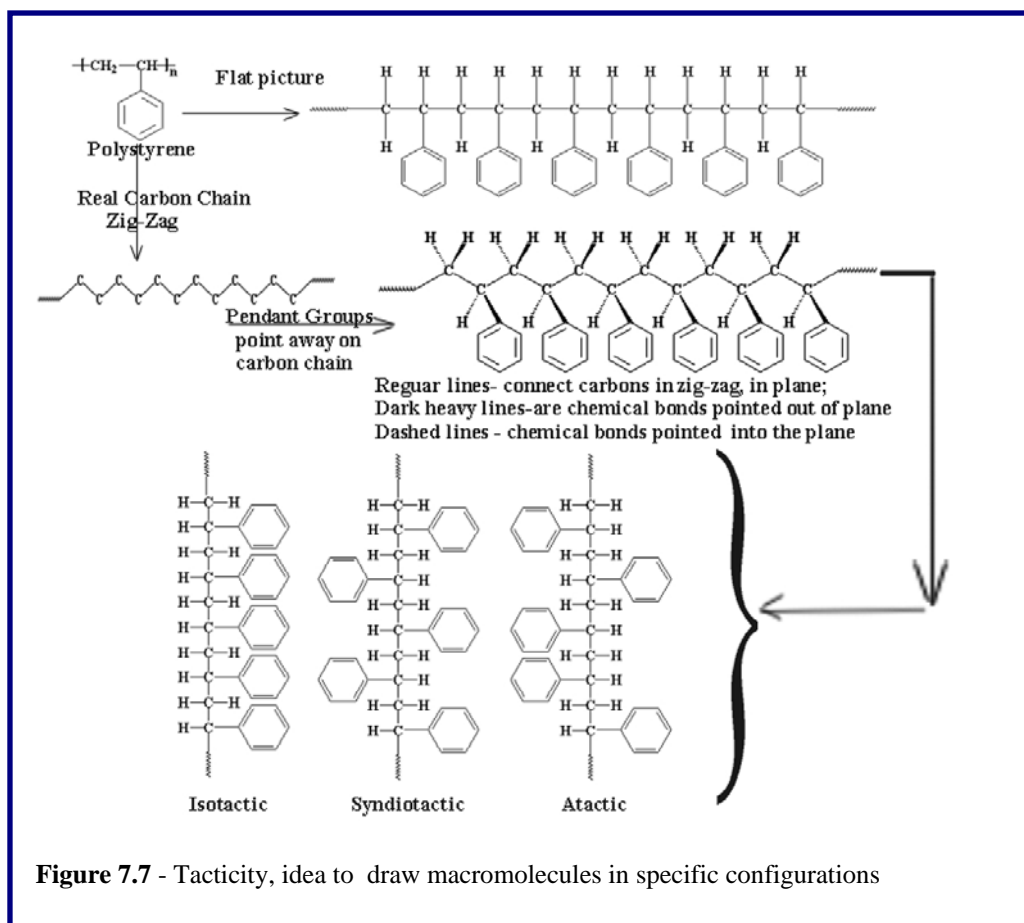
Figure 7.7 - Tacticity, idea to draw macromolecules in specific configurations

mers.   Atactic polystyrene is a hard plastic, and completely amorphous. It can't crystallize at all.

Then metallocene catalysis vinyl polymerization was invented and with it syndiotactic polystyrene became possible. It is not only crystalline, but it doesn't melt until 270 °C.

Another vinyl polymer, polypropylene is a good example of the effects of tacticity. At first, there was only atactic polypropylene. It is kind of soft and sticky, not very strong, and not much good for anything. Then along came two scientists named Robert L. Banks and J. Paul Hogan. They invented a new type of vinyl polymerization which ended up being named Ziegler-Natta polymerization. This new process could make isotactic polypropylene. This new polypropylene could crystallize, and could be used to make fibers, for things like indoor-outdoor carpeting.

7.5.2 Polymer Crystallinity

It is expected the polymers to line up all stretched out. But they can't always stretch out that straight. In fact, very few polymers can stretch out perfectly straight, and those are ultra-high molecular weight polyethylene, and aramids like Kevlar and Nomex. Most polymers can only stretch out for a short distance before they fold back on themselves.(figure 7. 8 A)

For polyethylene, the length the chains will stretch before they fold is about 100 angstroms. But not only do they fold like this. Polymers form stacks of these folded chains. There is a picture of a stack, called a lamella, (figure 7.8 B).

Sometimes part of a chain is included in this crystal, and part of it isn't. When this happens we get the kind of mess as in figure 7.8 C. The lamella is no longer neat and tidy, but sloppy, with chains hanging out of it everywhere!

Of course, being indecisive, the polymer chains will often decide they want to come back into the lamella after wandering around outside for awhile. (figure 7 D)

This is the *switchboard model* of a polymer crystalline lamella. When a polymer chain doesn't wander around outside the crystal, but just folds right back in on itself, like we saw in the first pictures, that is called the *adjacent re-entry model*.

7.5.3 Amorphousness and Crystallinity

If we look at those pictures up there, we can see that some of the polymer is crystalline, and some is not! Most crystalline polymers are not crystalline. The chains or parts of chains, that aren't in the crystals, have no order to the arrangement of their chains. They are in the *amorphous state*. Therefore, a crystalline polymer really has two components: the crystalline portion and the amorphous portion. The crystalline portion is in the lamellae, and the amorphous potion is outside the lamellae. If we look at a wide-angle picture of what a lamella looks like, we can see how the crystalline and amorphous portions are arranged.

Lamella grow like the spokes of a bicycle wheel from a central nucleus. (Sometimes call the lamella *lamellar fibrils*.) They really grow out in three dimensions, so they really look more like sphere than a wheel. This whole sphere is called a *spherulite*

In a sample of a crystalline sample there are many billions of spherulites. (figure 7.8 E). In between the crystalline lamellae there are regions when there is no order to the arrangement of the polymer chains. These disordered regions are the amorphous regions. As we can also see in the picture, a single polymer chain may be partly in a crystalline lamella, and partly in the amorphous state. Some chains even start in one lamella, cross the amorphous region, and then join another lamella. These chains are called *tie molecules*.

No polymer is crystalline. If we are making plastics, crystallinity makes a material strong, but it also makes it brittle. A completely crystalline polymer would be too brittle to be used as plastic. The amorphous regions give a polymer *toughness*, that is, the ability to bend without breaking.

However, for making fibres, the polymers must be as crystalline as possible. This is because a fibre is really a long crystal.

Many polymers are a mix of amorphous and crystalline regions, but some are highly crystalline and some are highly amorphous. Here are some of the polymers that tend toward the extremes:

Some Highly Crystalline Polymers: Polypropylene, Syndiotactic polystyrene, Nylon, Kevlar and Nomex, Polyketones.

Some Highly Amorphous Polymers: Poly(methyl methacrylate) Atactic polystyrene, Polycarbonate, Polyisoprene, Polybutadiene

Therefore, some polymers are highly crystalline and some are highly amorphous.

There are two important factors, polymer structure and intermolecular forces.

The polymer's structure affects crystallinity. If it is regular and orderly, it will pack into crystals easily. If not, it will not. It helps to look at polystyrene to understand how this works.

As we saw in figure 7.7, there are two kinds of polystyrene. There is atactic polystyrene, and there is syndiotactic polystyrene. One is crystalline, and one is very amorphous.

Figure 7.8- Packing macromolecules in a polymer. From lin up chain to lamella and spherullites
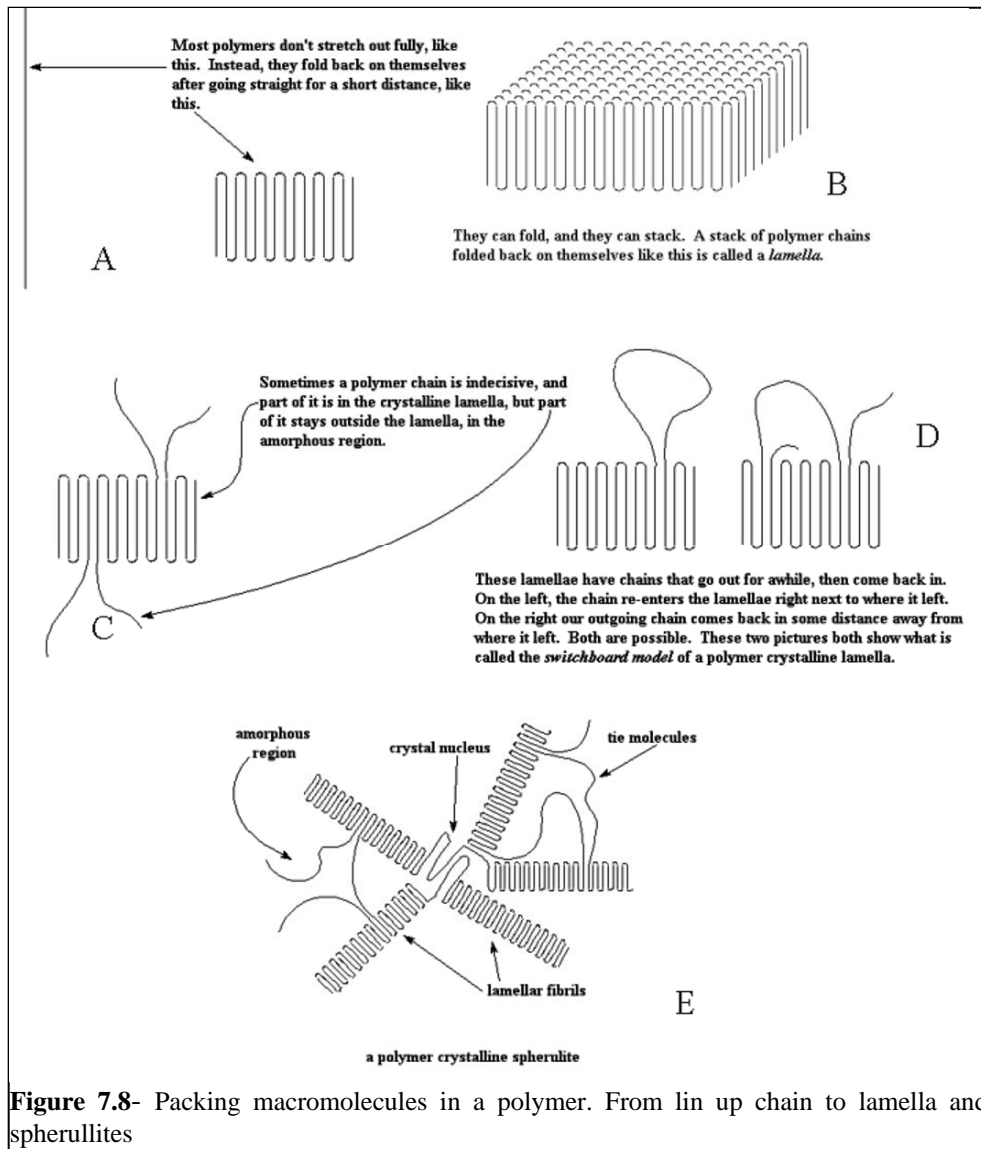
Syndiotactic polystyrene is very orderly, with the phenyl groups falling on alternating sides of the chain. This means it can pack very easily into crystals.

But atactic styrene has no such order. The phenyl groups come on any which side of the chain they please. With no order, the chains can't pack very well. The atactic polystyrene is very amorphous.

Other atactic polymers like poly(methyl methacrylate) and poly(vinyl chloride) are also amorphous. Stereoregular polymers like isotactic polypropylene and polytetrafluoroethylene are highly crystalline.

Polyethylene is another good example. It can be crystalline or amorphous. Linear polyethylene is nearly 100% crystalline. But the branched stuff just can't pack the way the linear stuff can, so it is highly amorphous.

7.5.4 Crystallinity and intermolecular forces

Intermolecular forces can be a big help for a polymer if it wants to form crystals.

A good example is nylon. we can see from the picture (figure 7.9) that the polar amide groups in the backbone chain of nylon 6,6 are strongly attracted to each other.

They form strong hydrogen bonds. This strong binding holds crystals together. Polyesters are another example. Let's look at the polyester we cal poly(ethylene terephthalate). The polar ester groups make for strong crystals. In addition, the aromatic rings like to stack together in an orderly fashion, making the crystal even stronger.

In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

The polar ester groups in this poly(ethylene terephthalate) hold the polyester into strong crystals.

The phenyl rings in poly(ethylene therephthalate) stack in an orderly fashion to form strong crystals.
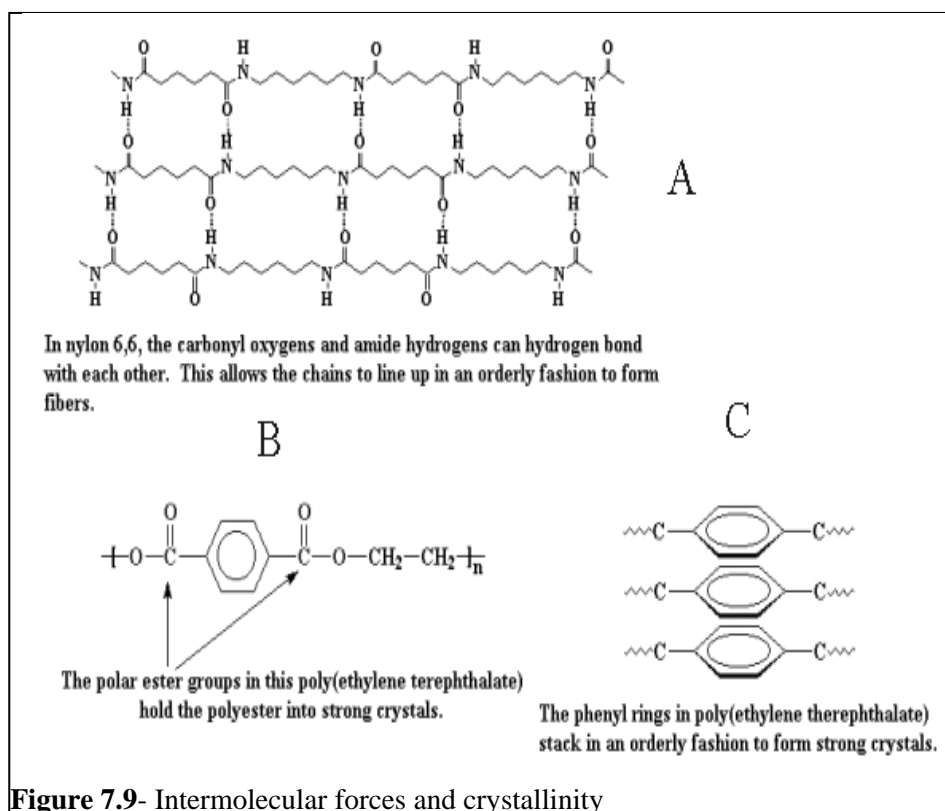
Figure 7.9- Intermolecular forces and crystallinity

Many polymers contain lots of crystalline material and lots of amorphous material. There is a way we can find out how much of a polymer sample is amorphous and how much is crystalline. This method has its own page, and it's called differential scanning calorimetry (see chapter dealing with calorimetry)

7.6 Melting and glass transition in polymers

There are a lot of important differences between the glass transition and melting.

The melting is something that happens to a crystalline polymer, while the glass transition happens only to polymers in the amorphous state. A given polymer will often have both amorphous and crystalline domains within it, so the same sample can often show a melting point *and* a Tg. However, the chains that melt are not the chains that undergo the glass transition.

There is another big difference between melting and the glass transition. When heat a crystalline polymer at a constant rate, the temperature will increase at a constant rate. The heat amount of heat required to raise the temperature of one gram of the polymer one degree Celsius is called the *heat capacity* as defined for any substance. When the polymer reaches its melting point the temperature will hold steady for awhile even though there is adding heat to the polymer. It will hold steady until the polymer has completely melted. Then the temperature of the polymer will begin to increase once again. The temperature rising stops because melting requires energy. All the energy is add to a crystalline polymer at its melting point goes into melting, and none of it goes into raising the temperature. This heat is called the **latent heat of melting**. (The word **latent** means hidden.)

Once the polymer has melted, the temperature begins to rise again, but now it rises at a slower rate. The molten polymer has a higher heat capacity than the solid crystalline polymer, so it can absorb more heat with a smaller increase in temperature. Two things happen when a crystalline polymer melts: It absorbs a certain amount of heat, the latent heat of melting, and it undergoes a change in it's heat capacity. Any change brought about by heat, whether it is melting or freezing, or boiling or condensation, which has a change in heat capacity, and a latent heat involved, is called a **first order transition**.

But when you heat *an amorphous polymer* to its Tg, something different happens. First when heat it, and the temperature goes up. It goes up at a rate determined by the polymer's heat capacity. When is reach the Tg, the temperature doesn't stop rising. There is no latent heat of glass transition. The temperature keeps going up. But the temperature doesn't go up at the same rate above the Tg as below it. The polymer does undergo an increase in its heat capacity when it undergoes the glass transition. Because the glass transition involves change in heat capacity, but it doesn't involve a latent heat, this transition is called **second order transition**

The plots (figure 7.10) show the amount of heat added to the polymer on the y-axis and the temperature that you'd get with a given amount of heat on the x-axis.
The plot on the left shows what happens when you heat a 100% crystalline polymer. It can be seen that it is discontinuous. That is the melting temperature. At that break, a lot of heat is added without any temperature increase at all. That's the latent heat of melting. We see the slope getting steeper on the high side of the break. The slope of this kind of plot is equal to the heat capacity, so this increase in steepness corresponds to our increase in heat capacity above the melting point.

In the plot on the right, which shows what happens to a 100% amorphous polymer when you heat it, we don't have a break. The only change we see at the glass transition temperature is an increase in the slope, which means, of course, that we have an increase in heat capacity. We can see a heat capacity change at the Tg, but no break, like in the plot for the crystalline polymer. As said before, there is no latent heat involved with the glass transition. And this is the difference between a first order transition like melting, and a second order transition like the glass transition.

A polymer chain that can move around fairly easily will have a very low Tg, while one that doesn't move so well will have a high one. This makes sense. The more easily a polymer can move, the less heat it takes for the chains to commence wiggling and break out of the rigid glassy state and into the soft rubbery state.

What makes one polymer move more easily than another does? Several things affect the mobility of a polymer chain.

A heat vs. temperature plot for an crystalline polymer,
on the left; and a amorphous polymer on the right.

Figure 7.10
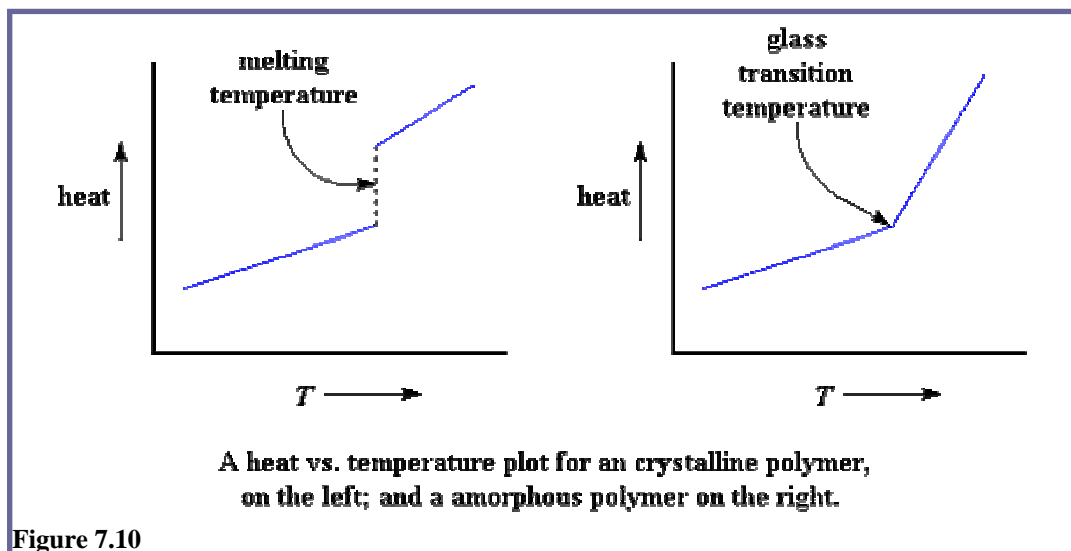
Backbone Flexibility

This is the biggest and most important one to remember. The more flexible the backbone chain is, the better the polymer will move, and the lower it's Tg will be. Let's look at some examples. The most dramatic one is that of **silicones**, and let us takes a look at one called polydimethylsiloxane.
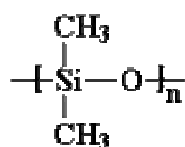
polydimethylsiloxane

This backbone is so flexible that polydimethylsiloxane has a Tg way down at -127^0 C. This chain is so flexible that it's a liquid at room temperature, and it's even used to thicken shampoos and conditioners.

At another extreme, poly(phenylene sulfone).
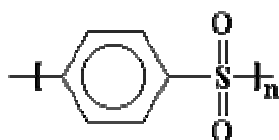
poly(phenylene sulfone)

This polymer's backbone is just plain stiff. It's so rigid that it doesn't have a Tg.

We can heat this to over 500^0 C and it will still stay in the glassy state. It will decompose from all the heat before it lets itself undergo a glass transition! In order to make a polymer that's at all processable we have to put some flexible groups in the backbone chain. Ether groups work nicely.
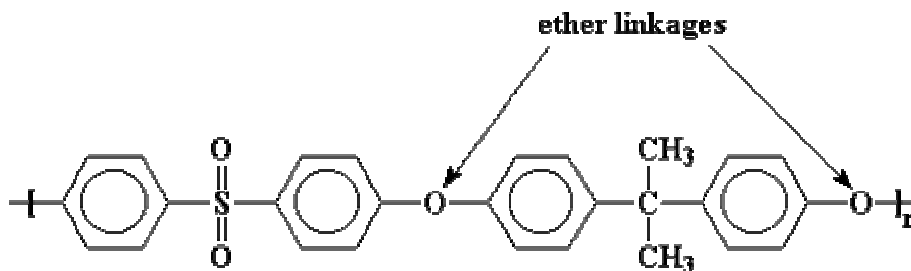
a poly(ether sulfone)

Polymers like this are called **poly(ether sulfones)**, and those flexible ether groups bring the Tg of this one down to a more manageable 190^0 C.

Pendant Groups (Fish Hooks and Boat Anchors)

Pendant groups have a big effect on chain mobility. Even a small pendant group can act as a fishhook that will catch on any nearby molecule when the polymer chain tries to move like corkscrew. Pendant groups also catch on each other when chains try to slither by each other. One of the best pendant groups for getting a high Tg is the big bulky adamantyl group. And adamantyl group is derived from a compound called adamantane.

adamantane

an adamantyl group attached to an R group.
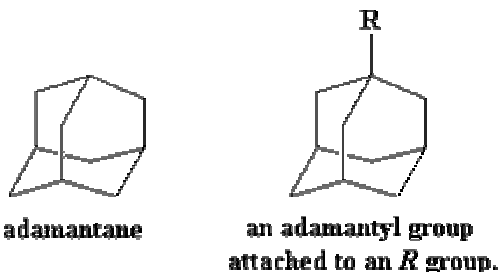
A big group like this does more than just act like hook that catches on nearby molecules and keeps the polymer from moving. It's a downright boat anchor. Not only does it get caught on nearby polymer chains, it's sheer mass is such a load for it's polymer chain too move that it makes the polymer chain move much more slowly. To see how much this affects the Tg, just take a look at two **poly(ether ketones)** one with an adamantane pendant group and one without.
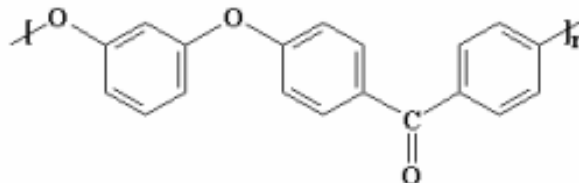
This poly(ether ketone) has a Tg of 119 ºC
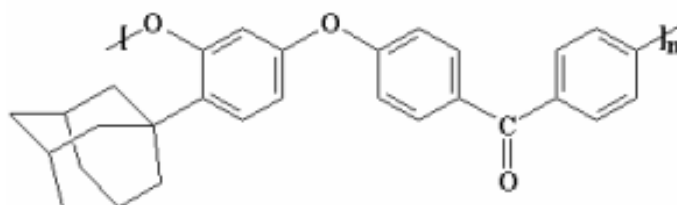
The Tg of the polymer on the top is already decent at 119^0C, but the adamantyl group raises even higher, to 225^0 C.

Pendant Groups:

Big bulky pendant groups can lower the Tg, too. The big

This poly(ether ketone) has a Tg of 225 ºC

pendant groups limit how closely the polymer chains can pack together. The further they are from each other, the more easily they can move around. This lowers the Tg, in the same way a **plasticizer** does. The fancy way to say(see Feynman lectures) that there is more room between the polymer chains is to say there is more *free volume* in the polymer. The more free volume, the lower the Tg generally. We can see this with a series of **methacrylate** polymers.

We can see a big drop each time we make that pendant alkyl chain one carbon longer. We start out at 120°C for poly(methyl methacrylate), but by the time we get to poly(butyl methacrylate) the Tg has dropped to only 20^0C, pretty close to room temperature.

$$\begin{array}{cccc}
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
-\!\!\!\begin{array}{c}|\\ \text{CH}_2-\text{C}\\ |\end{array}\!\!\!-_n & -\!\!\!\begin{array}{c}|\\ \text{CH}_2-\text{C}\\ |\end{array}\!\!\!-_n & -\!\!\!\begin{array}{c}|\\ \text{CH}_2-\text{C}\\ |\end{array}\!\!\!-_n & -\!\!\!\begin{array}{c}|\\ \text{CH}_2-\text{C}\\ |\end{array}\!\!\!-_n \\
\text{C}=\text{O} & \text{C}=\text{O} & \text{C}=\text{O} & \text{C}=\text{O} \\
\text{O} & \text{O} & \text{O} & \text{O} \\
\text{CH}_3 & \text{CH}_2 & \text{CH}_2 & \text{CH}_2 \\
 & \text{CH}_3 & \text{CH}_2 & \text{CH}_2 \\
 & & \text{CH}_3 & \text{CH}_2 \\
 & & & \text{CH}_3
\end{array}$$

Poly(methyl methacrylate)
Tg = 100-120 ºC

Poly(ethyl methacrylate)
Tg = 65 ºC

Poly(propyl methacrylate)
Tg = 35 ºC

Poly(butyl methacrylate)
Tg = 20 ºC
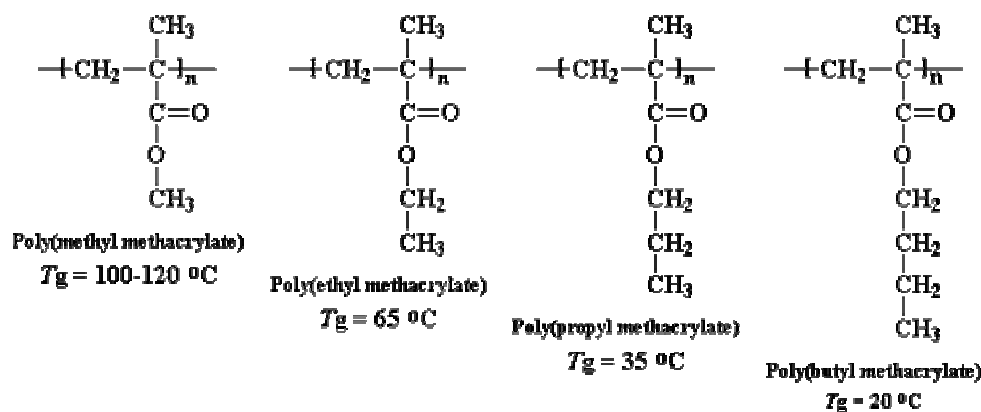
7.7 Polymer networks and gels

Many times the word gel is heard in our everyday life. Probably everyone is familiarized with such terms like silica gel, gel electrophoresis, or gel permeation chromatography. Lets just take a look at what the market does offer these days: ----a gel cake---------->

➡ Bath gels, rejuvenating gels, hair styling gels, and all you need for your personal care.
➡ Sun soothe sunscreen and after-sun gel made to help to reduce skin ageing due to extended exposure to the sun.
➡ A new gel to be used as an insect repellent.
➡ Gel used to make contact lenses.
➡ Pain killing gel and anti-inflammatory agents.
➡ Comfy gel soles for shoes.
➡ Super absorbent gel that absorbs 400 times its weight in water, to be used in place of soil for plants contained in vessels.
➡ Gel made of a thermoplastic resin to use for burning candles, with no dripping wax.
➡ Gel mattress that ensures a pleasant sleep. And so on...

One can assume that gels' application range is as huge as the inventors' imagination, and that is right: gels are everywhere.

The first thing we must bear in mind when speaking about gels is crosslinking.

Crosslinked polymers are insoluble in all solvents, but they can be swollen at different extent, depending on their crosslinking degree. In general, polymers become crosslinked within a solution

Depending on the amount of dissolved polymer, solutions can be dilute or concentrated. Let's take a look at the below pictures. There is no interaction at all between the dissolved coils in dilute solutions, as shown in the figure on the left. Even when the solution is highly viscous, such coils remain as unique entities moving freely among the solvent molecules, without exerting forces of any kind on each other. Consequently, no links can be established between them, as interference with each other is virtually non-existent.
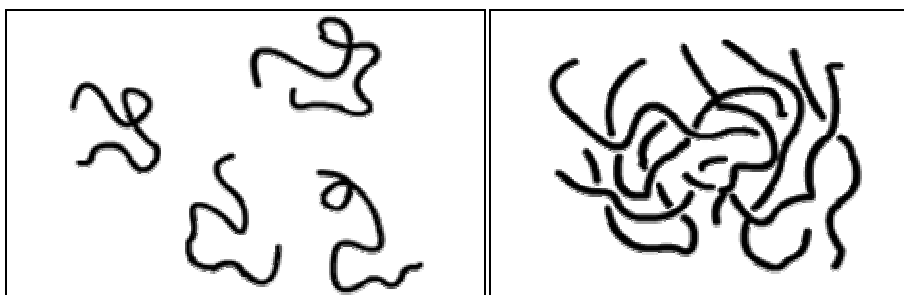
However, the situation is pretty different in concentrated solutions, represented on the right. As the number of molecules is increased, they are forced to come closer and interaction between them turns noticeable. The summation of intermolecular forces becomes a key factor, and the whole polymer mass no longer will show the same behaviour it displayed when coils were surrounded by vast domains of solvent.

Therefore, the viscosity increases drastically, and the solution begins to exhibit a transition from a concentrated solution to a gel, because such coils will establish linkages at some points, constituting gradually an only giant crosslinked coil, called a macroscopic gel. Such macroscopic gel is pictured schematically below, showing the crosslinks as solid circles.
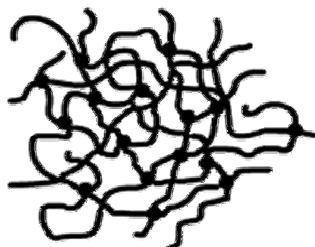
Have you asked yourself how these linkages between coils can be established? Surely, there must be some kind of bond able to hold the molecules together. Well, indeed there is. Usually such molecules become linked in two ways: through secondary interactions (secondary valence gels) and by means of covalent bonds (covalent gels). Let's discuss each of them in detail.

7.7.1 Secondary Valence Gels

Secondary interactions are reversible, and not only occur between different coils (intermolecular linkages), but also within the same coil (intramolecular linkages). Look at the pictures below. The one on the left shows a coil with intramolecular associations only. The picture on the right shows two coils with both intra and intermolecular linkages. The latter are represented by solid circles.
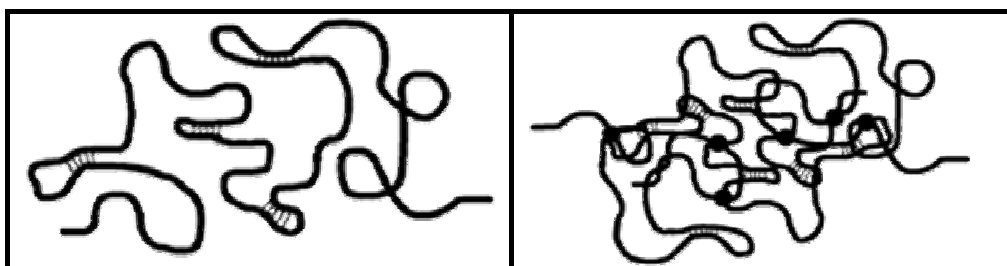
Normally, the formation of secondary valence gels depends on two factors: the strength of the intermolecular forces, which is a measure of the tendency of the polymer to establish non-covalent linkages, and the quality of the solvent.

If we consider the intermolecular forces, you might ask what type of polymers can form gels by means of secondary interactions when the solvent is water. Well, to find it out you could try an easy experiment in your kitchen. All you need is a small bowl and some gelatin previously stored in your refrigerator, like the delicious one that appears on the right. Now put a bit of gelatin into the bowl and warm it up a little. If you use a microwave, one minute is more than sufficient. Now look at the bowl. What happened?

Gradually the gelatin melted and became a viscous liquid! But this is no surprisingly enough. Let the gelatin to cool down, and... it will solidify again! Why?

Let's see. In the first place, it would help to understand what exactly gelatin is made of. Did you know it's mainly protein collagen, i.e. a natural polymer? This means that there are many amide groups in the backbone to establish bonds with each other.

Those are not covalent bonds, of course, but a particular kind of reversible linkage called hydrogen bond. The picture below shows those non-covalent linkages between protein chains. Hydrogen bond is a strong interaction that however is usually broken upon warming. Think about water: you need to warm it up to 100°C if you want it boiled! That's the temperature in which all the hydrogen bonds are broken, and the free water molecules switch from their liquid state to a gas state.
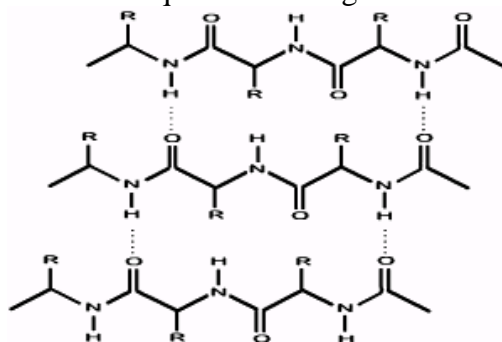
Also another natural occurring polymers form gels through secondary interactions, such as pectin, agar, and starch. That's why they are widely used in industry as thickeners, giving consistency to many foods.

However PVC, not a natural polymer indeed, can also form secondary valence gels if you choose an appropriate solvent. When PVC is mixed with such liquids called plasticizers (like phthalic, adipic, or sebacic acid esters for example) it constitutes thermo-reversible gels, commonly called "plasticized PVC", with rubbery or leathery consistency.

But what is an "appropriate" solvent when dealing with thermo-reversible secondary valence gels? Just think about it. Usually poor solvents ensure an incomplete solvation, hence a solvation equilibrium exists. As molecules remain tightly coiled in the presence of such solvents, they mainly establish intramolecular rather intermolecular linkages. The crosslinking density is therefore low, and the bonds established by secondary interactions are easily broken.

7.7.2 Covalent Gels

Up to now we've seen how secondary valence gels can be broken without difficulty when the secondary interactions that take place between coils are withdrawn. But can you break up covalent bonds in such an easy way? Well, the answer is no. There isn't any solvent powerful enough to cause the breaking of covalent bonds. Moreover, this type of linkage cannot be broken even by heat. Let us remember crosslinked thermosets. If it could, there wouldn't be increasing interest in the development of thermoplastic elastomers, for example.

Thus, covalent gels can be obtained in two ways: first, we can swell a previously crosslinked polymer, choosing a suitable solvent. Here's one example: polyacrylamide. It's soluble in water, but crosslinked polyacrylamide is not; it can only be swollen in water. If we prefer to crosslink a functional dissolved polymer we add another bi or multi-functional compound into the solution. Some examples are the epoxy resins or the diene polymers.

7.7.3 Mechanical Properties

As in gels, the coils remain fixed in space, not exchanging places as they do in concentrated solutions, the gel will not flow. That is an important property: imagine how it is for such products that are sold in tubes, such as toothpastes, cosmetics, or pharmaceuticals.

However, we might guess that the presence of the solvent within the reticular structure must have something to do with the behavior of such particular substances. Unlike solid molecules, each gel molecule could be considered as a dilute solution. This is a considerable advantage: it means that the coil segments can move rather freely, depending on the segment chemical structure, the concentration, the coil density, and obviously, the crosslinking degree. This movement is often called micro-brownian motion. That's why gels, under the influence of any deforming force, can react with an elastic retractive force. We then say gels have elasticity. Like solid polymers, the strength of gels increases with the crosslinking degree, i.e. their hardness and toughness turn higher. The properties of the solid state are usually maintained when the system goes into gel. This means that brittle polymers will lead to brittle gels, and rubbery polymers will form gels with certain toughness.

But in a general sense, are gels mechanically powerful? Can they be compared to solid bodies? To find a reasonable answer we analize the role that the solvent plays in such a system.

In solid polymers chains are close enough together. This means that the material can resist well any deformation without breaking up. But when solvent molecules come into play, as in gels, they penetrate among the chains, loosing them apart. Hence with separate chains acting as isolated entities, gels have no strength whatsoever to withstand a good deal of stress. Consequently, with some exceptions like plasticized PVC, we can conclude that gels, even the covalent ones, have poor mechanical properties most of the time.

Obviously, the strength will depend on the crosslinking degree. The more crosslinked is the material, the more elastic and stronger is it. For example, all the gels we have for our personal care, such as bath, hair styling, even painkillers or other pharmaceutical gels, will completely break when we touch them with our fingers, like in a cake. However, a mattress made of gels should be sufficiently elastic to make you feel comfortable, and strong enough so that it can stand your own weight without breaking when you lie down on it.

7.7.4 Gel Characterization

The different properties shown by gels, depending on their crosslinking degree, might lead us to another interesting question: how can these properties are measured?

As with solid polymers, in fact we can also evaluate mechanical properties on gels, provided they have a moderate crosslinking degree. If gels were not elastic enough, they would break before you could measure such parameters like tensile strength, elongation, and modulus. They would show a permanent deformation that would make difficult the quantitative evaluation of their mechanical properties.

However, if we are unable to measure mechanical properties for gels with a low crosslinking degree, we can establish another parameter which is characteristic of gels in particular: the swelling power.

What's that? In a physical sense, the swelling power gives us an idea about how much solvent can gels take up. Mathematically is a relationship between the weight (or volume) occupied by a swollen gel, Ws, and the weight (or volume) occupied by the corresponding dry gel, Wd. Of course, we can express all this by equations.

When considering weights, the equilibrium weight swelling ratio q_w is given by:

$$q_w = \frac{W_s}{W_d}$$

If volumes are considered, then the equilibrium volume swelling ratio q_v is defined by:

$$q_V = \frac{V_s}{V_d}$$

Doing a little more complex mathematical reasoning, you can also calculate the swelling degree percentage (%SD) given by:

$$SD = \frac{W_s - W_d}{W_d}$$

The swelling power depends mostly on the solvent and the polymer chain nature, and in polyelectrolytes (such as polyacrylic acid) also depends on the degree of dissociation. However, that a gel is soft doesn't necessarily mean it should have a high swelling power. Many times, low swelling power is attributed to polymer chains with low molecular weights.

The swelling power has a great significance for gels. The more solvent the gel takes up, the higher the swelling power is. That rings a bell. Remember superabsorbers?. As their name suggests, superabsorbers like polyacrylamide, poly(vinyl alcohol), and poly(acrylic acid) can take up enormous amounts of water.

7.7.5 A world of gels

Gels like these mentioned above, with a remarkable ability to absorb water or aqueous solvents, usually more than 20% their own weight, are called ***hydrogels***.

But we have many kinds of hydrogels in the market. There are porous and non-porous ones. *Macroporous hydrogels that are able to dry and swell back without significant changes in their macroscopic structure are known as **_aerogels_**.* On the other hand, dried non-porous hydrogels with capacity to absorb water by swelling are called **_xerogels_**.

While gels in general are widely used for a number of diverse applications, it's understandable that the interest for hydrogels is increasing constantly, particularly in their use as biomaterials.

From contact lenses and skin care uses to controlled drug release, application areas seem to be vast, especially with the advent of the so-called intelligent gels. Intelligent? Yes, they're smart enough because their swelling can be triggered by changes in such environmental factors like temperature, pH, solvent, ionic strength, light intensity, pressure, ultrasound irradiation, and magnetic or electric fields. Imagine that by varying the gel temperature in only 1°C, you can make the gel swell hundreds of times its own weight, or collapse, or even when it doesn't swell, it can display ability to change its physical properties.

7.7.6 Checking the Intelligence of "Intelligent Gels"

Since their discovery in 1975, intelligent gels have been tested in a number of different products. You might ask, for instance why gel soles are so comfortable. Well, that's because many of them are made using a viscoelastic gel that is soft at room temperature, but gets harder when making contact with the human body, i.e. it reacts with changes in temperature.

The ability to change their properties and the adherence to biological tissue is also another feature displayed by such hydrogels like poly(acrylic acid). This, coupled with the addition of some drugs into the gel matrix, makes them very useful for pharmaceutical applications like eye and nasal drops or sunscreens. That's because the gel becomes more viscous upon reaching the eye or nose, preventing the drops from dilution and washing by tears in the case of eye drops. Once inside the organ, the gel is capable to release the drug over a long period of time.

With sunscreens the procedure is different. Conventional sunscreens are usually greasy, so they're absorbed by the skin going directly into the bloodstream, where their utility is wasted. On the contrary, hydrogels are aqueous; they entrap the bioactive agent in micelles, so that it remains on the skin even longer.

7.7.7 Gels in our Body and more about....

Of course! Did you know that your muscles and internal organs are hydrogels? Sounds weird? It shouldn't... Just think you have lots of proteins (i.e. natural polymers) in your body. But these proteins are surrounded by an enormous quantity of water. After all, about 80% of the animal body is constituted by water!

Now put those proteins in contact with water, and what's going on here? Well, we have a big hydrogel! All soft parts of our body are just a big gel, where continuous change in molecular size as well as crosslinking degree is taking place.

Although hydrogels play a key role in the new trends of biotechnology, gel chemistry is not only circumscribed to organic molecules. In fact there are many inorganic gels, obviously derived from inorganic polymers particularly silicones and polysilanes.

There is another important branch of gel chemistry, named the sol-gel chemistry, which has been widely applied in the glass and ceramic fields, where research is still intense.

Commonly, the sol-gel process consists in the preparation of an inorganic network, working in solution at low temperatures. Such reaction involves three main steps: the formation of a colloidal suspension (called "sol"), the subsequent gelation of the sol in a continuous liquid phase ("gel"), and the removal of the solvent.

A great number of products are made by the sol-gel technology, such as fibers and composites, porous films, window insulators, superconductors, fillers, and optical, dielectic and electronic coatings. No surprisingly, the sol-gel process has even been applied for making high purity silica for optical fibers.

Lets summarize some things: High elasticity of polymer materials. Condition for realization of high-elastic state. Elasticity of a single polymer chain. Entropic nature of elasticity. Classical theory of high elsticity of polymer networks. Experimental deviations from the predictions of classical theory and their molecular origin.

Swelling of polymer gels in good solvents. Flory-Rehner theory. Superabsorbing properties of polyelectrolyte gels. Collpase of polyelectrolyte gels.

7.8 Dendrimers & Organic Nanoparticles

In recent years, a new structural class of macromolecules, the dendritic polymers, has attracted the attention of the scientific community. These nanometer sized, polymeric systems are hyperbranched materials having compact hydrodynamic volumes in solution and high, surface, functional group content. They may be water-soluble but, because of their compact dimensions, they do not have the usual rheological thickening properties that many polymers have in solution. Dendrimers, the most regular members of the class, are synthesized by step-wise convergent or divergent methods to give distinct stages or generations. Dendrimers are defined by their three components: a central core, an interior dendritic structure (the branches), and an exterior surface (the end groups). Over 50 compositionally different families of these nanoscale macromolecules, with over 200 end-group modifications, have been reported. They are characterized by nearly spherical structures, nanometer sizes, large numbers of reactive endgroup functionalities, shielded interior voids, and low systemic toxicity. This unique combination of properties makes them ideal candidates for nanotechnology applications in both biological and materials sciences. The spate of reports in the current literature has been directed toward their applications in a broad range of fields, including materials engineering, industrial, pharmaceutical, and biomedical applications. Specifically, nanoscale catalysts, lithographic materials, rheology modifiers, and targeted drug delivery systems, MRI contrast agents, and bioadhesives represent some of the potential applications.

Chapter 8

Nanomaterials World

8.1 What is nanoscience?

The word itself is a combination of nano, from the Greek "nanos" (or Latin "nanus"), meaning "Dwarf", and the word "Science." Nano refers to the 10^{-9} m, or one billionth. In these terms it refers to a meter, or a nanometer, which is on the scale of atomic diameters. For comparison, a human hair is about 100,000 nanometers thick!

Nanoscience is the study of atoms, molecules, and objects whose size is on the nanometer scale (1 - 100 nanometers).

Why is the study of nanoscience different than the same problems on a larger scale? Physics is different on the nanometer scale. Properties not seen on a macroscopic scale now become important- such as quantum mechanical and thermodynamic properties. Rather than working with bulk materials, one works with individual atoms and molecules. By learning about an individual molecule's properties, we can put them together in very well-defined ways to produce new materials with new and amazing characteristics.

Why is nanoscience suddenly becoming such a big field? There are multiple reasons for this. One is availability of new instruments able to "see" and "touch" at this scale. In the early 1980's the scanning tunneling microscope was invented at IBM-Zurich in Switzerland. This was the first instrument that was able to "see" atoms. A few years later, the Atomic Force Microscope was invented, expanding the capabilities and types of materials that could be investigated. Hence, Scanning Probe Microscopy was born, and since then multiple similar techniques have evolved from these instruments to "see" different properties at the nanometer scale. In addition, "older" techniques such as electron microscopy have continued to evolve as well, and now can image in the nanometer range. Currently, a large number of complementary instruments are developed that help scientists in the nano realm.

In addition to the enabling technologies, scientists have realized the potential of this research. By convincing politicians and leaders around the world, countries have instituted initiatives to promote nanoscience and nanotechnology in their universities and labs. With the recent increase in funding, many scientists are pursuing this research and the rate of discovery has increased dramatically. We taught that an introductory part for first year in each discipline is usefully.

8.2 Nanotechnolgy definition

A motivation in nanoscience is to try to understand how materials behave when sample sizes are close to atomic dimensions. In Figure 8.1 for example shows a picture of nanofibrils that are 10 to 100 times smaller in diameter than conventional textile fibers. In comparison to a human hair which is ca. 80,000 nm in diameter, the nanofibers are 1,000 times smaller in diameter. When the characteristic length scale of the microstructure is in the 1- 100 nm range, it becomes comparable with the critical length scales of physical phenomena, resulting in the so-called "size and shape effects." This leads to

unique properties and the opportunity to use such nanostructured materials in novel applications and devices. Phenomena occurring on this length scale are of interest to physicists, chemists, biologists, electrical and mechanical engineers, and computer scientists, making research in nanotechnology a frontier activity in materials science.

On tracking the nano evolution, it has been stated that no matter what the market outcomes in the near or long term, nanoscience will never be an industry itself but a science of many avenues of application, and possibility that could redefine the direction of several industries. This insight allows one to recognize that nanotechnology is not "a technology" but "a set of technologies," yielding a set of technical breakthroughs that will pass into many different markets.

Figure.8.1 A picture of nanofibrils shown with a Human hair for reference (Scanning Electron Microscopy)

Roughly, the world of nanotechnology may be divided into three broad categories: **nanomaterials** (generic word involving - *nanostructured materials, nanocomposites, nanopowders, etc* **nanotools, and nanodevices**. The various components of these categories are schematically illustrated in figure 8.2**.**

Nanotools. These include fabrication techniques; analysis and metrology instruments; and software for nanotechnology research and development. They are used in lithography, chemical vapor deposition (CVD), 3-D printing, and nanofluidics. Nanofluidics, the study of nanoscale fluid behavior, for example, the study of dynamics of droplets adsorbed onto surfaces under shearing, is mostly used in areas such as medical diagnostics and biosensors. Our body is the best example of nanofluidic applications-sanguine system, breathing system.

Hierarchical organization begins at the nanometer length scale and can comprise the unit cell of a crystalline structure, mers for polymers or proteins, aminoacids, etc to build our life. All are considered building –blocks and the methods and processes are actually well known categorized as bottom-up. That is contrary what we knew from up-down by miniaturizing the matter to micron and nanoscale.

Advances in nanotechnology give us methods, tools and instruments to do that. Succeeding levels of the hierarchy might include the scale of the grain size within a polycrystalline or composite material.

To synthesize the nanoscaled building blocks of our materials were invented a large number of methods many of them borrowed from macroscale: MBE- Molecular Beam Epitaxy, CVD-Chemical vapour deposition, sol-gel processes, atomic positioning in reactions of polymerization, architecturing and assembling using nanomanipulators from Atomic Force Microscopy (AFM), Plasma Chemistry, tools from genetic engineering, etc, etc.
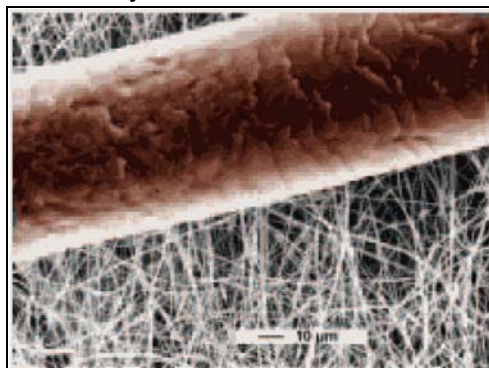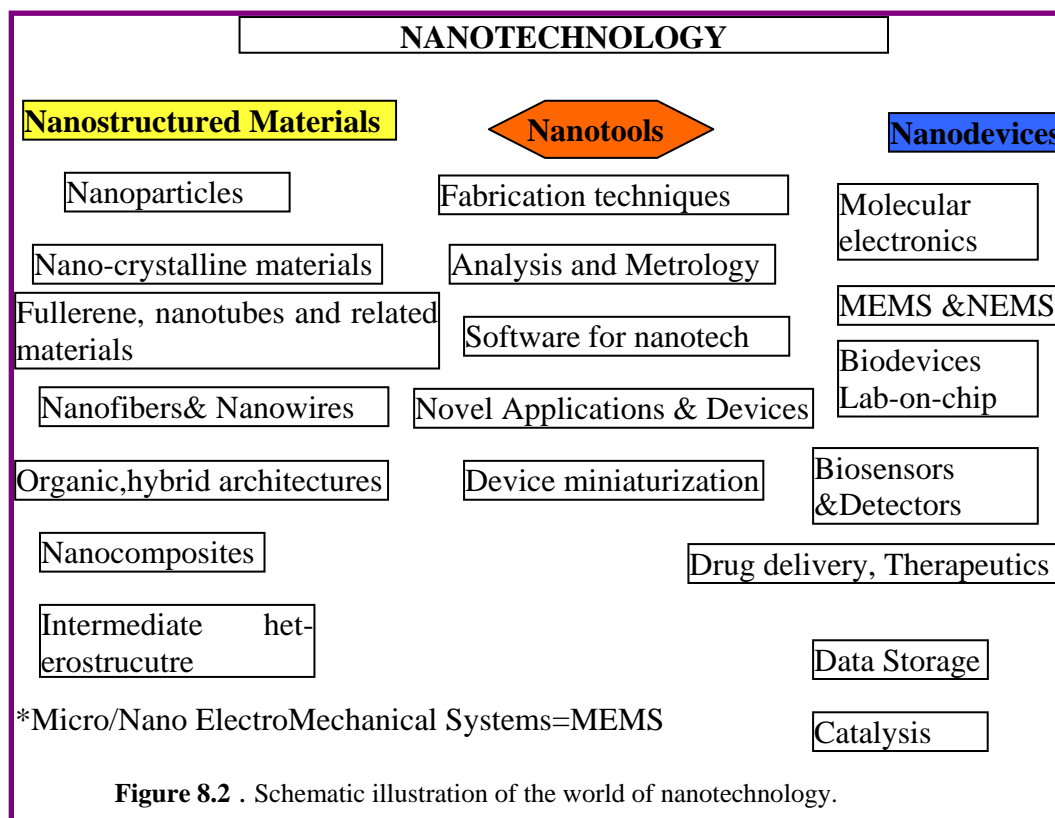
```
┌─────────────────────────────────────────────────────────────────┐
│                        NANOTECHNOLOGY                           │
│                                                                 │
│  Nanostructured Materials        Nanotools         Nanodevices  │
│                                                                 │
│    Nanoparticles          Fabrication techniques    Molecular   │
│                                                     electronics  │
│   Nano-crystalline materials  Analysis and Metrology            │
│                                                     MEMS &NEMS   │
│  Fullerene, nanotubes and related                               │
│  materials              Software for nanotech       Biodevices  │
│                                                     Lab-on-chip  │
│   Nanofibers& Nanowires    Novel Applications & Devices         │
│                                                     Biosensors   │
│  Organic,hybrid architectures   Device miniaturization &Detectors│
│                                                                 │
│   Nanocomposites                          Drug delivery, Therapeutics│
│                                                                 │
│  Intermediate      het-                                         │
│  erostrucutre                                      Data Storage │
│                                                                 │
│  *Micro/Nano ElectroMechanical Systems=MEMS        Catalysis   │
│                                                                 │
│        Figure 8.2 . Schematic illustration of the world of nanotechnology.│
└─────────────────────────────────────────────────────────────────┘
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Note: the fundamentals in matter constitution and organization remain atoms and molecules. With atoms and molecules, we can build new building-blocks which can be enriched with new properties such as self-assembling, self-organizing, interaction with viruses, microorganisms. They can be the LEGO-pieces in robotics, drug delivery, nanomedicine and nanobiotechnology, new energy sources, mimetic for biological systems and genetic engineering, molecular electronics, quantum computers.

Design and synthesis of supramolecular devices, self-organisation combined with recognition is exploited to acquire adaptive information transfer in, materials ("transcribing materials") with an original approach based on skill in methods of synthesis by combination and parallelization (combinatorial methods of synthesis).

In all methods, thermal physics is deeply involved because heat and work is everywhere.

To have a rough idea lets give some examples with nanomaterials world starting with some of them known of centuries: Aerosols, colloids, pigments, dye ; nanostructured materials- nanocrystals (nanocrystalline materials), nanoparticles with alloyed components, metal nanoparticles, amorphous nanoparticles, etc; nano-composites, dendrimers, etc.

8.3 Nanostructured materials

(NsM) are materials with a microstructure the characteristic length scale of which is on the order of a few (typically 1-100) nanometers. The microstructure refers to the chemical composition, the arrangement of the atoms (the atomic structure), and the size of a solid in one, two, or three dimensions. Effects controlling the properties of nanostructured materials include size effects (where critical length scales of physical phenomena become comparable with the characteristic size of the building blocks of the microstructure), changes of the dimensionality of the system, changes of the atomic structure, and alloying of components (e.g., elements) that are not miscible in the solid and/or the molten state.

The synthesis, characterization and processing of nanostructured materials are part of an emerging and rapidly growing field. Research and development in this field emphasizes scientific discoveries in the generation of materials with controlled microstructural characteristics, research on their processing into bulk materials with engineered properties and technological functions, and introduction of new device concepts and manufacturing methods.

8.3.1 Nanocrystalline Materials, Nanocrystals, Nanomaterials

Included here are ceramics, metals, and metal oxide nanoparticles. In the last two decades a class of materials with a nanometer-sized microstructure have been synthesized and studied. These materials are assembled from nanometer-sized building blocks, mostly crystallites. The building blocks may differ in their atomic structure, crystallographic orientation, or chemical composition. In cases where the building blocks are crystallites, incoherent or coherent interfaces may be formed between them, depending on the atomic structure, the crystallographic orientation, and the chemical composition of adjacent crystallites. In other words, materials assembled of nanometer-sized building blocks are microstructurally heterogeneous, consisting of the building blocks (e.g. crystallites) and the regions between adjacent building blocks (e.g. grain boundaries). It is this inherently heterogeneous structure on a nanometer scale that is crucial for many of their properties and distinguishes them from glasses, gels, etc. that are microstructurally homogeneous.

Grain boundaries make up a major portion of the material at nanoscales, and strongly affect properties and processing. The properties of NsM deviate from those of single crystals (or coarsegrained polycrystals) and glasses with the same average chemical composition. This deviation results from the reduced size and dimensionality of the nanometer-sized crystallites as well as from the numerous interfaces between adjacent crystallites. An attempt is made to summarize the basic physical concepts and the microstructural features of equilibrium and non-equilibrium NsM.

Nanocrystallites of bulk inorganic solids have been shown to exhibit size dependent properties, such as lower melting points, higher energy gaps, and nonthermodynamic structures. In comparison to macro-scale powders, increased ductility has been observed in nanopowders of metal alloys. In addition, quantum effects from boundary values become significant leading to such phenomena as quantum dots lasers.

One of the primary applications of metals in chemistry is their use as heterogeneous catalysts in a variety of reactions. In general, heterogeneous catalyst activity is surface dependent. Due to their vastly increased surface area over macro-scale materials, nanometals and oxides are ultra-high activity catalysts. They are also used as desirable starting materials for a variety of reactions, especially solid-state routes.

Nanometals and oxides are also widely used in the formation of nanocomposites.

Aside from their synthetic utility, they have many useful and unique magnetic, electric, and optical properties
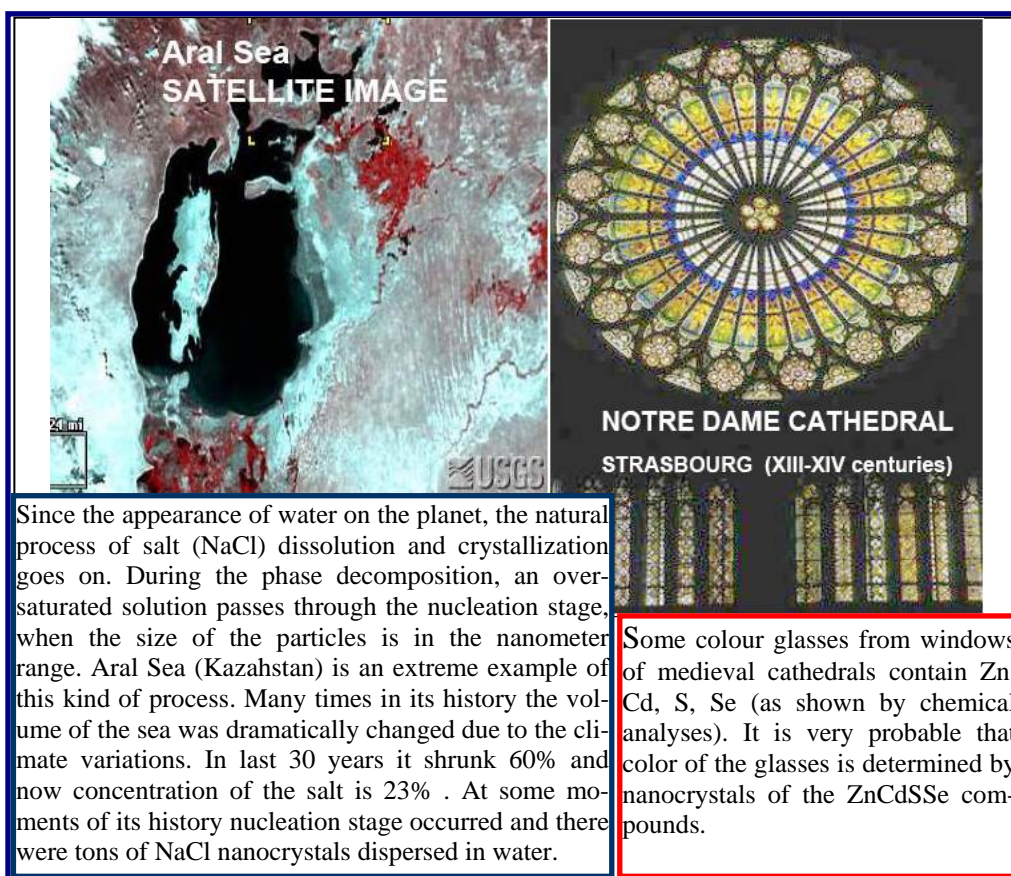
Nanocrystals exhibit a wide range of size-dependent properties. Variations in fundamental characteristics ranging from phase transitions to electrical conductivity can be induced by controlling the size of the crystals;

For example, in the prototypical material, CdS, the band gap can be tuned between 2.5 and 4 eV, while the radiative rate for the lowest allowed optical excitation ranges from several nanoseconds down to tens of picoseconds. The energy above the band gap required to add an excess charge increases by 0.5 eV, while the very notion of charge transport no longer seems to apply. The melting temperature varies from 1600 down to 400°C. The pressure required to induce transformation phase increases from 2 to 9 GPa, even as the number of nucleation events for the transition becomes one. This enormous range of fundamental properties is all realized in a material of a single chemical composition: CdS. The variation is achieved by reducing the size of the crystal, not by altering its chemical composition.

There are three major effects, which are responsible for these size variations in nanocrystal properties. *First, in nanocrystals the number of surface atoms is a large fraction of the total. Second, the intrinsic properties of the interior of nanocrystals are transformed by quantum size effects.* Third, each nanocrystals can be considered "a thermal isolated systems" and heat change is dominant by thermal radiation. In any material, surface atoms make a distinct contribution to the free energy, and the large changes in thermodynamic properties of nanocrystals (melting temperature depression, solid-solid phase transition elevation) can ultimately be traced to this. The surfaces of nanocrystals have until recently been thought of as largely disordered, yielding spherical or ellipsoidal shapes. Work that is more recent shows that nanocrystals assume regular shapes, with the same well-defined facets as are present in extended crystals.

Semiconductor Nanocrystals–also known as Quantum Dot can be used for: biotechnology, telecommunications, LED, Solar cells, or basically everywhere semiconductors are used
With these nanocrystals, you can control the electronic states; hence control the optical and electronic properties of the material.

Ancient example with nanocrystals

Since the appearance of water on the planet, the natural process of salt (NaCl) dissolution and crystallization goes on. During the phase decomposition, an over-saturated solution passes through the nucleation stage, when the size of the particles is in the nanometer range. Aral Sea (Kazahstan) is an extreme example of this kind of process. Many times in its history the volume of the sea was dramatically changed due to the climate variations. In last 30 years it shrunk 60% and now concentration of the salt is 23% . At some moments of its history nucleation stage occurred and there were tons of NaCl nanocrystals dispersed in water.

Some colour glasses from windows of medieval cathedrals contain Zn, Cd, S, Se (as shown by chemical analyses). It is very probable that color of the glasses is determined by nanocrystals of the ZnCdSSe compounds.

8.3.2 Colloids

The term *colloidal* refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1μm, or that in a system discontinuities are found at distances of that order. It is not necessary for all three dimensions to be in the colloidal range: fibers in which only two dimensions are in this range, and thin films, in which one dimension is in this range, may also be classified as colloidal. Nor is it necessary for the units of a *colloidal system* to be discrete: continuous network structures, the basic units of which are of colloidal dimensions also fall in this class (e.g. porous solids, gels and foams).

A *colloidal dispersion* is a system in which particles of colloidal size of any nature (e.g. solid, liquid or gas) are dispersed in a *continuous phase* of a different composition (or state).

The name *dispersed phase* for the particles should be used only if they have essentially the properties of a bulk phase of the same composition.

The term *colloid* may be used as a short synonym for colloidal system. The size limits given above are not rigid since they will depend to some extent on the properties under consideration. This nomenclature can be applied to coarser systems, especially when a gradual transition of properties is considered.

The description of colloidal systems often requires numbering of the components or constituents. It is felt that a fixed rule of numbering is unnecessarily restrictive. However, the author should make clear in all cases how he is numbering and in particular whether he is numbering by independent thermodynamic components (all neutral) or by species or constituents, of which some may be ionic, and which may be related by equilibrium conditions or by the condition of electroneutrality. In comparing English and French, it should be realized that the English word `component' is usually equivalent to the French `constituent' and the English `constituent' to the French `composant'.

A fluid colloidal system composed of two or more components may be called a *sol*, e.g. a protein sol, a gold sol, an emulsion, a surfactant solution above the critical micelle concentration an aerosol.

In a *suspension* solid particles are dispersed in a liquid; a *colloidal suspension* is one in which the size of the particles lies in the colloidal range.

In an *emulsion* liquid droplets and/or liquid crystals are dispersed in a liquid. In emulsions the droplets often exceed the usual limits for colloids in size. An emulsion is denoted by the symbol O/W if the continuous phase: is an aqueous solution and by W/O if the continuous phase is an organic liquid (an `oil'). More complicated emulsions such as O/W/O (i.e. oil droplets contained within aqueous droplets dispersed in a continuous oil phase) are also possible.

Photographic emulsions, although colloidal systems, are not emulsions in the sense of this nomenclature.

A *latex* (plural = latices or latexes) is an emulsion or sol in which each colloidal particle contains a number of macromolecules.

A *foam* is a dispersion in which a large proportion of gas by volume in the form of gas bubbles, is dispersed in a liquid, solid or gel. The diameter of the bubbles is usually larger than 1 micron, but the thickness of the lamellae between the bubbles is often in the usual colloidal size range.

The term *froth* has been used interchangeably with foam. In particular cases froth may be distinguished from foam by the fact that the former is stabilized by solid particles (as in *froth-flotation* q.v.) and the latter by soluble substances.

Aerosols are dispersions in gases. In aerosols, the particles often exceed the usual size limits for colloids. If the dispersed particles are solid, one speaks of *aerosols of solid particles*, if they are liquid of *aerosols of liquid particles*. The use of the terms solid aerosol and liquid aerosol is discouraged. An aerosol is neither `solid' nor `liquid' but, if anything, gaseous.

A great variety of terms such as dust, haze, fog, mist, drizzle, smoke, smog are in use to describe aerosols according to their properties, origin, etc. Of these only the terms fog and smoke are included in this nomenclature.

A *fog* is an aerosol of liquid particles, in particular a low cloud.

A *smoke* is an aerosol originating from combustion, thermal decomposition or thermal evaporation. Its particles may be solid (magnesium oxide smoke) or liquid (spraying from odorant bottle).

A *gel* is a colloidal system with a finite, usually rather small, yield stress. Materials such as silica gel which have passed a gel stage during preparation, are improperly called gels. A particular class Polymer gel has been detailed in section7.7

The term *xerogel* is used for such dried out open structures; and also for dried out compact macromolecular gels such as gelatin or rubber.

The term *aerogel* is used when the openness of the structure is largely maintained.

Colloidal dispersions may be *lyophobic* (*hydrophobic*, if the dispersion medium is an aqueous solution) or *lyophilic* (*hydrophilic*). *Lyophilic sols* are formed spontaneously when the dry coherent material (e.g. gelatin, rubber, soap) is brought in contact with the dispersion medium, hence they are thermodynamically more stable than in the initial state of dry colloid material plus dispersion medium. *Lyophobic sols* (e.g. gold sol) cannot be formed by spontaneous dispersion in the medium. They are thermodynamically unstable with respect to separation into macroscopic phases, but they may remain for long times in a metastable state.

Lyophilic sols comprise both *association colloids* in which aggregates of small molecules are formed reversibly and *macromolecules* in which the molecules themselves are of colloidal size.

Mixtures of lyophobic and lyophilic colloids, may form *protected lyophobic colloids*

The terms *lyophilic* (*hydrophilic, lipophilic, oleophilic*, etc.) and *lyophobic*, (*lipophobic*, etc.) may also be used to describe the character of interaction of a particular atomic group with the medium. In this usage the terms have the relative qualitative meaning of `solvent preferring' (water-preferring, fat-preferring etc.) and `solvent rejecting' (water-rejecting, fat-rejecting, etc.) respectively.

The terms `*solvent preferring*' or `*solvent rejecting*' always refer to a differential process usually in the sense of preferring the solvent above itself or preferring itself above the solvent but sometimes preferring one solvent (e.g. water) above another (e.g. oil).

A *colloidal electrolyte* is an electrolyte which gives ions of which at least one is of colloidal size. This term therefore includes hydrophobic sols, ionic association colloids, and polyelectrolytes. Ions of low relative molecular mass, with a charge opposite to that of the colloidal ion, are called *counterions*; if their charge has the same sign as that of the colloidal ion, they are called *co-ions*.

A *polyelectrolyte* is a macromolecular substance which, on dissolving in water or another ionizing solvent, dissociates to give *polyions* (*polycations* or *polyanions*)--multiply charged ions--together with an equivalent amount of ions of small charge and opposite sign. Polyelectrolytes dissociating into polycations and polyanions, with no ions of small charge, are also conceivable. A polyelectrolyte can be a *polyacid*, a *polybase*, a *polysalt* or a *polyampholyte*.

If all particles in a colloidal system are of (nearly) the same size the system is called *monodisperse*; in the opposite cases the systems are *heterodisperse*.

If only a few particle-sizes occur in a colloidal system the system is *paucidisperse* and if many particle-sizes occur *polydisperse*.

In heterodisperse systems the determination of particle mass or relative molecular mass gives averages, which depend on the method used. The most common averages are:

Number average relative molecular mass (= *number average molecular weight*)

$$\overline{M}_n = \frac{\sum n_i M_r(i)}{\sum n_i}$$

where n_i and $M_r(i)$ are the amount of substance and the relative molecular mass of the species i respectively.

Mass average relative molecular mass (= *mass average molecular weight*):

$$\overline{M}_m = \frac{\sum n_i \left(M_r(i)\right)^2}{\sum n_i M_r(i)}$$

Average relative molecular masses in which higher powers of occur $M_r(i)$ can be defined. Other definitions can be found in any textbooks in polymer science. The subscript r in the above definitions is generally omitted if there is no possibility of ambiguity.

8.3.2.1 PREPARATION AND PROCESSING OF COLLOIDAL SYSTEMS

Colloidal sols can be formed by dispersion methods (e.g. by mechanical subdivision of larger particles or by dissolution in the case of lyophilic sols) or by condensation methods (from supersaturated solutions or supercooled vapours, or as the product of chemical reactions) or by a combination of these two (e.g. in an electrical discharge). When a condensation method is applied, molecules (or ions) are deposited on nuclei, which may be of the same chemical species as the colloid (homogeneous nucleation) or different (heterogeneous nucleation).

An aggregate of a small number of atoms, molecules or ions is called an embryo. A critical embryo has that size at which the Gibbs energy at constant pressure and temperature is a maximum. A larger embryo is called a homogeneous nucleus. A nucleating agent is a material either added to or present in the system, which induces either homogeneous or heterogeneous nucleation. The rate of nucleation is the number of nuclei formed in unit time per unit volume.

Dialysis is the process of separating a colloidal sol from a colloid-free solution by a membrane permeable to all components of the system except the colloidal ones, and allowing the exchange of the components of small molar mass to proceed for a certain time.

The colloid-free solution obtained at equilibrium in dialysis is called equilibrium dialysate. Its composition approaches that of the dispersion medium (more precisely, the limit to which the composition of the dispersion medium tends at large distances from the particles). In the dialysis equilibrium an osmotic pressure difference exists between sol and equilibrium dialysate. After (complete or incomplete) dialysis two solutions are obtained. The one free from colloidal material is called dialysate; the other one, containing the colloidal particles may be called retentate, dialysis residue, or simply residue, but should not be called dialysate.

The ultrafiltrate, prepared by ultrafiltration (filtration through a dialysis membrane), is in general not of the same composition as the equilibrium solution. If dialysis is conducted in the presence of an electric field across the membrane(s) it is called electrodialysis. Electrodialysis may lead to local differences in concentration and density. Under the influence of gravity these density differences lead to large scale separation of sols of high and of low (often vanishingly low) concentrations. This process is called electrodecantation (electrophoresis convection).

Flotation is the removal of matter by entrainment at an interface. In particular, froth flotation is the removal of particulate matter by foaming (frothing).

Foam fractionation is a method of separation in which a component of the bulk liquid is preferentially adsorbed at the L/V interface and is removed by foaming.

The terms stable and stability are used in rather special and often different senses in colloid science: the relationship between these usages and the formal thermodynamic usage is outlined below. Thermodynamically stable or metastable means that the system is in a state of equilibrium corresponding to a local minimum of the appropriate thermodynamic potential for the specified constraints on the system (e.g. Gibbs energy at constant T and P). Stability cannot be defined in an absolute sense, but if several states are in principle accessible to the system under given conditions, that with the lowest potential is called the stable state, while the other states are described as metastable. Unstable states are not at a local minimum. Transitions between metastable and stable states occur at rates which depend on the magnitude of the appropriate activation energy barriers which separate them. Most colloidal systems are metastable or unstable with respect to the separate bulk phases, with the (possible) exception of lyophilic sols, gels and xerogels of macromolecules.

Colloidally stable means that the particles do not aggregate at a significant rate: the precise connotation depends on the type of aggregation under consideration. For example, a concentrated paint is called stable by some people because oil and pigment do not separate out at a measurable rate, and unstable by others because the pigment particles aggregate into a continuous network.

An aggregate is, in general, a group of particles (which may be atoms or molecules) held together in any way: a colloidal particle itself (e.g. a micelle, see below) may be regarded as an aggregate. More specifically, aggregate is used to describe the structure formed by the cohesion of colloidal particles.

Aggregation is the process or the result of the formation of aggregates. When a sol is colloidally unstable (i.e. the rate of aggregation is not negligible) the formation of aggregates is called coagulation or flocculation. These terms are often used interchangeably, but some authors prefer to introduce a distinction between coagulation, implying the formation of compact aggregates, leading to the macroscopic separation of a coagulum; and flocculation, implying the formation of a loose or open network which may or may not separate macroscopically. In many contexts the loose structure formed in this way is called a floc. While this distinction has certain advantages, in view of the more general (but not universal) acceptance of the equivalence of the words coagulation and flocculation, any author who wishes to make a distinction between them should state so clearly in his publication.

The reversal of coagulation or flocculation, i.e. the dispersion of aggregates to form a colloidally stable suspension or emulsion, is called deflocculation (sometimes peptization).

The rate of aggregation is in general determined by the frequency of collisions and the probability of cohesion during collision. If the collisions are caused by Brownian motion, the process is called perikinetic aggregation; if by hydrodynamic motions (e.g. convection or sedimentation) one may speak of orthokinetic aggregation.

In hydrophobic sols, coagulation can be brought about by changing the electrolyte concentration to the critical coagulation concentration (c.c.c.) .As the value of the critical coagulation concentration depends to some extent on the experimental circumstances (method of mixing, time between mixing and determining the state of coagulation, criterion for measuring the degree of coagulation, etc.) these should be clearly stated. The generalization that the critical coagulation concentration for a typical lyo-

phobic sol is extremely sensitive to the valence of the counterions (high valence gives a low critical coagulation concentration) is called the Schulze-Hardy rule.

If the critical coagulation concentration of a mixture of two electrolytes A and B corresponds to concentrations of the two components of c_A and c_B whereas the c.c.c.'s of A and B taken separately are c_{0A} and c_{0B} then the effects of the electrolytes are said to be additive if:

$$\frac{c_A}{c_{0A}} + \frac{c_B}{c_{0B}} = 1$$

they are synergistic if $\frac{c_A}{c_{0A}} + \frac{c_B}{c_{0B}} < 1$; and antagonistic if $\frac{c_A}{c_{0A}} + \frac{c_B}{c_{0B}} > 1$. It is often found

in the latter case that the individual values of $\frac{c_A}{c_{0A}}$ and/or $\frac{c_B}{c_{0B}}$ exceed unity. Addition of

small amounts of a hydrophilic colloid to a hydrophobic sol may make the latter more sensitive to flocculation by electrolyte. This phenomenon is called sensitization. Higher concentrations of the same hydrophilic colloid usually protect the hydrophobic sol from flocculation. This phenomenon is called protective action. Colloidally stable mixtures of a lyophobic and lyophilic colloid are called protected lyophobic colloids; although they may be thermodynamically unstable with respect to macroscopic phase separation, they have many properties in common with lyophilic colloids.

Sedimentation is the settling of suspended particles under the action of gravity or a centrifugal field. If the concentration of particles is high and interparticle forces are strong enough, the process of sedimentation may be better described as compaction of the particle structure with pressing out of the liquid. This particular kind of settling is also called subsidence. Sediment is the highly concentrated suspension which may be formed by the sedimentation of a dilute suspension.

Coalescence is the disappearance of the boundary between two particles (usually droplets or bubbles) in contact, or between one of these and a bulk phase followed by changes of shape leading to a reduction of the total surface area. The flocculation of an emulsion, viz. the formation of aggregates, may be followed by coalescence. If coalescence is extensive it leads to the formation of a macrophase and the emulsion is said to break. The breaking of a foam involves the coalescence of gas bubbles.

Coalescence of solid particles is called sintering.

Creaming is the macroscopic separation of a dilute emulsion into a highly concentrated emulsion, in which interglobular contact is important, and a continuous phase under the action of gravity or a centrifugal field. This separation usually occurs upward, but the term may still be applied if the relative densities of the dispersed and continuous phases are such that the concentrated emulsion settles downward. Some authors, however, also use creaming as the opposite of sedimentation even when the particles are not emulsion droplets. Cream is the highly concentrated emulsion formed by creaming of a dilute emulsion. The droplets in the cream may be colloidally stable or flocculated, but they should not have coalesced.

As a rule all colloidal systems, initially of uniform concentration, establish, when subjected to the action of gravity or a centrifugal field, a concentration gradient as a result of sedimentation or creaming but if the system is colloidally stable the particles in the sediment or cream do not aggregate and can be redispersed by the application of forces of the same magnitude as those which caused sedimentation or creaming.

The loss of the stability of a lyophilic sol (equivalent to a decrease in the solubility of the lyophilic colloid) quite often results in a separation of the system into two liquid phases. The separation into two liquid phases in colloidal systems is called coacervation. It occurs also, though rarely, in hydrophobic sols. The phase more concentrated in colloid component is the coacervate, and the other phase is the equilibrium solution. If coacervation is caused by the interaction of two oppositely charged colloids, it is called complex coacervation. Coacervation usually begins with the separation of the second phase in the form of small droplets which may coalesce to a continuous phase. Sometimes with extremely anisotropy particles the droplets have the shape of spindles or cylinders (tactoids). If the colloidal system is highly concentrated, droplets of the dilute phase are formed in the concentrated one (negative tactoids). The phenomenon of tactoid formation is not restricted to lyophilic systems.
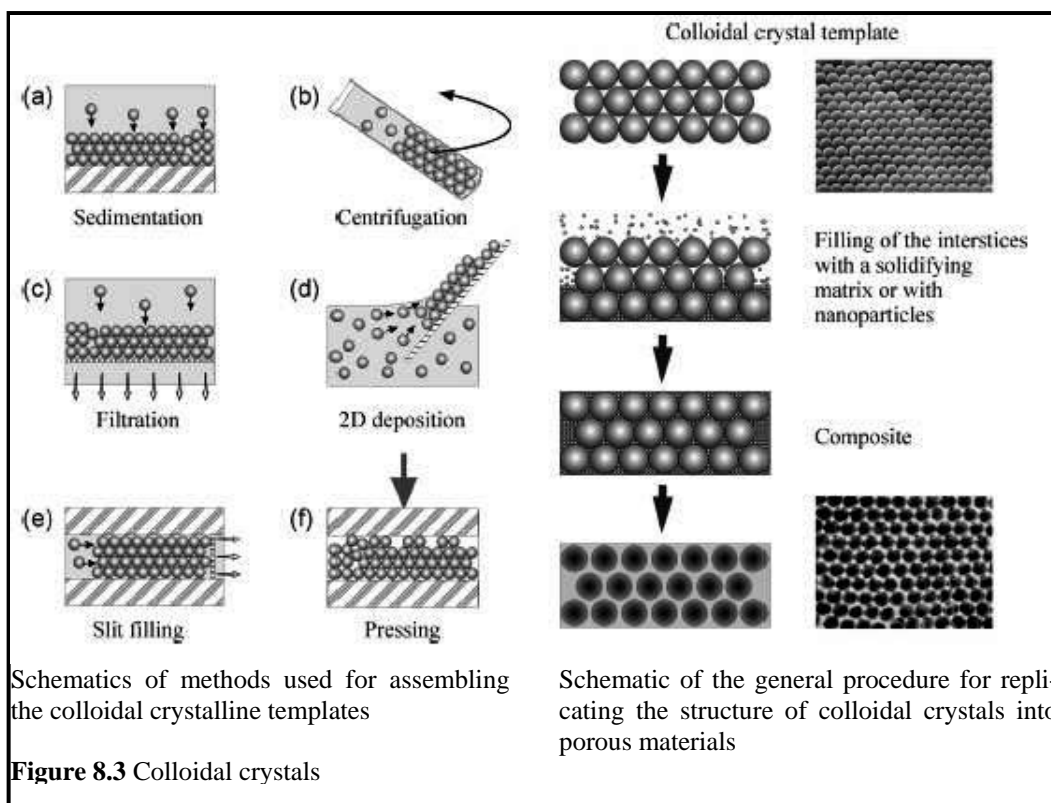
In some systems, sedimenting particles form layers separated by approximately equal distances of the order of the wavelength of light. This gives rise to strong colours when observed in reflected light and the system is said to form irridescent layers or schiller layers.

8.3.3 Colloidal crystals

The colloidal particles can ordering in crystals with long range order. The long-range ordering of particles in the structure of colloidal crystals results in a number of unique potentially useful properties, such as optical diffraction and photonic band gaps, maximal packing density and high surface/volume ratio. However, the materials obtained after the particulate arrays are dried are very brittle and can be re-dispersed in water. A fascinating example of how colloidal crystals can be turned into a durable material with remarkable properties is provided by the natural opals, which are formed when the voids between ordered sediments of silica particles are infiltrated by hydrated silica, which then solidifies.

A variety of artificial structures based on colloidal crystals have been synthesized recently using the 'fixing' concept suggested by the opals. In this approach Fig. 8.3 , the colloidal crystals are assembled in order to serve as templates, the voids of which are infiltrated by material that solidifies there. The original colloidal particles are subsequently removed, leaving behind a new material with pores that preserve the most valuable property of the colloidal crystals the long-ranged periodic structure. A major advantage of the colloidal crystal template method is the ability to control the dimensions of the pores easily by varying the size of the beads in the templates. the colloidal crystals are assembled in order to serve as templates, the voids of which are
infiltrated by material that solidifies there. The original colloidal particles are subsequently removed, leaving behind a new material with pores that preserve

the most valuable property of the colloidal crystals the long-ranged periodic structure

Schematics of methods used for assembling the colloidal crystalline templates

Schematic of the general procedure for replicating the structure of colloidal crystals into porous materials

Figure 8.3 Colloidal crystals

A major advantage of the colloidal crystal template method is the ability to control the dimensions of the pores easily by varying the size of the beads in the templates.

Latex and silica microspheres are the two major types of particles that are usually used for the colloidal crystal assembly, as they can be obtained both highly monodisperse and relatively cheaply. Central to the materials synthesis is the design of procedures for assembling the crystals and subsequently infusing them with appropriate media. A summary of the crystallization methods used by different investigators is represented in Fig. 8.3. The simplest method is gravitational sedimentation of the particles, usually combined with drying of the suspension from above. The process can be accelerated and the quality of the materials can be improved via centrifugation Fig. 8.3b. Another way to speed the process up is by filtration Fig. 8.3c , which also allows easy washing and subsequent infusion with different media. Of certain interest is the formation of crystalline sheets of specific thickness, for which the convective assembly method, Fig. 8.3d has been used after recent modificaions and improvements. Colloidal crystals can also form when the particles are confined in the thin film between two solid boundaries. This approach has also recently been used to assemble closely packed crystals, by filtering suspensions into a thin slit between two solid plates Fig. 8.3e. Finally, ordered structures between solid surfaces can be formed by pressing and compaction of particles in the dry, Fig. 8.3f .

8.4 Nanocomposites

The definition of nano-composite material has broadened significantly to encompass a large variety of systems such as one-dimensional, two-dimensional, three-

dimensional and amorphous materials, made of distinctly dissimilar components and mixed at the nanometer scale.

The general class of nanocomposite organic/inorganic materials is a fast growing area of research. Significant effort is focusing on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual parents but also on their morphology and interfacial characteristics.

Building blocks can subsequently be further organized through incorporation into a matrix material (e.g., a polymer,, carbon materials, wood, clay, etc) or through compaction of component heterogeneous nanoparticles into a composite whole (glass and ceramics). Nanocomposites are materials with a nanoscale structure that improve the macroscopic properties of products. Typically, nanocomposites are clay, polymer or carbon, or a combination of these materials with nanoparticle building blocks.

Nanocomposites, materials with nanoscale separation of phases can generally be divided into two types: multilayer structures and inorganic/organic composites. Multilayer structures are typically formed by gas phase deposition or from the self-assembly of monolayers. Inorganic/organic composites can be formed by sol-gel techniques, bridging between clusters (as in silsequioxanes), or by coating nanoparticles, in polymer layers for example. Nanocomposites can greatly enhance the properties of materials. For example, ppm level impurities can result in the formation of nanoscale aluminide secondary phases in aluminum alloys, increasing their strength and corrosion resistance. Magnetic multilayered materials are one of the most important aspects of nanocomposites as they have led to significant advances in storage media.

This rapidly expanding field is generating many exciting new materials with novel properties. The latter can derive by combining properties from the parent constituents into a single material. There is also the possibility of new properties which are unknown in the parent constituent materials.

The inorganic components can be three-dimensional framework systems such as zeolites, two-dimensional layered materials such as clays, metal oxides, metal phosphates, chalcogenides, and even one-dimensional and zero-dimensional materials such as (Mo3Se3-)n chains and clusters. Experimental work has generally shown that virtually all types and classes of nanocomposite materials lead to new and improved properties when compared to their macrocomposite counterparts. Therefore, nanocomposites promise new applications in many fields such as mechanically reinforced lightweight components, non-linear optics, battery cathodes and ionics, nano-wires, sensors and other systems.

The general class of organic/inorganic nanocomposites may also be of relevance to issues of bio-ceramics and biomineralization in which in-situ growth and polymerization of biopolymer and inorganic matrix is occurring. Finally, lamellar nanocomposites represent an extreme case of a composite in which interface interactions between the two phases are maximized. Since the remarkable properties of conventional composites are mainly due to interface interactions, the materials dealt with here could provide good model systems in which such interactions can be studied in detail using conventional bulk sample (as opposed to surface) techniques. By judiciously engineering the polymer-host interactions, nanocomposites may be produced with a broad range of properties.

Inorganic layered materials exist in great variety. They possess well defined, ordered intralamellar space potentially accessible by foreign species. This ability enables them to act as matrices or hosts for polymers, yielding interesting hybrid nano-composite materials.

Lamellar nano-composites can be divided into two distinct classes, intercalated and exfoliated. In the former, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well defined number of polymer layers in the intra-lamellar space. In exfoliated nano-composites the number of polymer chains between the layers is almost continuously variable and the layers stand >100 Å apart. The inter-calated nano-composites are also more compound-like because of the fixed poly-mer/layer ratio, and they are interesting for their electronic and charge transport proper-ties. On the other hand, exfoliated nano-composites are more interesting for their supe-rior mechanical properties.

The lamellar class of intercalated organic/inorganic nanocomposites and namely those systems that exhibit electronic properties in at least one of the components. This subclass of nano-composites offers the possibility of obtaining well ordered systems some of which may lead to unusual electrical and mechanical properties. Selected members of this class may be amenable to direct structural characterization by standard crystallographic methods. An important issue in this area is the few structural details that are available, therefore, any system which can be subjected to such analysis is of in-terest.

Nanocomposites also offer the possibility to combine diverse properties which are impossible within a single material, e.g. flexible mechanical properties and supercon-ducting properties. This work is now in its infancy and we propose to carry out exten-sive investigations in the next funding period. Another exciting aspect is the possibility of creating heterostructures composed of different kinds of inorganic layers, which could lead to new multifuntional materials.

In the past we have focused our efforts on creating such materials with conjugated and saturated organic macromolecules. Actually aree developed several general syn-thetic routes for inserting polymer chains into host structures and have designed many novel nanocomposites.

These include: In-situ intercalative polymerization (ISIP) of a monomer using the host itself as the oxidant. The rationale behind intercalative polymerization is that host matrices with high electron affinity can oxidatively polymerize appropriate monomers in their interior. Monomer intercalation followed by topotactic intralamellar solid state polymerization. This route creates conjugated polymers inside non-oxidizing hosts.

Direct precipitative encapsulation of polymer chains by colloidally dispersed sin-gle layers of a host. This approach gives access to a large variety of nano-composites with many kinds of polymers and hosts.

One model how to build a nanocomposites

One composite, multilayered (layer thickness aprox 1nm)

Figure 8.4 – Models in nanocomposites designing
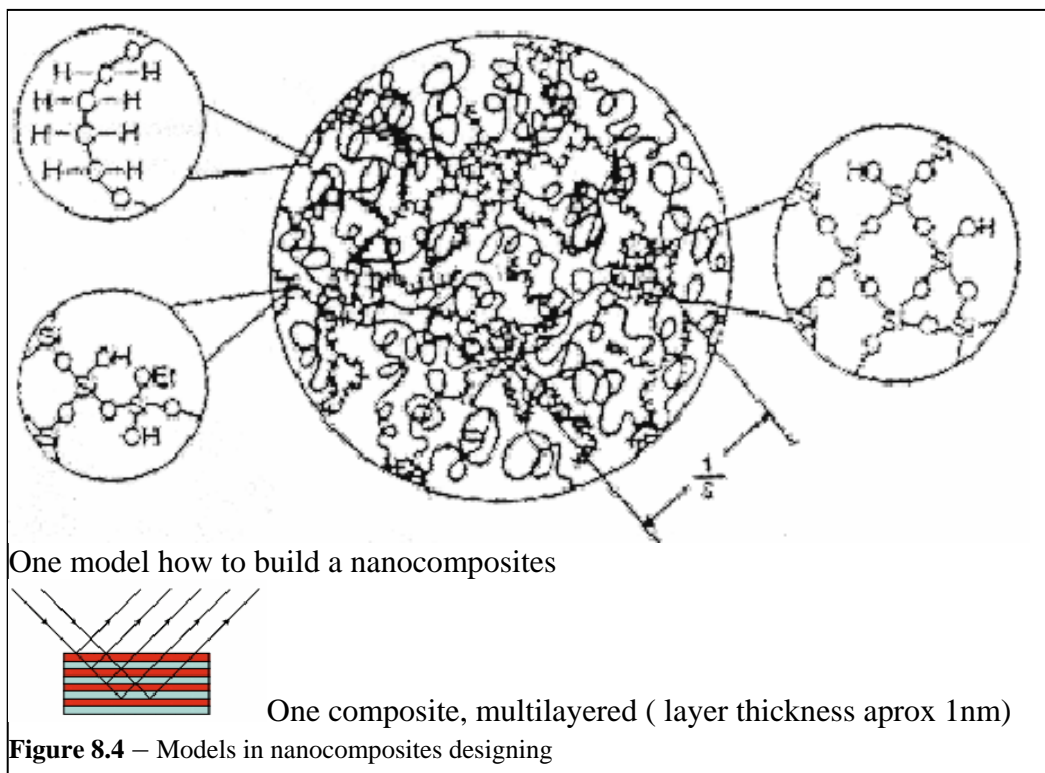
8.4.1 Polymer and Polymer-Clay Nanocomposites

The large industrial demand for polymers has lead to an equally large interest in polymer composites to enhance their properties. Clay-polymer nanocomposites are among the most successful nanotechnological materials today. This is because they can simultaneously improve material properties without significant trade offs.

Recent efforts have focused upon polymer-layered silica nanocomposites and other polymer/clay composites. These materials have improved mechanical properties without the large loading require by traditional particulate fillers. Increased mechanical stability in polymer-clay nanocomposites also contributes to an increased heat deflection temperature. These composites have a large reduction gas and liquid permeability and solvent uptake. Traditional polymer composites often have a marked reduction in optical clarity; however, nanoparticles cause little scattering in the optical spectrum and very little UV scattering. Although flame retardant additives to polymers typically reduce their mechanical properties, polymer-clay nanocomposites have enhanced barrier and mechanical properties and are less flammable. Compression-injection molding, melt-intercalation, and coextrusion of the polymer with ceramic nanopowders can form nanocomposites. Often no solvent or mechanical shear is needed to promote intercalation.

Properties and Applications

Advantages of Nanosized Additions The Nanocomposites 2000 conference has revealed clearly the property advantages that nanomaterial additives can provide in comparison to both their conventional filler counterparts and base polymer. Properties which have been shown to undergo substantial improvements include:

- Mechanical properties e.g. strength, modulus and dimensional stability
- Decreased permeability to gases, water and hydrocarbons
- Thermal stability and heat distortion temperature
- Flame retardancy and reduced smoke emissions
- Chemical resistance
- Surface appearance
- Electrical conductivity
- Optical clarity in comparison to conventionally filled polymers

Disadvantages of Nanosized Additions .To date one of the few disadvantages associated with nanoparticle incorporation has concerned toughness and impact performance. Some of the data presented has suggested that nanoclay modification of polymers such as polyamides, could reduce impact performance. Clearly this is an issue which would require consideration for applications where impact loading events are likely. In addition, further research will be necessary to, for example, develop a better understanding of formulation/structure/property relationships, better routes to platelet exfoliation and dispersion etc.

Particle Loadings

In addition it is important to recognise that nanoparticulate/fibrous loading confers significant property improvements with very low loading levels, traditional microparticle additives requiring much higher loading levels to achieve similar performance. This in turn can result in significant weight reductions (of obvious importance for various military and aerospace applications) for similar performance, greater strength for similar structural dimensions and, for barrier applications, increased barrier performance for similar material thickness.

Examples of Mechanical Property gains due to Nanoparticle Additions

There are data in literature relating to polyamide – montmorillonite nanocomposites indicates tensile strength improvements of approximately 40 and 20% at temperatures of 23ºC and 120ºC respectively and modulus improvements of 70% and a very impressive 220% at the same temperatures. In addition Heat Distortion Temperature was shown to increase from 65ºC for the unmodified polyamide to 152ºC for the nanoclay-modified material, all the above being achieved with just a 5% loading of montmorillonite clay. Similar mechanical property improvements were presented for polymethyl methacrylate – clay hybrids.

Further data relating to polyamide-6 polymers confirms these property trends. In addition, the further benefits of short/long glass fibre incorporation, together with nanoclay incorporation, are clearly revealed.

Areas of Application. Such mechanical property improvements have resulted in major interest in nanocomposite materials in numerous automotive and general/industrial applications. These include potential for utilisation as mirror housings on various vehicle types, door handles, engine covers and intake manifolds and timing belt covers. More general applications currently being considered include usage as impellers and blades for vacuum cleaners, power tool housings, mower hoods and covers for portable electronic equipment such as mobile phones, pagers etc.

Gas Barriers

The gaseous barrier property improvement that can result from incorporation of relatively small quantities of nanoclay materials is shown to be substantial. Data provided from various sources indicates oxygen transmission rates for polyamide-

organoclay composites which are usually less than half that of the unmodified polymer. Further data reveals the extent to which both the amount of clay incorporated in the polymer, and the aspect ratio of the filler contributes to overall barrier performance. In particular, aspect ratio is shown to have a major effect, with high ratios (and hence tendencies towards filler incorporation at the nano-level) quite dramatically enhancing gaseous barrier properties. Such excellent barrier characteristics have resulted in considerable interest in nanoclay composites in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles. The use of nanocomposite formulations would be expected to enhance considerably the shelf life of many types of food

Oxygen Barriers. A combined active/passive oxygen barrier system for polyamide-6 materials were developed Passive barrier characteristics are provided by nanoclay particles incorporated via melt processing techniques whilst the active contribution comes from an oxygen scavenging ingredient (undisclosed). Oxygen transmission results reveal substantial benefits provided by nanoclay incorporation in comparison to the base polymer (rates approximately 15-20% of the bulk polymer value, with further benefits provided by the combined active/passive system). It is suggests that the increased tortuosity provided by the nanoclay particles essentially slows transmission of oxygen through the composite and drives molecules to the active scavenging species resulting in near zero oxygen transmission for a considerable period of time.

Food Packaging (Triton Systems and the US Army are conducting further work on barrier performance in a joint investigation). The requirement here is for a non-refrigerated packaging system capable of maintaining food freshness for three years. Nanoclay polymer composites are currently showing considerable promise for this application It is likely that excellent gaseous barrier properties exhibited by nanocomposite polymer systems will result in their substantial use as packaging materials in future years. A somewhat more esoteric possibility arising from enhanced barrier performance recently suggested has been blown–films for artificial intestines!

Fuel Tanks The ability of nanoclay incorporation to reduce solvent transmission through polymers such as polyamides has been demonstrated. Data provided reveals significant reductions in fuel transmission through polyamide–6/6 polymers by incorporation of a nanoclay filler. As a result, considerable interest is now being shown in these materials as both fuel tank and fuel line components for cars. Of further interest for this type of application, the reduced fuel transmission characteristics are accompanied by significant material cost reductions.

Films. The presence of filler incorporation at nano-levels has also been shown to have significant effects on the transparency and haze characteristics of films. In comparison to conventionally filled polymers, nanoclay incorporation has been shown to significantly enhance transparency and reduce haze. With polyamide based composites, this effect has been shown to be due to modifications in the crystallisation behaviour brought about by the nanoclay particles; spherilitic domain dimensions being considerably smaller. Similarly, nano-modified polymers have been shown, when employed to coat polymeric transparency materials, to enhance both toughness and hardness of these materials without interfering with light transmission characteristics.

An ability to resist high velocity impact combined with substantially improved abrasion resistance was demonstrated.

Environmental Protection. Water laden atmospheres have long been regarded as one of the most damaging environments which polymeric materials can encounter. Thus an ability to minimise the extent to which water is absorbed can be a major advantage. Data indicates the significant extent to which nanoclay incorporation can reduce the extent of water absorption in a polymer. Similar effects have been observed with polyamide based nanocomposites. In addition, a significant effect of nanoclay aspect ratio on water diffusion characteristics in a polyimide nanocomposite. Specifically, increasing aspect ratio was found to diminish substantially the amount of water absorbed, thus indicating the beneficial effects likely from nanoparticle incorporation in comparison to conventional microparticle loading. Hydrophobic enhancement would clearly promote both improved nanocomposite properties and diminish the extent to which water would be transmitted through to an underlying substrate. Thus applications in which contact with water or moist environments is likely could clearly benefit from materials incorporating nanoclay particles.

Flammability Reduction. The ability of nanoclay incorporation to reduce the flammability of polymeric materials is a major theme. It was demonstrated the extent to which flammability behaviour could be restricted in polymers such as polypropylene with as little as 2% nanoclay loading. In particular heat release rates, as obtained from cone calorimetry experiments, were found to diminish substantially by nanoclay incorporation. Although conventional microparticle filler incorporation, together with the use of flame retardant and intumescent agents would also minimise flammability behaviour, this is usually accompanied by reductions in various other important properties. With the nanoclay approach, this is usually achieved whilst maintaining or enhancing other properties and characteristics.

8.5 Fullerenes

The discovery of fullerenes in 1985 by Curl, Kroto, and Smalley culminated in their Nobel Prize in 1996. Fullerenes, or Buck-minsterfullerenes, are named after Buckminster Fuller the architect and designer of the geodesic dome and are sometimes called bucky balls. The names derive from the basic shape that defines fullerenes; an elongated sphere of carbon atoms formed by interconnecting six-member rings and twelve isolated five-member rings forming hexagonal and pentagonal faces. The first isolated and characterized fullerene, C60, contains 20 hexagonal faces and 12 pentagonal faces just like a soccer ball and possess perfect icosahedral symmetry.

Figure 8.5- C_{60}

Fullerene physics and chemistry continues to be an exciting field generating many articles with promising new applications every year. Magnetic nanoparticles (nanomagnetic materials) show great potential for high-density magnetic storage media.

Recent work has shown that C60 dispersed into ferromagnetic materials such as iron, cobalt, or cobaltiron alloy can form thin films with promising magnetic properties. A number of organometallic-fullerene compounds have recently been synthesized. Of particular note are a ferrocene-like C60 derivative and pair of fullerenes bridged by a rhodium cluster. Some fullerene
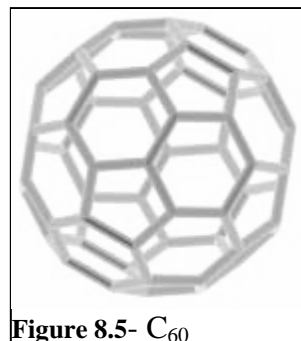
derivatives even exhibit superconducting character. There has been a report of a fullerene containing, superconducting field-effect device with a Tc as high as 117 K.

Buckyball was named "Molecule of the Year" for 1991 by *Science* magazine. In the December 20, 1991, issue of *Science*, the Editors made the following observations: "Fullerene science exhibits the classic profile of a major scientific breakthrough. Buckyballs were found by accident by researchers asking a completely different question. Then they were steadily explored - until they became widely available and the field exploded. Now, buckyball scientists are enjoying the exponential phase, in which almost everything is new and the unexpected is the expected. Eventually, the action will focus on a few promising research veins and the practical applications will bloom" (Koshland, Jr., 1991).

Since 1991, the pace of discovery in fullerene science has continued to accelerate. Researchers around the world are exploring both the basic science and potential applications of fullerenes. And the field has spawned important new areas of exploration, including carbon nanotubes and nanowires. In 1996, the Nobel Prize in Chemistry was awarded to the co-discoverers of C60, Richard Smalley, Robert Curl and Harry Kroto.

Other fullerenes were discovered shortly afterwards with more and fewer carbon atoms, ranging from 28 up into the hundreds, though C_{60} remains the easiest to produce, and cheapest, with prices rising rapidly for the larger fullerenes. The word 'fullerene' covers this collection of hollow carbon molecules made of a cage of interlocking pentagons and hexagons. Carbon nanotubes, made of graphite sheets of hexagonal arrays of carbon rolled into tubes, are close cousins in terms of production methods and some of their properties, and can be included in the fullerene family if their ends are closed, in which case they are like a buckyball extended into a tube by the insertion of carbons along its midriff. For the purposes of this report, the term fullerenes should not generally be taken to include carbon nanotubes.

8.5.1 Production methods

Fullerenes are in fact produced in small amounts naturally, in fires and lightning strikes, and there is some evidence that the massive Permian extinction of 250 million years ago was caused by the impact of an object containing buckyballs. However, they were first produced by man (at least knowingly) in the soot resulting from vaporizing graphite with a laser. The earliest bulk production process is the arc discharge (or Krätschmer-Huffman) method, using graphite electrodes, developed in 1990. This produces predominantly C_{60} and C_{70} but can be made to produce higher fullerenes, for instance by having more porous electrodes. Separation with solvents such as toluene can achieve near 100% purity for C60. A little later, a group at MIT started producing C60 in a benzene flame. And pyrolysis (transformation of a compound by heat, without burning) of a variety of aromatic compounds has also been used to produce fullerenes (aromatic compounds have benzene-derived ring structures. A typical attribute of aromatics is that they have bonding electrons free to move around, so-called delocalized electrons. Fullerenes themselves are aromatic). Methods such as sputtering and electron beam evaporation (with a graphite precursor) have been shown to preferentially produce higher fullerenes, such as C70, C76, C78, and C84.

8.5.2 Fullerene, properties

Physically, buckyballs are extremely strong molecules, able to resist great pressure—they will bounce back to their original shape after being subjected to over 3,000 atmospheres. Their physical strength does seem to offer potential in materials.

However, like nanotubes, they do not bond to each other chemically, sticking together instead through much weaker forces—van der Waals—the same forces that hold layers of graphite together. This gives buckyballs, like graphite, potential as a lubricant, though the molecules tend to be too small for many applications, getting stuck in crevices. Buckyballs with shells around them, known as nano-onions, or bucky-onions, are larger and potentially better as a lubricant. A technique for creating these with quite high purity using an underwater arc approach was demonstrated in December 2001 by a group from the University of Cambridge in the UK and the Himeji Institute of Technology in Japan.

Although buckyballs do not stick together well, this does not mean they do not have applications in solids. When incorporated in relatively low amounts in a polymer matrix they can be held in place and impart some of their strength and low density to the material. Companies such as BuckyUSA are working with the tire industry to establish whether C70 would be a superior additive to carbon black.

Fullerenes and related substances have shown considerable potential as catalysts (basically, substances that enhance a reaction without being consumed themselves). It has used bucky-onions to convert ethylbenzene into styrene, one of the ten most important industrial chemical processes. Existing approaches are limited to a maximum yield of 50% but the researchers achieved styrene yields of 62% in preliminary experiments, and expect further improvement. The bucky-onions seem, however, to be a precursor to the catalyst as they were converted in the reaction into a material that had lost the regular, concentric-layer structure of bucky-onions, and looked more or less disordered, but was an effective catalyst (*Angewandte Chemie International Edition, 41, 1885–1888*). This soot contains a variety of carbon forms that can be partially like fullerenes (composed of hexagons and pentagons) but probably with open areas that serve as catalytic sites. The soot can be used for hydrogenation/dehydrogenation of aromatics, for upgrading of heavy oils, and for conversion of methane into higher hydrocarbons by pyrolytic or reforming processes.

Fullerenes have interesting electrical properties, which have led to suggestions of use in a number of electronics-related areas, from data storage devices to solar cells.

Researchers at Virginia Tech have used ultra-thin layers of fullerenes as electron acceptors in flexible organic solar cells. Currently the efficiency is about a fifth of conventional silicon photovoltaics (so about 3-4%, compared to 15-20% for mass market silicon solar cells) but the researchers expect to be able, through better control of the nanostructure, to equal or exceed the efficiency of current silicon-based devices.

The same properties also offer potential use in photodetectors for X-rays. Another use of the electrical properties of fullerenes is in fuel cells: replacing large polymer molecules in the electrolytic membrane of direct methanol fuel cells (with personal electronics being the intended application). The result is a fuel cell capable of operating at lower temperatures than those with polymer-only membranes, Also it has been using fullerenes in work on hydrogen-based fuel cells, exploiting their ability to help move protons around (proton exchange membranes are the basis of such fuel cells).

Fullerenes have been inserted into nanotubes, the result sometimes being referred to as 'peapods'. The earliest work on this was done early in 2002 in South Korea (Seoul National University) and the US (University of Pennsylvania in Philadelphia), using C82 and C60 respectively. The fullerenes alter the electrical behavior of the nanotubes, creating regions of varying semiconducting properties, effectively producing a series of

tiny transistors within a nanotube. The properties can be modified by moving the location of the enclosed fullerenes and researchers at Michigan State University have even suggested using this to create memory devices. Such work is still at the very early research stage and applications should not be expected any time soon, if ever (there are many competing approaches to nanoelectronics and memory).
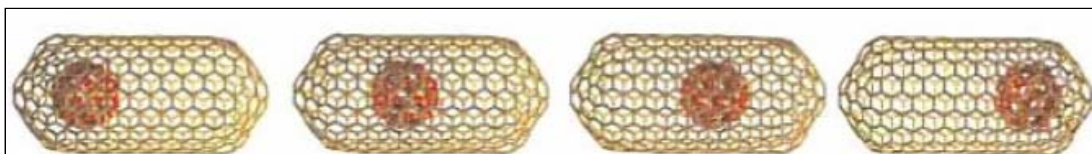
Computer simulation of nanotube-based memory element. The nanotube holds a C60 molecule inside. The C60 carries a net charge because it contains an alkali atom in the hollow cage. The C60 can be shifted from one end to the other by applying an electric field between the ends of the capsule. The two energy minima of this system, with the C60 bonded to either end of the capsule, can be associated with bit 0 and bit 1. (David Tomanek, Michigan State University,http://www.pa.msu.edu/~tomanek).

Fullerene-based materials may have important photonic device applications (photonics being essentially the equivalent of electronics but using light instead of electricity). Fullerenes exhibit a very large non-linear optical response (i.e. their optical properties change with exposure to light) and may well be suitable for a range of telecommunications applications. The non-linear optical properties may be enhanced by the addition of one or more metal atoms externally to the fullerene cage as well as within the cage itself.

Fullerenes are also effective at mopping up free radicals, which damage living tissue. This has led to the suggestion that they might protect the skin in cosmetics, or help hinder neural damage caused by radicals in certain diseases, research on which in rats has already shown promise. The size of C60 is similar to many biologically active molecules, including drugs, and steroid hormones. This gives it potential as a foundation for creating a variety of biologically active variants. Buckyballs have a high physical and chemical affinity for the active site on an important enzyme for HIV, called HIV protease, and block the action of the enzyme. HIV protease is the target of existing AIDS drugs but resistance has developed to a set of these drugs since they all have similar actions. Buckyballs target HIV protease differently so their effect should not be subject to resistance already developed.

As previously mentioned, the neuroprotective potential of C60 has already been demonstrated, and vesicles made out of them could be used to deliver drugs. Applications for buckyballs with other atoms trapped inside them, referred to as endohedral fullerenes, are mentioned later. Considerable interest was generated in the second half of 2001 by research at Lucent's Bell Labs that showed that buckyballs could be made superconducting at above the temperature of liquid nitrogen, a very important find because liquid nitrogen is relatively cheap to produce but lower temperatures are much harder to maintain.

Fullerenes and their derivatives have indeed been shown to be superconducting, but only at very low temperatures (a few tens of degrees centigrade above absolute zero).

Around the same time there was also a claim that a polymer had been created out of buckyballs that was magnetic at room temperature, making the first non-metallic magnetic material. Though no wrong-doing has been suggested in this case, these re-

sults also have not been reproduced. Besides which, in terms of potential value, this result was trumped shortly afterwards by the creation of a polymer (without buckyballs) that was also shown to be magnetic at room temperature, and considerably more so.

Fullerenes can also be used as precursors for other materials, such as diamond coatings or nanotubes

On the esoteric side, fullerenes have been used in fundamental research in quantum mechanics, being the largest particles in which the wave/particle duality of matter has been demonstrated, by getting a C60 molecule to appear to pass through two different slits simultaneously, a famous experiment normally performed with electrons, photons or single atoms.

8.5.3 Functionalization

Chemical groups can be attached to a fullerene's carbon atoms, a process called functionalization, modifying their properties. The number of carbon atoms available to do this has led to the epithet "molecular pincushion", especially within the context of medical applications such as those being developed by the company C Sixty.

Research on functionalization of fullerenes has been particularly active in recent years, with aims varying from the creation of polymers to biologically active variants.

A nice illustration of the lengths to which functionalization can be taken comes from a group at the University of Tokyo in Japan and their creation of molecular 'shuttlecocks' (see picture). These have potential in liquid crystal applications, which goes beyond liquid-crystal displays as there is growing interest in their use in areas such as nonlinear optics, photonics and molecular electronics (*Nature 419, 702–705*).
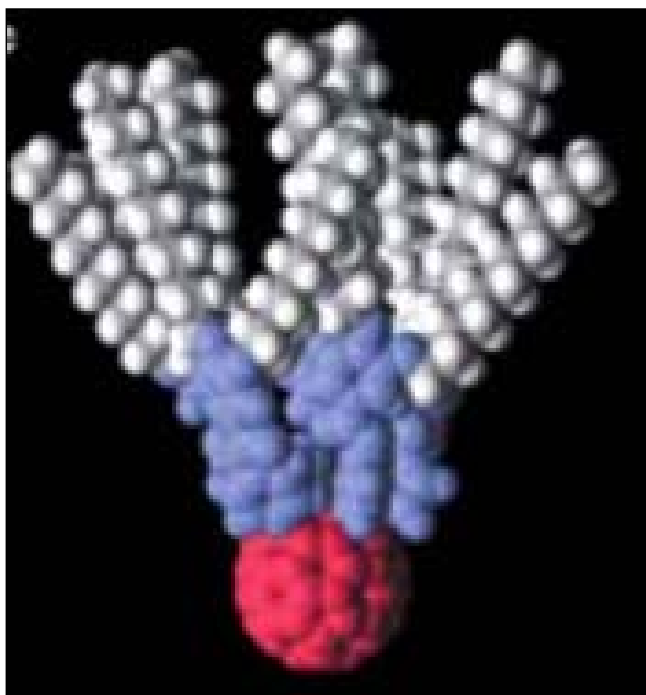
8.5.4 Endohedral fullerenes

An area of research that has been at least as active as functionalization of fullerenes is that of putting atoms inside them. The results are called endohedral fullerenes, which are described with the notation X@C60, where X is the trapped atom (or atoms) and C60 could be any fullerene. Reactive elements can be stabilized inside the fullerene cage. The contained element can also change the electronic and magnetic properties of the fullerene (the caged atom can contribute electrons to the fullerene molecule). The creation of endohedral fullerenes has proved challenging. Simple approaches involve creating the fullerenes in the presence of the element to be encapsulated, but this produces a low yield, typically less than 1%. Alternatively, fullerenes can be mixed with the substance to be encapsulated and subjected to high temperatures and pressures, or a chemical approach can be taken to open up the fullerene to let the other substance in.A huge number of elements have been encapsulated in fullerenes, including the noble gases, which have no desire to bond with the surrounding carbon atoms but can be used

in applications such as magnetic resonance imaging (MRI). Using endohedral fullerenes for medical imaging applications requires them to be water soluble. The higher fullerenes (above C60) have derivatives that are generally more soluble, but they are more expensive to produce. C60 endohedral fullerenes are generally less soluble and air-sensitive, but relatively cheap to produce. Functionalization has managed to improve solubility and also stability in air.
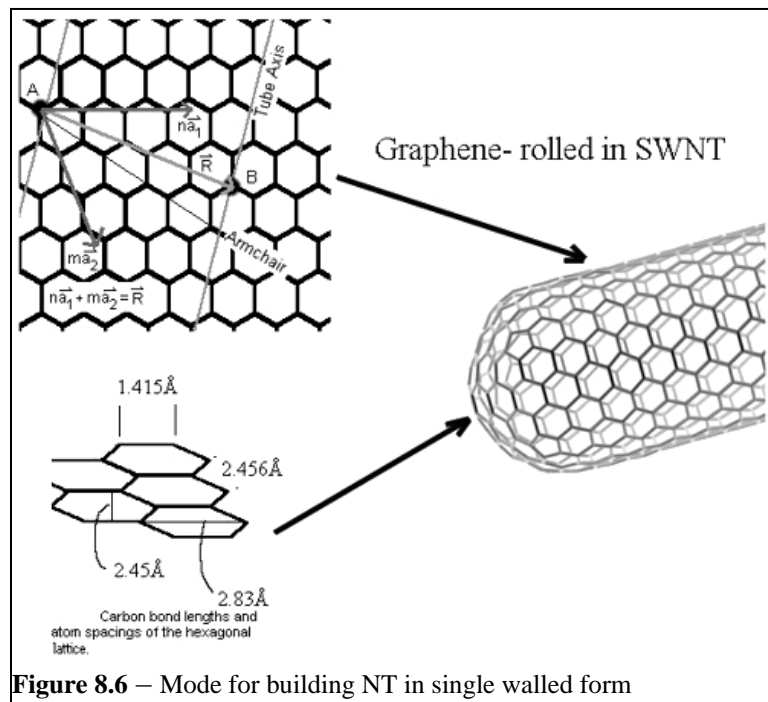
8.6 Nanotubes

Carbon nanotubes (CNTs) are hollow cylinders of carbon atoms. Their appearance is that of rolled tubes of graphite such that their walls are hex-agonal carbon rings and are often formed in large bundles. The ends of CNTs are domed structures of six-membered rings capped by a five membered ring. Generally speaking, there are two types of CNTs: single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). As their names imply, SWNTs consist of a single, cylindrical graphene layer, where as MWNTs consist of multiple graphene layers telescoped about one another (figure 8.6)

Carbon nanotubes (CNTs) were first isolated and characterized by Ijima in 1991. Since then dozens of research articles have been published, and new applications for CNTs have been proposed every year. The unique physical and chemical properties of CNTs, such as structural rigidity and flexibility continue to generate considerable interest. Additionally, CNTs are extremely strong, about 100 times stronger (stress resistant) than steel at one-sixth the weight. CNTs can also act as either conductors or semiconductors depending on their chirality, possess an intrinsic superconductivity, are ideal thermal conductors, and can also behave as field emitters.

8.6.1 Basic Structure

Simply put, carbon nanotubes exist as a macro-molecule of carbon, analagous to a sheet of graphite (the pure, brittle for m of cabon in your pencil lead) rolled into a cylinder (figure 8.6). Graphite looks like a sheet of hexagonal rings of carbon, called

Figure 8.6 – Mode for building NT in single walled form

graphene. Sheets of graphite lay stacked on top on one another, but they slide past each other and can be separated easily. However, when coiled, the carbon arrangement becomes very strong. In fact, nanotubes have been known to be up to one hundred times as strong as steel and almost two millimeters long! These nanotubes have a hemispherical "cap" at each end of the cylinder. They are light, flexible, thermally stable, and are

chemically inert. They have the ability to be either metallic or semi-conducting depending on the "twist" of the tube.

Types of SWNTs

Nanotubes form different types, which can be described by the chiral vector (n, m), where n and m are integers of the vector equation R = na$_1$ + ma$_2$. The chiral vector is determined by the diagram at the left in figure 8.6. Imagine that the nanotube is unraveled into a planar sheet. Draw two lines along the tube axis where the separation takes place. In other words, if we cut along the two and then match their ends together in a cylinder, we get the nanotube. Now, find any point on one of the lines that intersects one of the carbon atoms (point A). Next, draw the Armchair line, which travels across each hexagon, separating them into two equal halves. Now that you have the armchair line drawn, find a point along the other tube axis that intersects a carbon atom nearest to the Armchair line (point B). Now connect A and B with our chiral vector, R. The wrapping angle; (not shown) is formed between R and the Armchair line. If R lies along the Armchair line (=0°), then it is called an "Armchair" nanotube. If =30°, then the tube is of the "zigzag" type. Otherwise, if 0°<angle<30° then it is a "chiral" tube. The vector a$_1$ lies along the "zigzag" line. The other vector a$_2$ has a different magnitude than a$_1$, but its direction is a reflection of a$_1$ over the Armchair line.

When added together, they equal the chiral vector R. The values of n and m determine the chirality, or "twist" of the nanotube. The chirality in turn affects the conductance of the nanotube, it's density, it's lattice structure, and other properties. A SWNT is considered metallic if the value n - m is divisible by three. Otherwise, the nanotube is semiconducting. Consequently, when tubes are formed with random values of n and m, we would expect that two-thirds of nanotubes would be semi-conducting, while the other third would be metallic, which happens to be the case.

Given the chiral vector (n,m), the diameter of a carbon nanotube can be determined using the relationship

$$d = (n^2 + m^2 + nm)^{1/2} \ 0.0783 \ nm$$

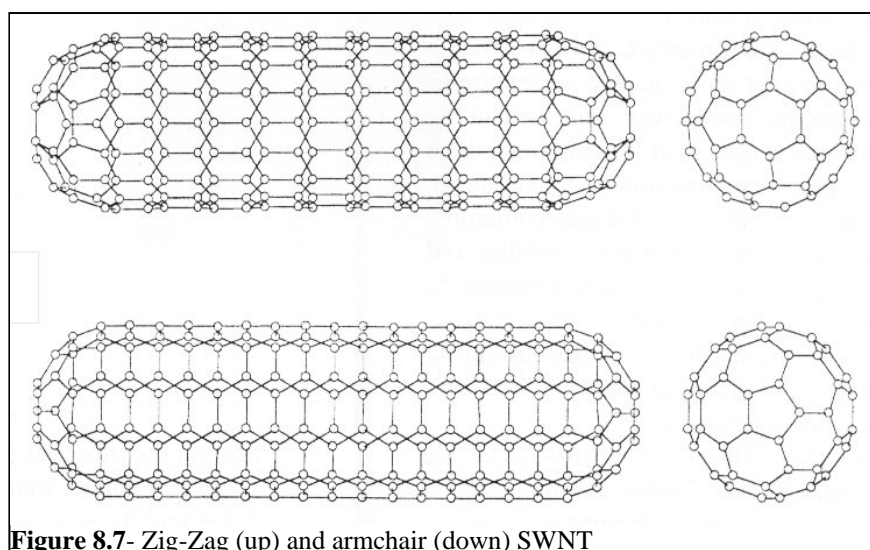The both types of SWNTs in zig-zag and armchair are sketched in figure 8.7

Figure 8.7- Zig-Zag (up) and armchair (down) SWNT

8.6.2 Basic properties

Are sumarized in table 8.1

Table 8.1			
Average Diameter of SWNT's			1.2-1.4 nm
Distance from opposite Carbon Atoms			2.83 Å
Analogous Carbon Atom Separation			2.456 Å
Parallel Carbon Bond Separation			2.45 Å
Carbon Bond Length			1.42 Å
C - C Tight Bonding Overlap Energy			~ 2.5 eV
Group Symmetry (10, 10)			C_{5V}
Lattice: Bundles of Ropes of Nanotubes	Triangular Lattice (2D)		
Lattice Constant			17 Å
Lattice Parameter:			
	(10, 10) Armchair		16.78 Å
	(17, 0) Zigzag		16.52 Å
	(12, 6) Chiral		16.52 Å
Density:			
	(10, 10) Armchair		1.33 g/cm^3
	(17, 0) Zigzag		1.34 g/cm^3
	(12, 6) Chiral		1.40 g/cm^3
Interlayer Spacing:			
	(n, n) Armchair		3.38 Å
	(n, 0) Zigzag		3.41 Å
	(2n, n) Chiral		3.39 Å
.			
Optical Properties			
Fundamental Gap:			
	For (n, m); n-m is divisible by 3 [Metallic]		0 eV
	For (n, m); n-m is not divisible by 3 [Semi-Conducting]		~ 0.5 eV
.			
Electrical Transport			
Conductance Quantization	n x (12.9 k)$^{-1}$		
Resistivity	10^{-4} -cm		
Maximum Current Density	10^{13} A/m^2		
Thermal Transport			
Thermal Conductivity	~ 2000 W/m/K		
Phonon Mean Free Path	~ 100 nm		
Relaxation Time	~ 10^{-11} s		
Elastic Behavior			
Young's Modulus (SWNT)	~ 1 TPa		
Young's Modulus (MWNT)	1.28 TPa		
Maximum Tensile Strength	~30 GPa		

8.6.3 Carbon Nanotube-Based Nanodevices

Carbon nanotubes are a hot research area at the moment. The excitement has been fueled by experimental breakthroughs that have led to realistic possibilities of using them commercially. Applications could include field emission-based flat panel displays, novel semiconducting devices, chemical sensors, and ultra-sensitive electromechanical sensors. The utility of carbon nanotubes for molecular electronics or computers, first predicted by theory and simulations, is now being explored through experiments to fabricate and conceptualize new devices based on simulations. Carbon nanotubes are now the top candidate to replace silicon when current chip features cannot be made any smaller in 10-15 years time. Calculations show that nanotubes can have metallic or variable semiconducting properties with energy gaps ranging from a few meV to a few tenths of an eV. Experiments probing the density of states confirm these predictions.

Conductivity measurements on single nanotubes have shown rectification effects for some nanotubes and ohmic conductance for others. These properties suggest that nanotubes could lead to a new generation of electronic devices. Simulations to investigate the interaction of water molecules with a nanotube tip revealed an atomistic understanding of the interaction, which is critical in designing commercial-quality flat panel displays around carbon nanotubes. Their use as ultra-sensitive electromechanical sensors has also been explored.

8.7 Polyhedral Silsesquioxanes (Inorganic-Organic Hybrid Nanoparticles)

Hybrid inorganic-organic composites are an emerging class of new materials that hold significant promise. Materials are being designed with the good physical properties of ceramics and the excellent choice of functional group chemical reactivity associated with organic chemistry. New silicon-containing organic polymers, in general, and polysilsesquioxanes, in particular, have generated a great deal of interest because of their potential replacement for and compatibility with currently employed, silicon-based inorganics in the electronics, photonics, and other materials technologies. Hydrolytic condensation of trifunctional silanes yields network polymers or polyhedral clusters having the generic formula $(RSiO1.5)n$. Hence they are known by the "not quite on the tip of the tongue" name silsesquioxanes. Each silicon atom is bound to an average of one and a half (sesqui)

Figure 8.8- One Silsesquioxanes: $C_{32}H_{96}N_8O_{20}Si_8 \cdot xH_2O$(Octakis(tetramethylammonium) substituted

oxygen atoms and to one hydrocarbon group (ane). Typical functional groups that may be hydrolyzed/condensed include alkoxy- or chlorosilanes, silanols, and silanolates. (figure 8.8)
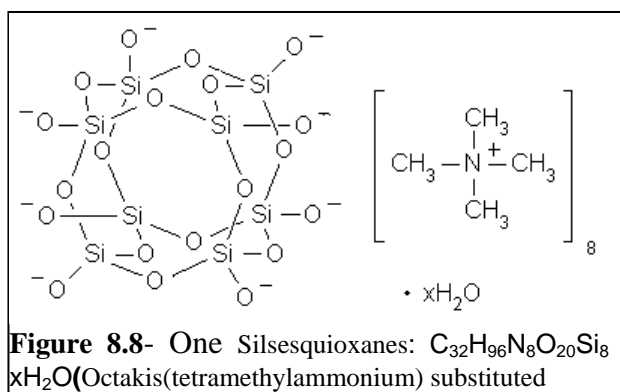
Synthetic methodologies that combine pH control of hydrolysis/condensation kinetics, surfactant-mediated polymer growth, and molecular templating mechanisms have been employed to control molecular scale regularity as well as external morphology in the resulting inorganic/organic hybrids (from transparent nanocomposites, to

mesoporous networks, to highly porous and periodic organosilica crystallites) all of which have the silsesquioxane (or RSiO1.5) stoichiometry. These inorganic-organic hybrids offer a unique set of physical, chemical, and size dependent properties that could not be realized from just ceramics or organic polymers alone. Silsesquioxanes are therefore depicted as bridging the property space between these two component classes of materials. Many of these silsesquioxane hybrid materials also exhibit an enhancement in properties such as solubility, thermal and thermomechanical stability, mechanical toughness, optical transparency, gas permeability, dielectric constant, and fire retardancy, to name just a few.

8.8 Nano-Intermediates

Nanostructured films, dispersions, high surface area materials, and supramolecular assemblies are the high utility intermediates to many products with improved properties such as solar cells and batteries, sensors, catalysts, coatings, and drug delivery systems. They have been fabricated using various techniques. Nanoparticles are obvious building blocks of nanosystems but, require special techniques such as self-assembly to properly align the nanoparticles. Recent developments have lead to air resistant, room temperature systems for nanotemplates with features as small as 67 nm. More traditionally, electron-beam systems are used to fabricate devices down to 40 nm.

8.9 Nanophases, nanopowders

Nanocrystalline materials in general nanoparticles (nanopowders) from amorphous to crystalline, alloyed materials or coated with shells, encapsulated nanoparticles. Nanophases are single or multiple phases in a single nanoparticle: Encapsulated nanoparticles with coated surface, or in thin polymeric shell that enables compatibility of the particles with a wide variety of fluids, resins and polymers. Nanophases are developed to permit the dispersion in water and a variety of polar and non-polar organic fluids. This allows concentrated, ready-to-use nanoparticle dispersions, eliminating the need for customers to disperse the nanoparticles themselves.

Nanophase's family are nanocrystalline materials, and then nanoengineers those materials to fit an application need.

An enhanced capability of Nanophases is ability to confine complex multi-component materials. This process has demonstrated the ability to produce homogeneous mixed metal oxide nanopowders where the component materials form solid solutions with well-defined single/multiple crystalline phases. Nanocrystalline metal oxides having up to four metallic elements have been successfully produced. A wide variety of single-phase pure and mixed rare earth oxides, as well as pure and mixed transition metal oxides and main group metal oxides. The materials produced by specific processes have application in ultrafine polishing and chemical-mechanical planarization (CMP), catalysis, fuel cells, electronic materials, and advanced imaging, personal care, sunscreens, abrasion-resistant applications, environmental catalysts, antimicrobial products, and a variety of ultra-fine polishing applications, including semiconductor wafers, hard disk drives, and optics.

Various applications include wood preservation, anti-fouling and anti-microbial coatings, fuel cells, catalytic converters, UV-attenuation coatings, scratch resistant coatings, charge dissipating coatings, deodorant/antiperspirants, depilatory/shaving products, and others.

PVS (Physical Vapor Synthesis)

In this process, electrical arc discharge energy is first applied to a solid precursor (typically metal) in order to generate a vapor at high temperature. A reactant gas is then added to the vapor, which is then cooled at a controlled rate and condenses to form nanoparticles. The nanomaterials produced by the PVS process consist of discrete, fully-dense particles of defined crystallinity. This method typically produces particles with average sizes ranging from 8-75 nm. In addition, this process has been used to generate additional materials such as a variety of doped zinc oxides, selected rare earth and transition metal oxides, and transparent conductive oxides such as antimony-tin oxide and indium-tin oxide.

Synthesis in arc electric discharge submersed in fluid (nanoarc synthesis-NAS)

Like the PVS process, the NAS process uses arc energy to produce nanoparticles. The NAS process, however, is capable of using a wide variety precursor formats and chemical compositions, thereby greatly expanding the number of materials that can be manufactured as nanopowders,discrete, fully-dense particles of defined crystallinity, with average sizes ranging from 7-45 nm.

This process has demonstrated the ability to produce homogeneous mixed metal oxide nanopowders where the component materials form solid solutions with well-defined single crystalline phases. Nanocrystalline metal oxides having up to four metallic elements have been successfully produced.

The NAS process has the capability to produce a wide variety of single-phase pure and mixed rare earth oxides, as well as pure and mixed transition metal oxides and main group metal oxides..

Nanoparticle Coatings - Discrete Particle Encapsulation

Coating the surface of the nanoparticles with a thin polymeric shell that enables compatibility of the particles with a wide variety of fluids, resins and polymers. In this way, the nanoparticles retain their original chemical and physical properties, but the coating can be tailored for wide variety of applications and environments, ranging from extremely non-polar (hydrophobic) to very polar systems.

Nanoparticle Dispersions

Application areas as diverse as cosmetics, coatings, polishing and catalysis all require that the particles are initially well dispersed and that the particles stay well dispersed (i.e. do not aggregate or "crash out" in the application environment) in order to exhibit their full activity.

Aqueous Dispersions

Oftentimes, the electrostatic requirements for aqueous dispersion stability can be directly engineered at the particle surface using the PVS or NAS processes. In other cases, depending upon the application pH requirements, a compatible dispersant chemistry is selected which allows the particles to maintain a high electrostatic charge even after the natural isoelectric point of the particles is crossed. Under these conditions, the particles repel one another and do not aggregate. This dispersant chemistry is used in conjunction with specialized processing to produce highly stable, concentrated aqueous dispersions of the nanoparticles. In addition, once the particles are well dispersed in water, a variety of further processing options can be accessed: additional complimentary chemistries can be added, the pH can be altered to suit a particular application, or the particle size distribution can be tailored to meet a specific requirement.

Organic Dispersions

In polar and non-polar organic fluids, nonionic steric stabilizers are employed. These dispersants prevent the particles from forming larger aggregates through repulsive forces extending from the particle-continuous phase interface.

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Carbon Nanotubes - A Time Line

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Chapter 9

The Pressure

The pressure P is the ratio of the force F applied to a surface A: $d\vec{F} = Pd\vec{A}$

Pressure = force / area. SI unit = *Pascal (Pa) = 1 Newton / m².*

Atmospheric pressure: the column of the atmosphere air pressing down on a given unit area.

9.1 The pressure in gases

Gases consist of molecules that are constantly moving through space in strait lines, randomly, and with various speeds. The average kinetic energy of the gas molecule is proportional to the absolute (K) temperature – meaning, the higher the temperature, the faster the gas particles move.

The gas molecules collide with each other without loosing any kinetic energy – like billiard balls. The molecules volume is tiny compared to that of the container – the assumption that in comparison the gas molecules take up not volume is used. Gas molecules have no attraction between themselves.

Figure 9.1 − The pressure definition for a gas as results of the molecules impacts on walls and as force per area for any body

The collisions against the sides of the container constitute the pressure of the gas.

Kinetic molecular theory establishes pressures from the molecules collisions with walls, defines kinetic temperature.

STP = Standard Temperature and Pressure = 1atm =
760 mm Hg = 760 torr
1atm = 101,325 Pa; T=273K

Barometer -Torricelli
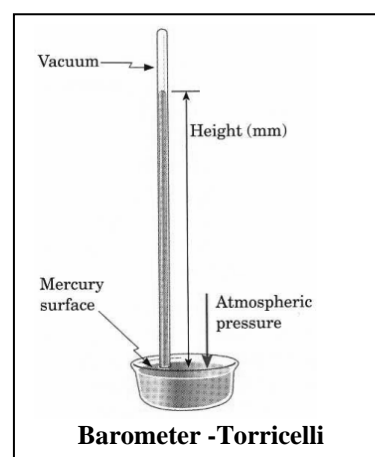
9.2 The pressure in liquids

The measurements of the hydrostatic pressure employee a large variety of methods depending of the pressure range. Roughly, the range of the pressures can be subdivided in: low pressure (<1atm), atmospheric pressures (1-100atm), high and ultrahigh pressures specific for: supercritical fluids (10-20Kbar), diamond synthesis (30-100Kbar), metallic hydrogen (1Mbar), nuclear fusion. At very high pressure the pressure is generated by solid compression. The pressure is transmitted to reaction volume in a quasi-hydrostatic manner.

Low pressures are specific in vacuum technique: for vacuum- $1-10^{-3}$torr, high vacuum- up to 10^{-6} torr, ultrahigh vacuum ($10^{-8}-10^{-12}$torr).

The range of atmospheric pressures is measured with manometers, at high pressure by fixed point transition, at low pressure with McLeod manometer and pressure gauges.

Direct measurements: Direct measurement pressure gauges, U-tube Manometer, McLeod gauge, Bourdon gauge Diaphragm gauges - Mechanical linkage type, Strain gauge type, Capsule type, Capacitance Manometer.

Indirect measurements: Thermal Conductivity gauges - **Pirani gauge, Thermistor gauge,Thermocouple gauge,** Calibration of thermal gauges. Ionization type gauges, Principle of ionization, Discharge tube, Hot filament gauge, Extension of range using **Bayard-Alpert type gauge**, **Cold cathode Penning gauge**

9.2.1 The manometer (U-tube)

Is a device employed to measure pressure. There is a variety of manometer designs. A simple, common design is to seal a length of glass tubing and then bend the glass tube into a U-shape. The glass tube is then filled with a liquid, typically mercury, so that all trapped air is removed from the sealed end of the tube. The glass tube is then positioned with the curved region at the bottom. The mercury settles to the
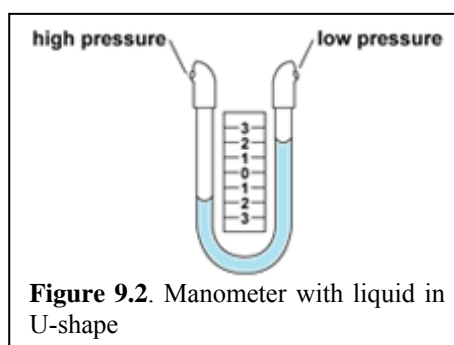
Figure 9.2. Manometer with liquid in U-shape

bottom. The various types of manometers have much in common with the U-tube manometer, which consists of a hollow tube, usually glass, a liquid partially filling the tube, and a scale to measure the height of one liquid surface with respect to the other. One end of the hollow tube of a manometer is the high-pressure end and the other the low-pressure. If the low-pressure end is open to atmospheric pressure, the remaining end may be used to measure vacuum or gage pressure.

The barometer- is a specific manometer designed to measure the atmosphere pressure. To understand how the height of a column of mercury can be used as a unit of pressure and how the unit of torr is related to the SI unit of Pascal consider the following mathematical analysis of the behavior of the manometer.

The force exerted by the column of mercury in a tube arises from the gravitational acceleration of the column of mercury. Newton's Second Law provides an expression for this force:

$$F = m\,g$$

In this equation, m is the mass of mercury in the column and $g = 9.80665$ m^2/sec is the gravitational acceleration. This force is distributed over the cross-sectional area of the column (A). The pressure resulting from the column of mercury is thus

$$P = \frac{mg}{A} = \rho g H$$

This equation clearly shows that the height of a column of mercury is directly proportional to the pressure exerted by that column of mercury. The difference in heights of the two columns of mercury in a manometer can thus be used to measure the difference in pressures between the two sides of the manometer.

The relation between torr and Pa is also evident. Using ρ_{Hg} = 13.5951 g cm^{-3}, one finds that 1 torr = 133 Pa or 1 atm = 760 torr = 101 kPa.

9.2.2 Well-type manometer

One leg of this manometer has a relatively small diameter, and the second leg is a reservoir. The cross-sectional area of the reservoir may be as much as 1500 times that of the vertical leg, so that the level of the reservoir does not change appreciably with a change of pressure. Small adjustments to the scale of the vertical leg compensate for the little reservoir level change that does occur. Readings of differential or gage pressure may then be made directly on the vertical scale. Mercurial barometers are commonly made as well-type manometers (Figure 9.3).
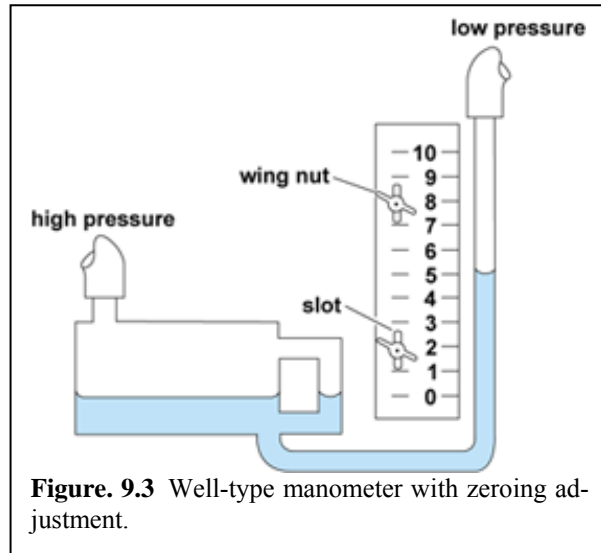
Figure. 9.3 Well-type manometer with zeroing adjustment.

9.2.3 Inclined-tube manometer

This is used for gage pressures below 250 mm of water differential.

The leg of the well-type manometer is inclined from the vertical to elongate the scale Figure 9.4. Inclined double-leg U-tube manometers are also used to measure very low differential pressures. Water or some other low-specific-gravity liquid is employed for this application.

9.2.4 Micromanometer

Micromanometer U-tubes have been made using precision-bore glass tubing, a metallic float in one leg, and an inductive coil to sense the position of the float. A null-balance electronic indicator can detect pressure changes as minute as 13 micrometers of water. Such devices are normally used as laboratory standards.
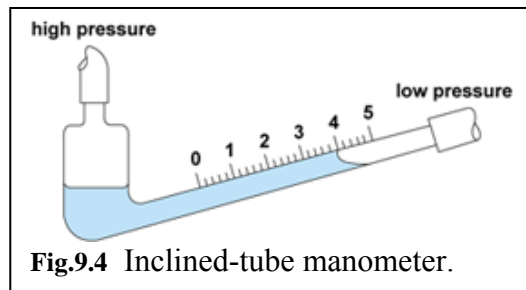
Fig.9.4 Inclined-tube manometer.

9.3 Pressure guages

9.3.1 Expansible metallic-element gages, Bourdon models

"In 1849 the Bourdon tube pressure gauge was patented in France by Eugene Bourdon. It is still one of the most widely used instruments for measuring the pressure of liquids and gases of all kinds, including steam, water, and air up to pressures of hundred atmospheres. Eugene Bourdon founded the Bourdon Sedeme Company to manufacture his invention. The American patent rights to Eugene Bourdon's gauge were bought by Edward Ashcroft in 1852. Ashcroft played an important role in the widespread adoption of steam power in this country. He renamed Bourdon's gauge, the Ashcroft gauge"

Bourdon gauge is a thin-walled metal tube, somewhat flattened and bent into the form of a C. Attached to its free end is a lever system that magnifies any motion of the free end of the tube. On the fixed end of the gauge is a fitting you thread into a gas pressure system. As the tube straightens, the pointer moves around a dial that indicates the pressure in atm or bar. Bourdon gauges are in wide use throughout industry, due to their low cost and freedom from the operational limitations of liquid gages. There are three classes (Figure 9.5): A-bourdon, B-diaphragm, and C-bellows. All forms as single elements are affected by variations in external (atmospheric) pressures and hence are generally used as gage elements. Accuracies vary depending on materials, design, and precision of components. These elements may be designed to produce either motion or force under applied pressure. The more common motion type may directly position the pointer of a concentric indicating gage; position a linkage to operate a recording pen, or pneumatic relaying system to convert the measurement into a pneumatic signal; or position an electrical transducer to convert to an electrical signal.

Bourdon-spring gages (figure 9.5 A), in which pressure acts on a shaped, flat-
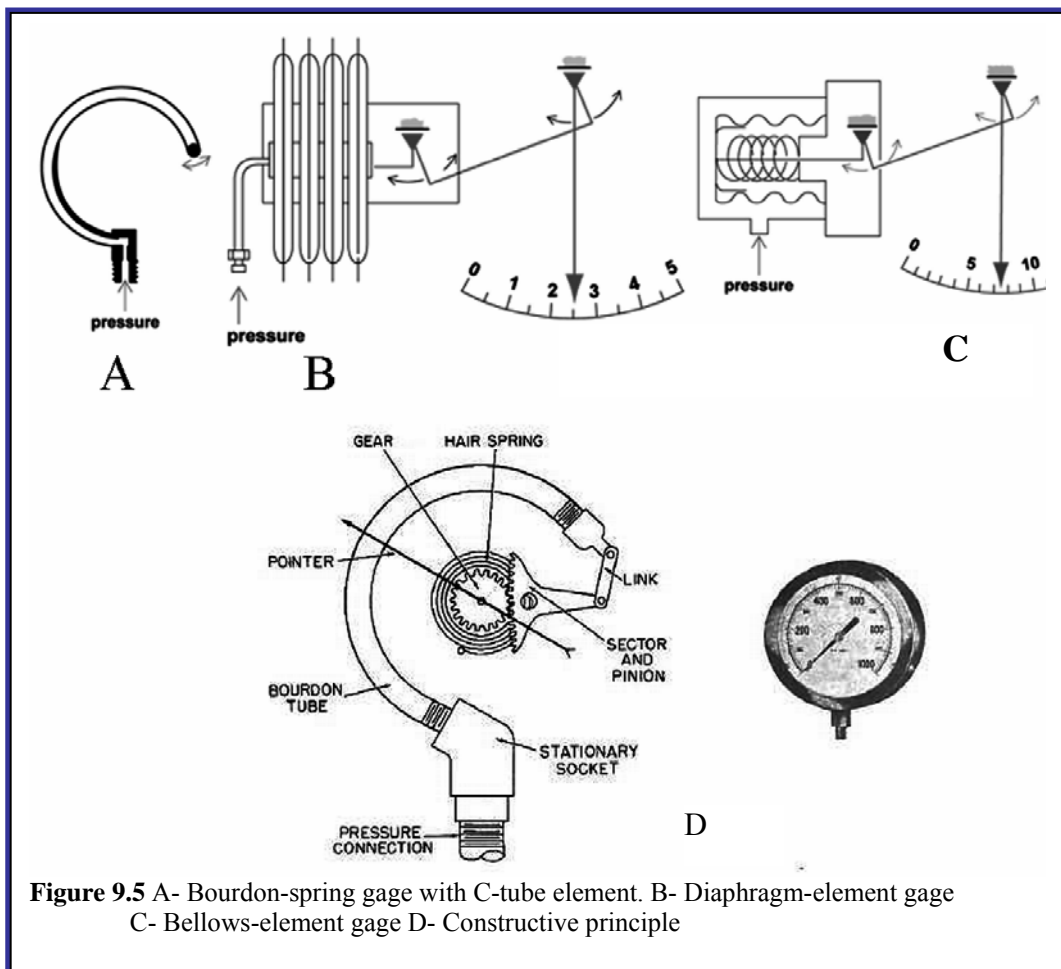
Figure 9.5 A- Bourdon-spring gage with C-tube element. B- Diaphragm-element gage
C- Bellows-element gage D- Constructive principle

tened, elastic tube, are by far the most widely used type of instrument. These gages are simple, rugged, and inexpensive. Common types have a C-, spiral-, helix-, or twisted-tube element. While most bourdons are metal, improved accuracy is sometimes accomplished with quartz bourdons.

In **diaphragm-element** gages, pressure applied to one or more contoured diaphragm disks acts against a spring or against the spring rate of the diaphragms, producing a measurable motion . Size, number, and thickness of the disks determine the range. For lower pressures, slack membrane diaphragms are used, opposed by a calibration spring; these instruments can detect differential pressures as low as 0.25 mm of water (2.5 pascals).

In bellows-element gages, pressure in or around the bellows moves the end plate of the bellows against a calibrated spring, producing a measurable motion .

Advances in the quality of metals and in the manufacture of metallic-element gages have led to a corresponding improvement in the quality of this type of gage. This is also true of the bourdon and diaphragm elements.

One side of the diaphragm is exposed to the pressure being measured, while the other side is exposed to the pressure of the atmosphere. Any increase in the pressure line moves the diaphragm upward against the spring, moving the pointer to a higher reading. When the pressure decreases, the spring moves the diaphragm downward, rotating the pointer to a lower reading. Thus, the position of the pointer is balanced between the pressure pushing the diaphragm upward and the spring action pushing down. When the gauge reads 0, the pressure in the line is equal to the outside air pressure.

9.3.2 Electrical pressure transducers

Pressure transducer: instrument component which detects a fluid pressure and produces an electrical, mechanical, or pneumatic signal related to the pressure. In general, the complete instrument system comprises a pressure-sensing element such as a bourdon tube, bellows, or diaphragm element: a device which converts motion or force produced by the sensing element to a change of an electrical, mechanical, or pneumatic parameter; and an indicating or recording instrument. Frequently the instrument is used in an autocontrol loop to maintain a desired pressure. Although pneumatic and mechanical transducers are commonly used, electrical measurement of pressure is often preferred because of a need for long-distance transmission, higher accuracy requirements, more favorable economics, or quicker response. Especially for control applications, pneumatic pressure signal transmission may be desirable over electrical where flammable materials are present.

Electrical pressure transducers may be classified by the operating principle as resistive transducers, strain gages, magnetic transducers, crystal transducers, capacitive transducers, and resonant.

9.3.2.1 THE STRAIN GAUGES, RESISTIVE PRESSURE TRANSDUCERS

Pressure is measured in these transducers by an element that changes its electrical resistance as a function of pressure (figure 9.6)

The strain gauge has been in use for many years and is the fundamental sensing element for many types of sensors, including pressure sensors, load cells, torque sensors, position sensors, etc. The majority of strain gauges are foil types, available in a wide choice of shapes and sizes to suit a variety of applications. They consist of a pattern of resistive foil which is mounted on a backing material. They operate on the principle that as the foil is subjected to stress, the resistance of the foil changes in a defined way. The strain gauge is connected into a Wheatstone Bridge circuit with a combination of four active gauges (full bridge), two gauges (half bridge), or, less commonly, a single gauge (quarter bridge). In the half and quarter circuits, the bridge is completed

with precision resistors. A detailed procedure for measurements is described in annex of this chapter.

Another variety of strain gage transducer uses integrated circuit technology. Resistors are diffused onto the surface of a silicon crystal within the boundaries of an area which is etched to form a thin diaphragm. Conductive pads at the ends of the resistors and fine wires provide the electrical connection to external electronic circuitry. Often four resistors are connected in a bridge circuit so that an applied pressure leaves one pair of resistors in compression and the other pair in tension, yielding the maximum output change.
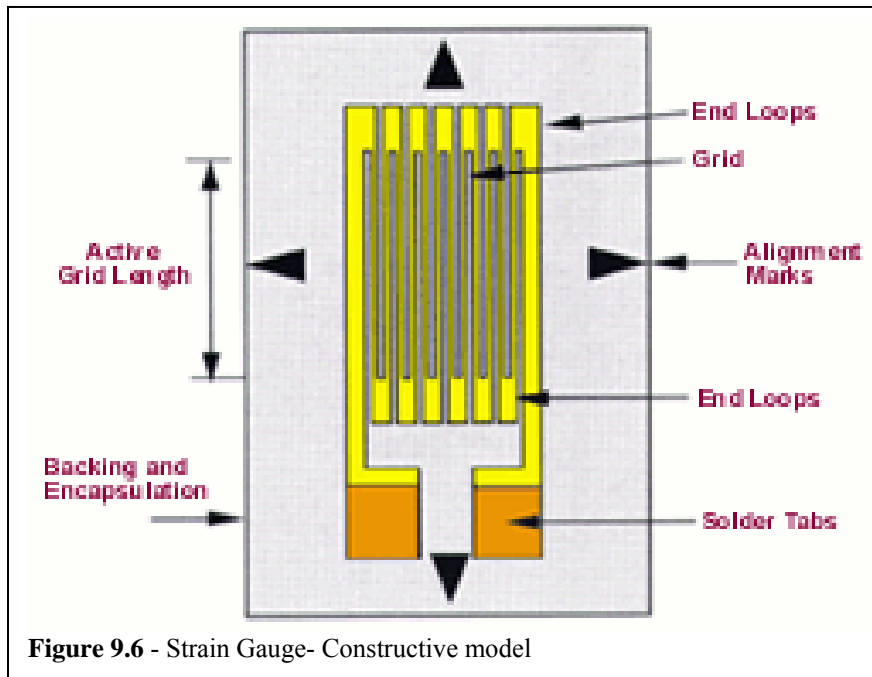
Figure 9.6 - Strain Gauge- Constructive model

9.3.2.2 MAGNETIC PRESSURE TRANSDUCERS

In this type, a change of pressure is converted into change of magnetic reluctance or inductance when one part of a magnetic circuit is moved by a pressure-sensing element bourdon tube, bellows, or diaphragm.

Reluctance-type pressure transducer

This type produces in a magnetic circuit a change of magnetic reluctance which is directly related to pressure. The change of reluctance is usually within one or two coils, wound intimately about the magnetic material in the magnetic circuit. A representative re-

Figure 9.7 Reluctance-type pressure transducer

luctance-changing device is shown in figure 9.7. A bourdon-type or other pressure-sensing device rotates the armature. The reluctances in the magnetic paths A and B are determined chiefly by the lengths of the air gaps between the armature and the core. The

inductance and inductive reactance of each winding depend on the reluctance in its magnetic path. If the armature is at a neutral symmetrical position, the air gaps are equal, and the inductive reactances XLA and XNB are equal. Change of pressure decreases one air gap and increases the other, thus changing the ratio of the inductive reactances XLA and XLB. These changes can be used in a variety of circuits to produce an electrical signal which is a measure of pressure. The signal is transmitted to a measuring or controlling instrument.

Inductive-type pressure transducer

A change in inductance and inductive reactance of one or more windings is produced by the movement of a magnetic core that is positioned by a bourdon tube or other pressure-sensing element. Unlike the action of a reluctance-type transducer, the inductance change is caused by a change in air gap within the winding, rather than in a relatively remote portion of the magnetic circuit. Figures 9.8 hows a representative ratio-type inductive device. The pressure-sensing element moves the core in response to changes of pressure. When the core is in a central position, the inductances of the two coils are equal. When a pressure change moves the core, the ratio of the two inductances is changed. Energy is supplied to the coils by the same bridge circuit that measures the ratio of inductances.

| Inductive pressure transducer | Linear variable differential transformer |
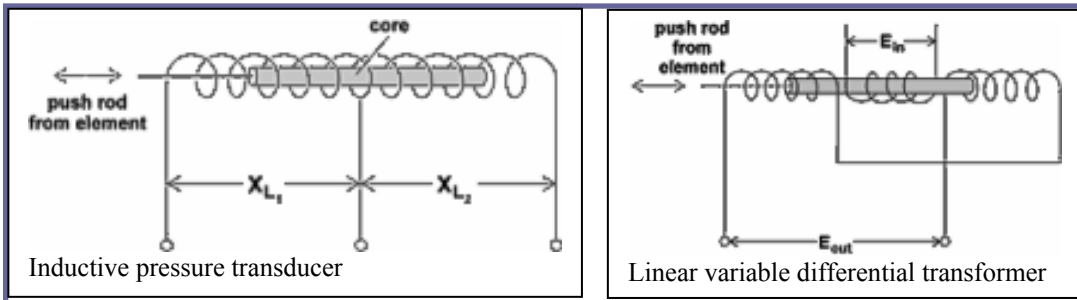
Figure 9.8- Inductive pressure transducer

Another form of inductive pressure transducer is the linear variable differential transformer (figure 9.8 right). When the core is centered, equal voltages are induced in two oppositely wound secondary windings and the output voltage is zero. A change of pressure moves the core, increasing the voltage induced in one secondary and decreasing the voltage induced in the other. The change in output (differential) voltage is thus a measure of the pressure.

9.3.3 Other pressure transducers

Piezoelectric pressure transducers

Some crystals produce an electric potential when placed under stress by a pressure-sensing element. The stress must be carefully oriented with respect to a specific axis of the crystal. Suitable crystals include naturally occurring quartz and tourmaline, and synthetic crystals such as Rochelle salts and barium titanate. The natural crystals are more rugged and less subject to drift. Although the synthetic crystals offer much higher voltage output, an amplifier is usually required for both types. Crystal transducers offer a high speed of response and are widely used for dynamic pressure measurements in such applications as ballistics and engine pressures.

Capacitive pressure transducers

Almost invariably, these sense pressure by means of a metallic diaphragm, which is also used as one plate of a capacitor. Any variation in pressure changes the distance

between the diaphragm and the other plate or plates, thereby changing the electrical capacitance of the system. The change in capacitance can be used to modify the amplitude of an electrical signal.

Resonant transducers

This transducer consists of a wire or tube fixed at one end and attached at the other (under tension) to a pressure-sensing element. The wire is placed in a magnetic field and allowed to oscillate at its resonant frequency by means of an electronic circuit. As the pressure is increased, the element increases the tension in the wire or tube, thus raising its resonant frequency. This frequency may be used directly as the transducer output or converted to a dc voltage or digital output through the use of intermediate electronics.

9.4 Vacuum Techniques

Vacuum technology has advanced considerably over the last 25 years and very low pressures are now routinely obtainable.

Units used in vacuum science and technology

- The SI unit of pressure is the Pascal ($1\ Pa = 1\ N\ m^{-2}$)
- Normal atmospheric pressure (1 atm.) is 101325 Pa or 1013 mbar (1 bar = 10^5 Pa).
- An older unit of pressure is the Torr (1 Torr = 1 mmHg). One atmosphere is ca. 760 Torr (i.e. 1 Torr = 133.3 Pa).
- 1 Torr = 1 mm Hg at 0°C, standard gravity
- 1 atm = 760 Torr

Whilst the mbar is often used as a unit of pressure for describing the level of vacuum, the most commonly employed unit is still the Torr. (The SI unit, the Pa , is almost never used !).

Classification of the degree of vacuum is hardly an exact science - it very much depends upon who you are talking to - but as a rough guideline is in bellow classification:

Rough (low) vacuum	$1 - 10^{-3}$ Torr
Medium vacuum	$10^{-3} - 10^{-5}$ Torr
High vacuum (HV)	$10^{-6} - 10^{-8}$ Torr
Ultrahigh vacuum (UHV)	$< 10^{-9}$ Torr

Otto von Guericke (originally spelled *Gericke*) (1602 - 1686) was the mayor of Magdeburg from 1646 to 1676. During this time he investigated vacuum and air pressure, invented the vacuum pump, and made the Magdeburg hemi-spheres, which he demonstrated again in Berlin in 1663 with even more (24) horses.

Virtually all surface studies are carried out under UHV conditions - the question is **why**?. We will address this question in surface science sections.

9.4.1 Pro vacuum, Physics and Chemistry

Vacuum is needed to disclose some aspects of the physics and chemistry of surfaces and interfaces. Surfaces and interfaces are everywhere and many related phenomena are common in daily life (texture, friction, surface tension, corrosion, heterogeneous catalysis). We are here concerned with understanding the microscopic properties of surfaces, asking questions like: what is the atomic structure of the surface compared to that of the bulk? What happens to the electronic properties and vibrational properties upon creating a surface? What happens in detail when we adsorb an atom or a molecule on a surface? In some cases, establishing a connection to the macroscopic surface phenomena is possible in others the microscopic origin of these phenomena is still completely unclear. We will mostly concentrate on simple model systems like the clean and defect-free surface of a single-crystal substrate. Such things do of course only exist in theory but the technological progress in the last 30 years (see below) has made it possible to get close to this ideal. This together with the progress in surface science theory makes it meaningful to compare experimental results to first-principles calculations. Why does one want to study surfaces and interfaces in the first place? Here are some motivating aspects.

One of the most important motivations in surface science is the understanding of heterogeneous catalysis. The fact that the presence of a solid could accelerate a chemical reaction without modifying the solid was first discovered in the early 19th century. Knowledge about catalysis has then rapidly grown and been the basis of the developing chemical industry. In the beginning, the microscopic mechanism of the catalytic process was, of course, unknown. Much was tried and ``good'' catalysts were made from experience. A typical surface science experiment on an ``ideal'' single crystal surface in ultra-high vacuum (UHV) is rather far away from the conditions a real catalyst is working in: the catalyst may be made of small metal particles dispersed on an inert substrate in a high pressure of gas at elevated temperature. Nevertheless, the surface science approach can give important information about many fundamental processes in catalysis. But there are of course situations where this is not enough.

Therefore, one tries to move into a direction where one is closer to the real catalyst but still very controlled. One for example can, study the catalytic properties of well-defined metal clusters on a well-defined surface. The ultimate goal is of course to really understand the catalytic reaction in all steps and to improve the catalyst (make it cheaper or more efficient).

Closely related to this is the issue of corrosion. Questions are: what are the chemical reactions leading to corrosion? How do they take place on the surface and what can we do to prevent them?

Another reason for the growing interest in surfaces is related to the semiconductor industry. There is a strong need to build smaller and smaller structures to get higher integration on computer chips. One consequence of small structures is that the relative importance of the surfaces is increasing. Another, more practical, consequence is the need to build these structures with high precision and to have flat interfaces between them. This is also an issue in the growth of thin and ultra-thin films and multilayers needed for semiconductors, magnetic storage, coatings and so on. One wishes to learn how to grow thin and uniform films of material A on material B. Even if such a film

growth is not possible (for example because A forms drops and clusters on B) one might still find a way to grow the film adding by using so-called ``surfactants''. Surface Science research on semiconductor surfaces is much closer to the real technological world than the research in heterogeneous catalysis. Most semiconductor devices are made of Si, grown on the surface of a single-crystal waver.

Related to the increased importance of surfaces in connection to smaller semiconductor structures is the field of nano technology. The importance of surface (or even edge and kink) effects is obvious. In addition to this, the surface is the ideal starting point for building very small structures. A promising current research field is for example the study of structural formation by self-organization.

A more fundamental issue is that surfaces and interfaces provide a unique opportunity to study (nearly) two-dimensional electronic systems. The most famous examples for this are the integer and the fractional quantum hall effect where a two-dimensional electron gas is generated in a semiconductor heterostructure (we will later see how) and studied at very low temperature and in high magnetic fields. Another example might be the electronic structure of the new high T_c superconductors and related compounds where much of the interesting physics goes on in the two-dimensional copper oxide planes. Yet another example are quasi two-dimensional electronic states on surfaces which can by used to study a lot of interesting many-body effects.

Historically, the interest in surfaces is an old one. People where always fascinated by the more macroscopic phenomena of surface colour and texture. It was also realized early that very little oil spreads over enormous areas on the surface of water. Catalysis was discovered, as mentioned above, in the first half of the 19th century. In the 1870ies the theory of surface thermodynamics was essentially completed by J.W. Gibbs.

Systematic experimental studies where pioneered in the beginning of last century by I. Langmuir. His studies of gas-surface interactions where even closely related to technical progress in electrical lamps. Around the same time, the basis of two other very important surface science experimental techniques was discovered: Einstein developed the theory of the photoelectric effect and Davisson and Germer showed that electrons behave like ``matter waves'' and can be diffracted from a crystal. We will come back to these two types of experiments later. In the 30s and 40s of last century tremendous theoretical progress about the surface and interface electronic structure was made (electronic surface states and semiconductor junctions) and the transistor was invented. Well-controlled experimental work first took off in the 60s when it became possible to generate vacuum conditions which were so good that surfaces could be cleaned and kept clean for a time long enough to do some useful experiments with them. Many experimental techniques were introduced, in particular the use of electron spectroscopy turned out to be essential for the progress in surface science. In the 80s the scanning tunnelling microscope was invented. It lead to a wide range of real-space studies on a truly atomic scale. The key-ingredient to surface science experiments is ultra-high vacuum. This means pressures in the 10^{-9} mbar range and below. Only such a low pressure will assure that a surface stays clean for a time long enough to do some experiments (we will see later how to obtain a clean surface). In the following, some important parts of UHV technology are described. To get a feel for it we will go down to the lab during the exercise and look at the hardware

9.4.2 Pumping and bake out

In order to achieve UHV conditions in UHV chamber two stages of pumping are needed (see Fig 9.9).
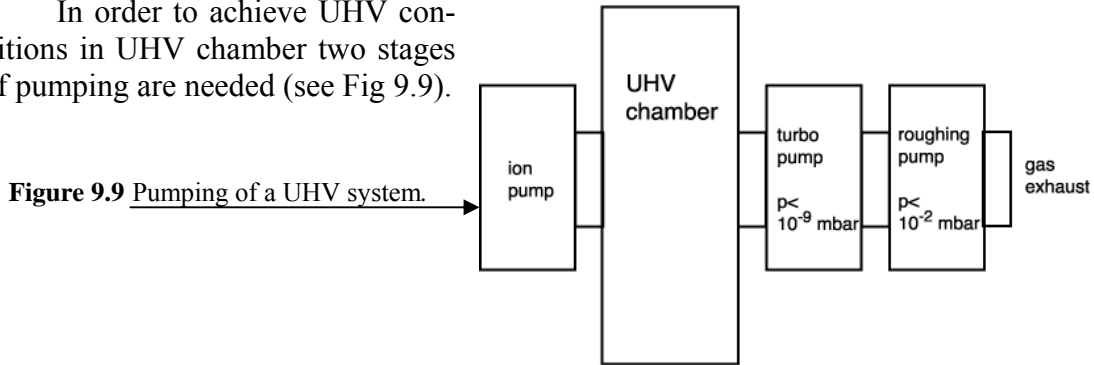
Figure 9.9 <u>Pumping of a UHV system.</u>

9.4.3 Vacuum pump

A vacuum pump is a pump that generates vacuum or further reduces the pressure of an existing vacuum. A vacuum pump can be a positive displacement pump that transports a gas load from an inlet port to an outlet, or exhaust, port. Vacuum pumps can also work on a momentum transfer principle, cryogenic entrapment principles as well as the positive displacement principle. The vacuum pump was invented by Otto von Guericke.

Types of Vacuum Pumps
- Transfer: roots blower ; rotary compression
- Diffusion pump
- turbomolecular pump
- entrapment pump: ion pump; cryo-pump

The changeover occurs at 10^{-2} - 10^{-3} Torr for typical vacuum systems.

Aspirator

9.4.3.1 VACUUM SYSTEM COMPONENTS

➢ **Aspirator**

Principle of operation: Bernoulli's Principle (moving fluid reduces pressure). Pump operation is based on bulk flow of fluids. Ultimate vacuum is approximately 24 Torr (vapor pressure of water at 25°C)

➢ **Rotary oil pump, Principle of operation**
1. Begin expansion cycle
2. Seal off expanded volume
3. Compress gas out exhaust

Pump operation is based on bulk flow of gas; hence the pump works in the viscous flow regime.

Used for obtaining "rough" vacuum (10^{-3} Torr), which is the lower limit of the viscous flow regime.

Pump must have a belt guard (to prevent fingers and hair from getting caught!). Trap vapors entering pump (to prevent degradation of pump oil and seals). Do not pump on atmosphere (the pump would overheat since it is not designed to be an air compressor!).

Figure 9.10: A oil-sealed rotary vane pump. Principle of operation: (a) gas from the vacuum system is expanded into the pump and (b) the gas is pushed through the pump exhaust

A roughing pump is used to pump the system down in the 10^{-3} mbar region. A typical pump is an oil-sealed rotary vane pump as shown in Fig. 9.10. The operation principle of this pump makes it obvious

why there are two stages on the vacuum system: the rotary vane pump will work fine when the pressure is high enough to ensure a gas flow through the pump but hopeless when the mean free path of the molecules is very long.

➢ **Diffusion pump**

Diffusion pumps are a type of vacuum pump designed to acheive better vacuums than possible by use of mechanical pumps alone. They use a high speed jet of fluid to direct residual gas molecules in the pump throat down into the bottom of the pump and out the exhaust. The high speed jet is generated by boiling the fluid (typically silicone oil) and directing the vapor through a mul-tistage jet assembly. Often several jets are used in series to enhance the pumping action.

Unlike mechanical pumps, diffusion pumps have no moving parts and as a result are quite dura-ble and reliable. They can function over pressures ranging from about 10^{-10} torr (10 nPa) to about 10^{-2} torr (1 Pa). Diffusion pumps can-not discharge directly into the at-mosphere, so a mechanical fore-pump is typically used to main-tain an outlet pressure around 0.1
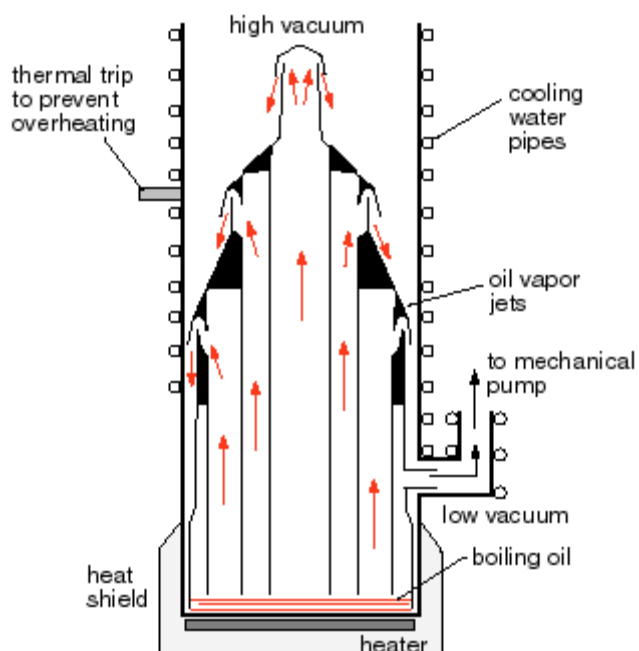
Figure 9.11- Principle for a diffusion pump, based on oil vaporization and dragging molecules from UHV chamber by the cycle: adsorbtion -condensation-desorbtion -transfer to low vacuum pump. Momentum transfer by vapour jet stream.

torr (10 Pa). One major disadvantage of diffusion pumps is the tendency to backstream oil into the vacuum chamber. This oil can contaminate surfaces inside the chamber or upon contact with hot filaments or electrical discharges may result in carbonaceous or siliceous deposits. Due to backstreaming, diffusion pumps are not suitable for use with highly sensitive analytical equipment or other applications which require an extremely clean vacuum environment. Often cold traps and baffles are used to minimize back-streaming, although this results in some loss of pumping ability.

Principle of operation-figure 9.11. The momentum transfer by vapor jet stream. Individual molecules are "pushed" toward exhaust by jet stream; hence, the pump works in the molecular flow regime. Used for obtaining "high" vacuum (10^{-6} Torr)

Safety considerations:

Rotary oil pump must be on to reduce the pressure to $<10^{-2}$ Torr (otherwise, hot oil could combust in presence of oxygen). Diffusion pump must be cooled with water or air (to prevent overheating) . Vacuum line must be protected with a trap (to prevent mi-gration of diffusion pump oil).

➤ Turbomolecular pump

The pump of choice for the second stage is a so-called turbomolecular pump (see Figure). Ultrafast fan blades knock molecules out of vacuum system. Turbomolecular pumps use a rapidly spinning turbine rotor to push gas from the inlet of the pump towards the exhaust, in order to create or maintain a vacuum. Most turbomolecular pumps employ multiple stages consisting of rotor/stator pairs mounted in series. The rotor of the pump is build such that the gas molecules collide with the fast moving rotor and thereby attain an impulse in the direction of the roughing pump. In order to achieve efficient pumping the speed of the rotor has to be very high. Typical values are up to 80 Krpm. Gas captured by the upper stages is pushed into the lower stages and successively compressed to the level of the fore-vacuum pressure. As with the diffusion pump, a mechanical vacuum pump is usually employed to reduce the exhaust pressure.
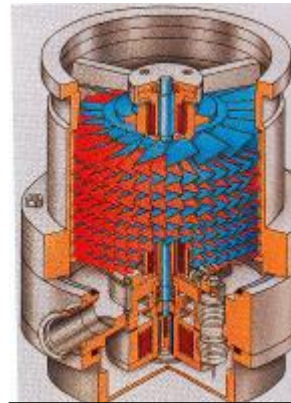
Figure 9. 12- Turbomolecular pump

The maximum compression varies linearly with circumferential rotor speed. In order to obtain extremely low pressures on the order of 10^{-10} torr, rotation rates of 20,000 to 30,000 revolutions per minute are often necessary. Unfortunately, the compression ratio varies exponentially with the square root of the molecular weight of the gas. Thus, heavy molecules are pumped much more efficiently than light molecules. Most gases are heavy enough that this isn't really an issue, however hydrogen and helium are not pumped efficiently.

➤ Ion Pump

Once the low pressure has been achieved it can also be maintained by another type of pump, the so-called ion pump shown in Figure 9.13

The rest gas in that pump is ionized by a plasma discharge due to the high voltage between anode and cathode.

The ionization probability is increased by the presence of the magnetic field which makes the electrons travel on spiral trajectories. When the ions hit the Titanium cathode they can be buried in it or react with it. Additionally, Ti is sputtered off the cathodes and deposited on other parts of the pump. This Ti can react with the rest gas and increases the pumping effect. The ion pump does not remove the rest gas from the system.

Figure 9.13- Ion pump- The residual gas carried by ionization. (More details in a plasma physics course)

It just binds it such that it cannot contribute to the pressure any more. The current provided by the high-voltage power supply is proportional to the pressure in the system. Ion pumps can therefore be used to estimate the pressure. The ion pump can be operated at pressures between 10^{-3} and 10^{-11} mbar.

In order to reach a low pressure in a short time it is necessary to perform a so-called bakeout of the whole vacuum system. During the bakeout the system is heated to at least 100-200 C for an extended period of time (24h). The heating causes a fast removal of the impurities adsorbed on the walls of the vacuum system (mostly water). The need for baking systems renders working with UHV chambers rather time-consuming. It also requires that the system is build only of components which can withstand high temperatures for a long period of time.

- ➢ **Cryo pump:** The molecules are frozen out
- ➢ **Sorption pump:** Molecules diffuse into absorbing material
- ➢ **Sputter ion pump**: molecules are ionized and buried
- ➢ **Cold trap**: Prevents pump oil from contaminating vacuum system. Prevents organic solvents from reaching pump (and degrading oil and seals). Acts as a pump by condensing molecules Principle of operation: freeze out contaminants. Never pump air through a liquid nitrogen trap (oxygen will condense and can explode). Put a test tube into a dewar of liquid nitrogen; condense liquid oxygen.
- ➢ **Regulators** (figure 9.15)
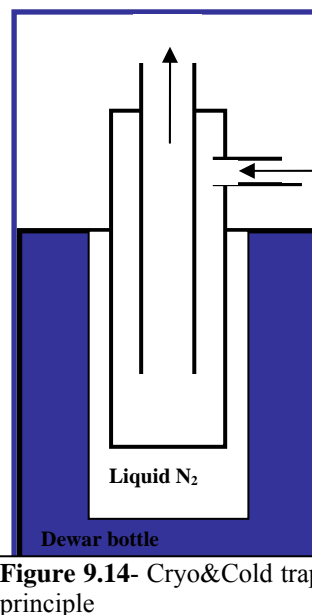
Figure 9.14- Cryo&Cold trap principle

Gas flow from a pressurized cylinder is controlled with: Main cylinder valve, Pressure regulator, Outlet valve. Valves are either open or closed; when open, the pressure is equal on both sides (assuming no or slow gas flow). The regulator allows for an adjustable pressure difference between both sides.
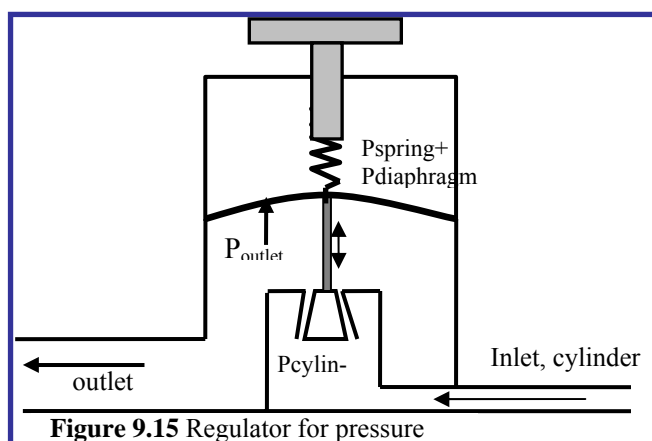
Figure 9.15 Regulator for pressure

The cylinder pressure $P_{cylinder}$ forces the valve closed and seals the regulator. The valve is attached to a flexible diaphragm that is connected to the pressure adjusting spring, which exert opening pressures $P_{diaphragm}$ and P_{spring} on the valve, respectively.

Compressing the spring pushes against the diaphragm and valve, allowing gas from the cylinder to flow past the valve. This gas exerts closing pressure p_{outlet} against the diaphragm, which closes the regulator. At equilibrium the opening and closing pressures balance each other $P_{cylinder} + P_{outlet} = P_{spring} + P_{diaphragm}$.Thus, an increase in the spring pressure causes an increase in the outlet gas pressure.

9.5 Vacuum measurement

The determination of a gas pressure that is less in magnitude than the pressure of the atmosphere. This low pressure can be expressed in terms of the height in millimeters of a column of mercury which the given pressure (vacuum) will support, referenced to zero pressure. The height of the column of mercury which the pressure will support may also be expressed in micrometers. The unit most commonly used is the torr, equal to 1 mm of mercury (mmHg). The unit of pressure in the International System (SI) is the pascal (Pa), equal to 1 newton per square meter (1 torr = 133.322 Pa).

In the laboratory, measurement of vacuum is important because the vacuum level has a significant effect on most physical, chemical, and biological processes.

Vacuum measurement is used, for example, in the manufacturing of television sets (evacuation of picture tubes); in metallurgy (treatment of metals attacked by common gases); and in the pharmaceutical industry (distilling heat-sensitive compounds).

Pressures above 1 torr can be easily measured by familiar pressure gages, such as liquid-column gages, diaphragm-pressure gages, bellows gages, and bourdon-spring gages. At pressures below 1 torr, mechanical effects such as hysteresis, ambient errors, and vibration make these gages impractical.

Pressures below 1 torr are best measured by gages which infer the pressure from the measurement of some other property of the gas, such as thermal conductivity or ionization.

The thermocouple gage, in combination with a hot- or cold-cathode gage (ionization type), is the most widely used method of vacuum measurement today.

Other gages used to measure vacuum in the range of 1 torr or below are the McLeod gage, the Pirani gage, and the Knudsen gage.

The McLeod gage is used as an absolute standard of vacuum measurement in the $10\text{-}10^{-4}$ torr ($10^3\text{-}10^{-2}$ Pa) range.

The Knudsen gage is used to measure very low pressures. It Measure pressure in terms of the net rate of transfer of momentum (force) by molecules between two surfaces maintained at different temperatures (cold and hot plates) and separated by a distance smaller than the mean free path of the gas molecules.

9.5.1 McLeod gage

Instrument used to measure vacuum by application of the principle of Boyle's law. A known volume of a gas whose pressure is to be measured is trapped by raising the level of a fluid (mercury or oil) by means of a plunger, by lifting a reservoir, by using pressure, or by tipping the apparatus. As the fluid level is further raised, the gas is compressed into the capillary tube (see figure 9.16). Obeying Boyle's law, the compressed gas now exerts enough pressure to support a column of fluid high enough to read. Readings are somewhat independent of the composition of the gas under pressure. It is widely used as a standard of pressure between 10 torr (103 Pascals)
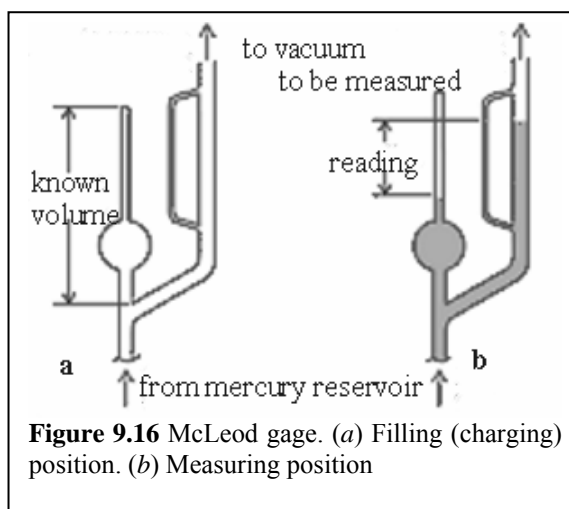

Figure 9.16 McLeod gage. (*a*) Filling (charging) position. (*b*) Measuring position

and 10^{-5} torr (10^{-3} Pascal) and is often used to calibrate other vacuum instruments. Some disadvantages of this gage are that readings are not continuous, the operator must be skilled in taking visual readings, and mercury or oil vapor may diffuse into the gas being measured. Condensable gases cannot be measured with a McLeod gage, although use of a sorption trap or cold trap may allow some measurements.

9.5.2 Ionization gage

Ionization gauges are triodes mounted in a glass bulb connected to the apparatus in which the pressure is to be measured. They are electrically connected as shown in Figure 9.17. In the hot-filament ionization gage the electrons emitted by a filament are attracted toward a positively charged grid electrode. Collisions of electrons with gas molecules produce ions, which are then attracted to a negatively charged electrode. The current measured at this electrode is directly proportional to the pressure or gas density. The ratio of this ion current to the current of bombarding electrons or grid current is proportional to the pressure at pressures below about 10^{-4} torr. An ionization gauge may be made from an ordinary three-element radio tube equipped with a glass connection to the vacuum system. Such gauges are useful for the pressure range from 10^{-3} to 10^{-6} torr.

Measurements with it are possible to a pressure of 10^{-9} torr. The upper end of a glass bulb supports the plate assembly, while the lower end supports the combined grid and filament assembly. The grid is made from a piece of nickel screen rolled to form a cylinder. This is bound mechanically to the central glass tube through the bottom by wrapping it with wire, and it is connected electrically to the grid electrode with one

Figure 9.17- Ionization gauge

loose end of the wrapping wire. There are two filaments, but only one is used. The other is held in reserve to be used if the first is accidentally burned out. Expensive auxiliary electrical instruments are required for this gauge The plate may be outgassed with high-frequency currents or by electron bombardment. In the latter case, an alternating potential of 200-500 volts is applied between the filaments and the plate. The amount of heat developed depends on the emission from the filament, and this is controlled by the filament current. Outgassing of the plate and glass walls of the gauge is necessary if quantitative measurements are to be made. However, for hunting leaks it is necessary only to outgas the plate once. At a given pressure, the ratio of plate to grid current is different for different values of the grid current. For this reason, it is necessary to adjust the grid current to some definite value, usually in the range of 10 to 50 milliamperes.

In the cold-cathode (Philips or Penning) ionization gage a high voltage is applied between two electrodes. Fewer electrons are emitted, but a strong magnetic field deflects the electron stream, increasing the length of the electron path that increases the chance for ionizing collisions of electrons with gas molecules. An advantageous feature of this gage is that it does not burn out. However, it becomes contaminated very easily if

operated at high pressures or if used in a dirty system. Pressure measurement range of this type of gage is 10^{-2} torr to 10^{-7} torr . All ionization gages should be calibrated for the gas to be measured, due to the variation of ionization efficiency

9.5.3 Pirani gage

Instrument used to measure vacuum by utilizing a resistance change due to a temperature change in a filament. This fine-wire filament, one of the four electrical resistances forming a Wheatstone bridge circuit, is exposed to the vacuum to be measured. Electric current heats the wire; the surrounding gas (in the vacuum) conducts heat away from the wire. At a stable vacuum, the wire quickly reaches equilibrium temperature. If the pressure rises, the gas carries away more heat, and the temperature of the wire decreases. Since the resistance of the filament is a function of temperature, the electrical balance of the Wheatstone bridge is changed. The output meter is usually a microammeter calibrated in torrs or millitorrs.

The calibration depends upon the thermal conductivity of the gas, and therefore the readings obtained must be adjusted for various gases. Accuracy is of the order of ±5% of scale. Pressure measurement range of this type of gage is usually 1 to 10^{-4} torr. The Pirani gauge construction: The Pirani gauge consists of a heated filament of platinum, tungsten, or some other metal with a high temperature coefficient of electrical resistance. The filament is exposed to the residual gases and is cooled by them. The temperature of the filament is determined by the heat conductivity of the residual gas, which, in turn, depends on the pressure. The filament may be operated in several ways. Pirani gauges work from ambient pressure down to about 10^{-3} mbar.
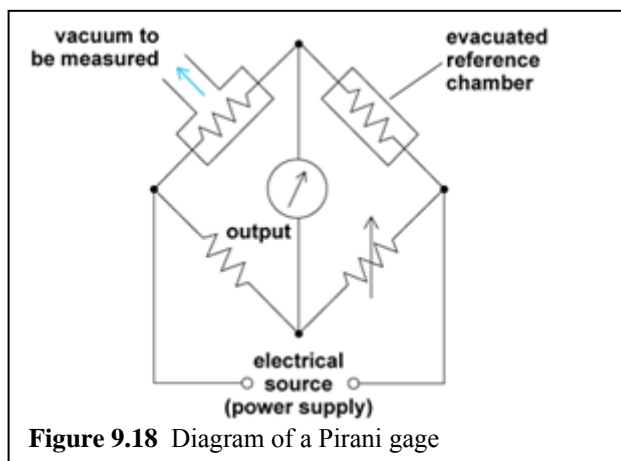
Figure 9.18 Diagram of a Pirani gage

9.5.4 The Langmuir gauge

Langmuir's viscosity gauge is made with a flattened quartz fiber about 50m thick and from five to ten times as wide. This quartz ribbon is about 5 cm long and is mounted in one end of a glass tube about 25 mm in diameter. When this ribbon is set vibrating in a high vacuum, the amplitude changes very slowly because the damping by the residual gas is almost negliglble, and, owing to the low internal viscosity of fused quartz, the loss of vibrational energy from this source is also low. From atmospheric pressure down to a few millimeters of mercury, the damping produced by the molecules of the residual gas is nearly independent of pressure. Over the transition range of pressure, where the damping varies from this constant value to zero, the time required for the amplitude of vibration to decrease to half value is an index of the pressure.

Within this range the relation between the time, the pressure, *P*, and the molecular weight of the residual gas is given by the following formula:

$$P\sqrt{M} = \frac{a}{t} - b$$

Here a and b are constants of the gauge. The value of the ratio b/a may be obtained by observing the damping time, to, for an essentially perfect vacuum, that is, a pressure of 10^{-6} torr less. For this pressure the left side of the equation can be set equal to zero. The values of a and b are determined from a second measurement of the time t_1 at a definite pressure P_1. This pressure is determined with a McLeod gauge. M is approximately 29 for air. The gauge may also be calibrated by subjecting it to saturated mercury vapor at a definite temperature at which the vapor pressure of mercury is known. The range over which the gauge is most useful lies between the pressures 2×10^{-2} and 5×10^{-5}.

9.5.5 Others techniques

➢ **The Knudsen gauge:** designed based on Knudsen phenomenon
➢ **Thermocouple gauge: P**rinciple of operation: pressure dependence of thermal conductivity. Only works at relatively high pressures because thermal conductivity eventually becomes too small.
➢ **Capacitance manometer:** Principle of operation: mechanical deflection of membrane (which is one plate of a capacitor) alters capacitance in an electronic circuit. Only works at relatively high pressures because deflection eventually becomes too small

Several interesting data in vacuum techniques
- ML- monolayer desorbtion; Mean free Path (MFP)- details in kinetic physics (vol III)

Degree of Vacuum	Pressure (Torr)	Gas Density (molecules m^{-3})	Mean Free Path (m)	Time / ML (s)
Atmospheric	760	2×10^{25}	7×10^{-8}	10^{-9}
Low	1	3×10^{22}	5×10^{-5}	10^{-6}
Medium	10-3	3×10^{19}	5×10^{-2}	10^{-3}
High	10-6	3×10^{16}	50	1
UltraHigh	10^{-10}	3×10^{12}	5×10^{5}	10^{4}
We can therefore conclude that the following requirements exist for: Collision Free Conditions=> $P < 10^{-4}$ Torr Maintenance of a Clean Surface=> $P < 10^{-9}$ Torr				

Composition of gas in vacuum chamber is very different from atmosphere
pumps remove certain gasses preferentially

Component	Volume % in dry air	Volume % in ion pumped chamber at 2×10^{-9} torr
N_2	78 %	trace
O_2	21 %	trace
Ar	0.93 %	trace
CO_2	0.03 %	3 %
CH_4	trace	3 %
H_2O	trace	5 %
CO	trace	6 %
H_2	trace	78 %

Table for pressure conversion

	mbar	Pascals (N/m^2)	atmos-pheres	Torr (mmHg)	microns (µm Hg)	psi (lb/in^2)	dyne/ cm^2	molecules / m^3
1 mbar =	1	100	9.87×10^{-4}	0.75	750	0.0145	1000	2.65×10^{22}
1 Pa =	0.01	1	9.87×10^{-6}	7.5×10^{-3}	7.5	1.45×10^{-4}	10	2.65×10^{20}
1 atm =	1010	10,100	1	760	7.6×10^5	14.69	1.01×10^6	2.69×10^{25}
1 Torr =	1.333	133.3	1.31×10^{-3}	1	1000	0.0193	1333	3.53×10^{22}
1 µm =	1.33×10^{-3}	0.133	1.31×10^{-6}	0.001	1	1.93×10^{-5}	1.333	3.53×10^{19}
1 psi =	68.94	6.89×10^3	0.068	51.71	5.17×10^4	1	6.89×10^4	1.83×10^{24}
1 dyne/ cm^2 =	0.001	0.10	9.87×10^{-7}	7.50×10^{-4}	0.75	1.45×10^{-5}	1	2.65×10^{19}
1 mole-cule/m^3 =	3.77×10^{-23}	3.77×10^{-21}	3.72×10^{-26}	2.83×10^{-23}	2.83×10^{-20}	5.47×10^{-25}	3.77×10^{-20}	1

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Books on surface science.

1. H. Lüth *Surfaces and Interfaces of Solid Materials* (Springer Study edition) An excellent book, mostly focused on the surfaces of semiconductors.

2. T. A. Delchar, and D. P. Woodruff, Modern *Techniques of Surface Science* (Cambridge Solid State Science Series). A very good book which is mainly concerned with technique (as the title indicates). If you work in the field this book is a ``must''.
3. A. Zangwill *Physics at Surfaces* (Cambridge Univ. Press). This book is complementary to the first. It is more about theory and concepts than about technique.
4. M. C. Desjonqueres, D. Spanjaard. *Concepts in Surface Physics* (Springer Series in Surface Sciences). A modern and theory-focused book.

Chapter 10

Zeroth law of thermodynamics

Regardless of how thorough the method or how strong the desire to define every new concept in terms of old ones, sooner or later the physicist, the chemist or the engineer will have to mention **thermal equilibrium** and **temperature**. Experimental observation and generalization led to the general axiom of the thermal equilibrium.

The zeroth law's whole experimental evolution and axiomatization is based on temperature, the representation of the subjective, empirical system's property of being hotter or colder than another.

The zeroth law seems self-evident and was taken for granted by physicists throughout the development of thermodynamics. Usually, we are expecting that relationships are transitive: If A is in thermal equilibrium with B and B is in thermal equilibrium with C then A is in thermal equilibrium with C. That is, allows us the temperature definition; Objects at thermal equilibrium have the same temperature.

10.1 Thermal equilibrium

Example: let us consider two closed systems, the boundaries of which do not allow work to be exchanged (for instance two arbitrary quantities of air found inside airtight rigid containers; "arbitrary" is being used to specify that the neither the mass, volume or pressure of any system is specified). When two such systems are put in contact with each other we can usually notice changes taking place inside both systems.

In our previous example these changes can be confirmed by recording the pressure with respect to time. Usually, after a certain amount of time these changes cease.

We can say a system's state is one of equilibrium when after long enough time there are no changes taking place inside it. In particular, when the closed system is unable to interact by exhanging work, in our previous example the long lasting system's state is one of thermal equilibrium.

Summary: If a body with a higher temperature is put in contact with one having a lower temperature, the first will exchange heat towards the second. Both bodies will approach the same temperature and, if there are no losses, will maintain this temerature constant. We say that the two bodies are in **thermal equilibrium**. The thermal equilibrium is the main subject of the zeroth law of thermodynamics.
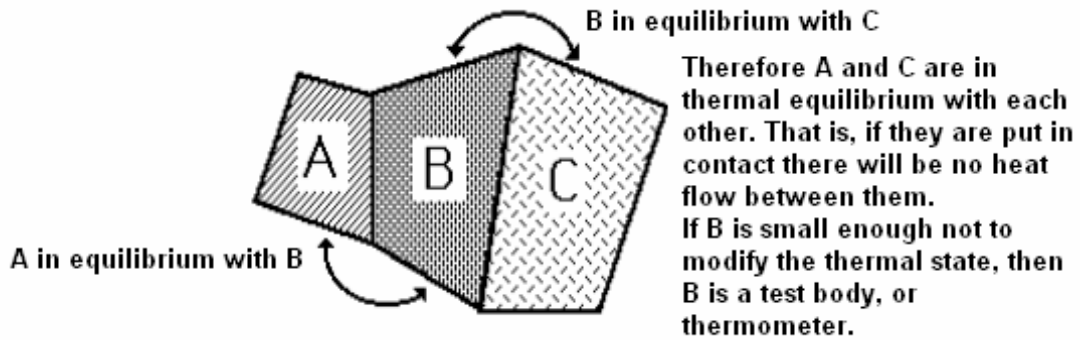
Figure 10.1: Stating the zeroth law in terms of thermal equilibrium.

Let (A) and (B) be closed systems that interact and reach thermal equilibrium, such as the ones in the previous example. The same experiment can be conducted using system (A) and a third system (C), which is also a closed system that cannot exchange work. It is experimentally shown that if the systems (B) and (C) are each in thermal equilibrium with system (A), when they are placed in direct contact, neither (B) or (C) will suffer any changes in time. This second observation can be stated: If systems (B) and (C) are each in thermal equilibrium with a third system, then (B) and (C) are in thermal equilibrium with each other.

More than a century ago Maxwell found this brief formulation to have the value of a law in physics. After Maxwell's death, almost half a century after the first and second laws of thermodynamics had already been formulated this was recognized as being *the zeroth law of thermodynamics.*The zeroth law was first formulated and named such by Fowler.

Thermal equilibrium, as defined in figure 10.1 has a wide application range. A few of its applications are summed in figure 10.2

Comments

Every law of thermodynamics can be considered a way of definig a new property of the system, such as internal energy with the first law and entropy with the second; this way the zeroth law defines the thermodynamic property called *temperature*. Taking into account the countless experimental results on which the zeroth law and thermometry are based, we accept temperature as being the property whose numerical value shows if a system is in thermal equilibrium with another. Two systems are in thermal equilibrium when their temperatures are identical.
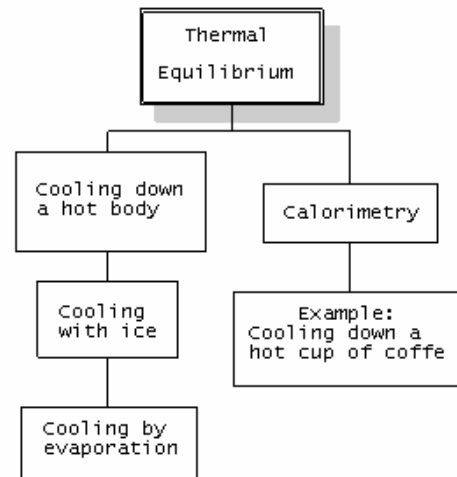
Figure 10.2: Applications of thermal equilibrium

10.2 Empirical temperature

The zeroth law's formulation respects the laws of logics which show that for any equivalence relation corresponds a repartition into equivalence classes and each such class is defined by a certain dimension (property or symbol).

In the case of thermic equilibrium a function of state called temperature θ can thus be attributed to each such class. The state parameters of body A can be chosen to be x,y and those of body B being α, β, therefore:

$$\theta_A = f_1(x, y); \ \theta_B = f_2(\alpha, \beta)$$

and for thermal equilibrium we should have: $f(x, y, \alpha, \beta) = 0$,

this meaning that the function has a minimum, and this is zero. For the given case we have:

$$\theta = f_1(x, y) = f_2(\alpha, \beta)$$

formulation, which introduces the notion of *empirical temperature.*

As a consequence of this formulation, we obtain the qualitative character of temperature but also one should take notice of the intuitive character regarding order. Any given body A found at a temperature different to that of B will change the state of B in a determined direction.

The correlation between internal energy and temperature. Thermodynamics admits that any given part of the system, no matter how small, is for a relatively short period of time a body at thermal equilibrium. Obviously this new axiom allows the solving of all common issues of thermal contact in chemical thermodynamics, whilst in the case of statistic mechanics electrons and ions from a certain region of plasma are given different temperatures.

The result of this approach is materialized in the necessity that the thermal equilibrium state of a system be completely defined by the external parameters and a propertary parameter: temperature (all thermal equilibrium parameters are functions of external parameters ($a=x, y$ or α, β) and temperature (θ) for instance). The system's energy is $U=U(\theta, a)$; it is correlated to temperature. This allows one to have: $\theta = \theta(a, U)$ (for equilibrium), the consequence of the correlation between energy and temperature.

Ergodicity. Systems whose states of internal equilibrium are characterized by parameters depending only on energy and external parameters are called ergodic systems (studied by thermodynamics).

The state of internal equilibrium must correspond to dynamic states of the system compatible with internal energy at equilibrium. The dynamic state of the system is described as being a point in the phases space (see chapters in kinetics theory and statistical physics) and is represented on a energy surface through the figurative point {p,q}. It is the result of the movement of the system's particles which at any given time have a given momentum, p, and position (the microstate of the system's particle).

Considering that the dynamic state of a system ("the phase" in the phases space) is represented on an energy surface through the point (p1,q1,…).The theory of ergodicity states that for a given period of time, parameters should have punctual values; it would be advised that regions with surfaces defined on energy surfaces should be used instead of points (quasi-ergodicity theory).

From the point of view of statistic mechanics the ergodicity theory requires the equality of the two averages, one in time and one in space, on a system with the given

energy U (microcanonic assembly) or that of a dynamic function, f(p,q) of the system, that is:

$$\overline{f(p,q)} == \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^\tau f(p,q)dt = \langle f(p,q) \rangle = \frac{\int_S f(p,q)d\mathbb{P}}{\int_S dP}$$

where P is the occurance probability of f(p,q) on a number of equivalent systems that concur to the achieving of the microstate of the system with the energy U.

The zeroth law shows that the equations above, in symbolic form, can be fulfilled in by indicating the number of parameters necessary and sufficient (degrees of freedom) to completely characterize a system; for an isotropic system with *c* components at equilibrium, this number is *c+2* (concentrations, temperature, pressure) in the absence of electrical, magnetic fields, etc.

10.3 The general axiom of thermodynamic equilibrium

In previous discussions only a few aspects of the concept of thermodynamic equilibrium as a limit state of transformation, from which the system cannot evolve by spontaneous processes have been presented.

One must keep in mind that this concept is usually associated with the immobility of the system or with a constant permanent value of some proprietary parameters, which don't, however, make up the necessary and sufficient characteristic of the state of equilibrium. Truthfully, a solid body can be kept motionless on a sloped surface by friction; a system composed of hydrogen and oxygen remains unchanged at low temperatures in the absence of catalysts; the flow of heat between two reservoirs separated by a thermally conducting wall in which a constant profile of temperature variation is established etc. The state of (internal) equilibrium corresponds to a state of the system which can be obtained through a quasistatic transformation in both ways: in this case the conditions of symmetrical values of the physical dimensions that characterize the transformations in either direction are fulfilled (for instance: work and heat are equal and of opposite signs).

The general axiom of thermodynamics corresponds to the affirmation that in *an isolated system, after long enough time, a state of thermodynamic equilibrium, in which no spontaneous transformation will take place, will be achieved.* In the paragraph of Boltzman's theorem H the significance of this transformation towards equilibrium was shown, and, in a qualitative form, the correlation between the microscopic and the macroscopic aspects of the phenomenon, considering the greater probability of this state compared to all other possible states of the system. Due to the discontinuity of molecular scale systems fluctuations from the state of equilibrium appear and thus the physical values measured in thermodynamics are only averages. Since these fluctuations increase with the decreasing of the number of particles that make up the system, laws and applications of thermodynamics are limited to normal systems, made up of a very large number of particles. In the case of a lower number of particles when the fluctuations are quite significant, the methods of statistic physics must be applied, some cases actually leading to contradictions between the conclusions established by thermodynamics and the properties of the systems of this type. Similarly, the extending of thermodynamics to astronomical systems (with an infinite number of particles) is incorrect; for such systems the notion of most probable state is senseless, since all the states are equally probable, and the fluctuations reach astronomical proportions. Both limitations are conse-

quences of the statistic character of the second law of thermodynamics. It is noticed that the isolated system is, from a molecular point of view, a conservative mechanical system made up of a large number of molecules and at thermodynamical equilibrium all thermodynamic variables reach certain constant values, contradicting Poincare's theorem (see Theorem H, in vol III), which states that the molecular system must tend to a quasi-periodic movement.

The general axiom stated above is, at thermal equilibrium, limited in the form of the *zeroth law*.

TEMPERATURE

Is a measure of how **hot** or **cold** an object is.
Is measured by a **thermometer**.

Thermometers are based on physical properties of objects that change with temperature, for example:

- ➤ volume of a liquid
- ➤ length of a solid
- ➤ pressure of a gas
- ➤ electrical resistance of a solid
- ➤ electrical potential difference between two solids

Some Temperatures

- ■ Lowest laboratory T ~ 10^{-7} °K

- ■ In nuclear fusion, T ~ 10^{13} °K

- ■ In big bang, T ~ 10^{40} °K or more

Temperature (K)

10^9	
10^8	← Hydrogen bomb
10^7	← Interior of the Sun
10^6	← Solar corona
10^5	
10^4	
10^3	← Surface of the Sun
	← Copper melts
10^2	← Water freezes
	← Liquid nitrogen
10	← Liquid hydrogen
1	← Liquid helium

Lowest temperature
achieved ~10^{-7} K
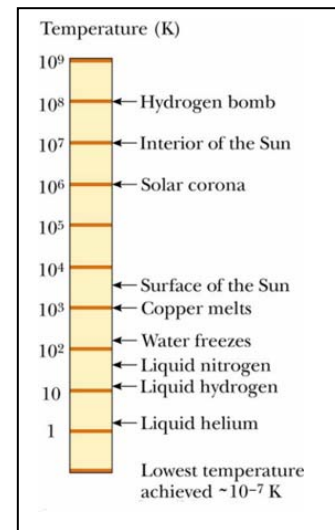
Temperature	Nature	Definitions	conversions
Kelvin	Absolute	A temperature scale whose zero point is absolute zero, the temperature of 0 entropy at which all molecular motion stops, -273.15° C. The *size* of a degree Kelvin is the same as the *size* of a degree Celsius	$K = {}^0C + 273.15$ Kelvin is a unit of temperature where one degree K is 1/279.16 of the temperature of the triple point of water (near freezing).
Rankine	Absolute	An absolute temperature scale with whose degrees are the size of Fahrenheit degrees. $${}^{\circ}R = {}^{\circ}F + 459.69.$$	$${}^{\circ}R = {}^{\circ}F + 459.69.$$
Celsius		A scale for measuring temperature in which the freezing and boiling temperatures of water are defined to be 0^0C and 100^0C, respectively.	
Fahrenheit		A scale for measuring temperature in which the freezing and boiling temperatures of water are be 32 ${}^{\circ}F$ and 212 ${}^{\circ}F$, respectively. The original definition of 0 ${}^{\circ}F$ was the freezing point of a water ice slurry	${}^0F = (9/5){}^0C + 32$

	Fahrenheit	Celsius	Kelvin
Boiling Point of Water	212°F	100°C	373 K
Freezing Point of Water	32°F	0°C	273 K
Absolute Zero	-459°F	-273°C	0 K
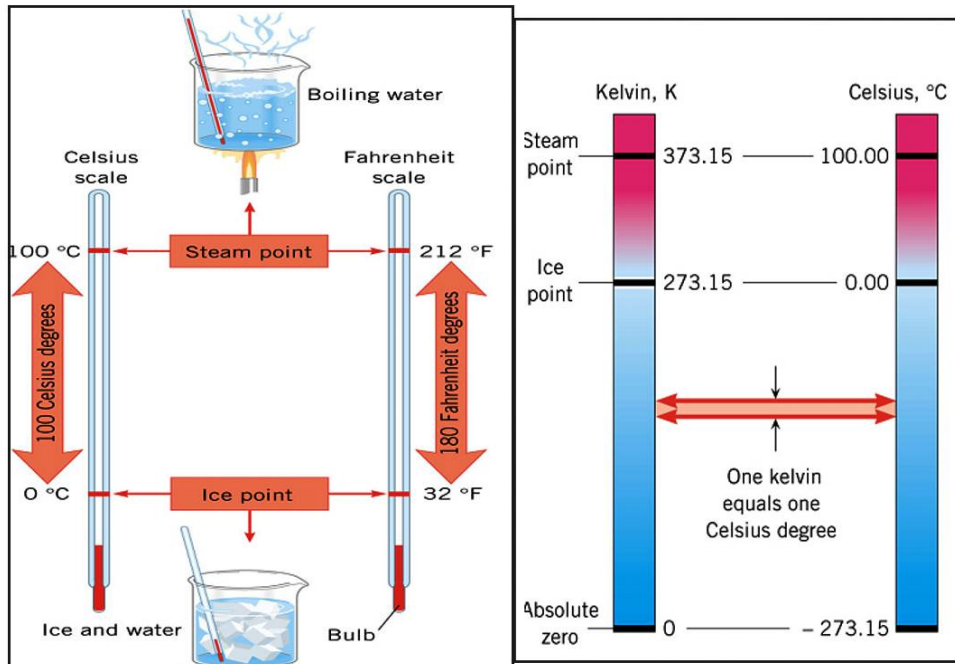
Celsius & Fahrenheit

Kelvin & Celsius

Chapter 11

Temperature

- Temperature (sometimes called thermodynamic temperature) is a measure of the average kinetic energy of the particles in a system.
- Adding heat to a system causes its temperature to rise.
- While there is no maximum theoretically reachable temperature, there is a minimum temperature, known as absolute zero, at which all molecular motion stops. Temperatures are commonly measured in the *Kelvin* or *Celsius* scales, with *Fahrenheit* still in common use in the Unites States.

There are lot of fileds in physics where temperatures are encountered in different forms and definitions

- Temperature is an important quantity in thermodynamics and kinetic theory, appearing explicitly for example in the ideal gas law
- Thermodynamically, temperature is given by the Maxwell relation (see vol II):

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

  where U is internal energy and S entropy, V-volume.
- The quantity (1/kT), where k is Boltzmann's constant, arising frequently in thermodynamics is defined as $\beta = 1/kT$, a quantity sometimes known as thermodynamic beta
- **Absolute temperature:** Temperature measured relative to absolute zero. Absolute temperature scales include Kelvin and Rankine.
- **Absolute zero:** The temperature at which all-molecular motion stops, equal to 0 Kelvin or -273.15° Celsius. However, quantum mechanically, molecules cannot cease all motion (as this would violate the Heisenberg uncertainty principle), so at 0 K they still vibrate with a certain small but nonzero energy known as the zero-point energy;
- **Blackbody temperature:** The effective temperature at which a blackbody emits blackbody radiation
- **Debye temperature:** In Debye theory, the Debye temperature θ_D is the temperature of a crystal's highest normal mode of vibration, i.e., the highest temperature that can be achieved due to a single normal vibration. The Debye temperature is given by:

$$\theta_D = \frac{h\nu_{max}}{k}$$

  where h is Planck's constant, and ν_{max} is the Debye frequency, a characteristic frequency of a given crystal given by:

$$\nu_{max} = \left(\frac{3N}{4\pi V} \right)^{1/3} \nu_s$$

where N/V is the number density of atoms and c_s is the effective speed of sound in the solid (more details in any solid state class)

- **Potential temperature:** The temperature for a volume of dry air at pressure P and temperature T would have if compressed adiabatically to/from P_0=1 atmosphere, given by :

$$\theta = T \left(\frac{P_0}{P} \right)^{(\gamma-1)/\gamma}$$

where γ is the heat capacity ratio of the gas.

- **Temperature wave:** A wave which exists on the surface of a solid due to thermal heating and subsequent loss of heat by thermal conduction. The functional form is:

$$T(x,t) = T_0 + \sum_{k=1}^{\infty} T_k e^{\beta_k x} \cos(k\omega t - \beta_k x - \Phi_k)$$

where β_k is the thermal absorption coefficient. (when solve out heat conduction with periodic source of heating)

There are few temperature definitions where we encounter a series of specific temperatures, which relate physical properties with the average kinetic energy in a body.

Many of them will be considered in solid state and statistical physics.

11.1 Kinetic Temperature

The kinetic theory has expressed for a ideal gas a direct relation Pressure-Average Kinetic Energy. By comparison with the ideal gas law, we can find a direct relation absolute temperature- Average kinetic energy. (see vol III - kinetic theory)

$$pV = nRT \Leftrightarrow pV = \frac{2}{3} N \left[\overline{\frac{mv^2}{2}} \right]$$

and

$$T = \frac{2}{3} \frac{N}{nR} \left[\overline{\frac{mv^2}{2}} \right] = \frac{2}{3} \cdot \frac{1}{k} \left[\overline{\frac{mv^2}{2}} \right]$$

or in concise form:

$$\overline{E}_{kin} = \left[\overline{\frac{mv^2}{2}} \right] = \frac{3}{2} kT$$

The kinetic energy is referring to the translation motion of the molecule, being a consequence of the limits in the model hypothesis for the ideal gas (point-like molecules and no any internal structure). The main conclusion from kinetic model is the univocity kinetic energy- temperature. In conclusion, for each freedom degree (rotation, vibration) where a kinetic energy is defined there is a correspondent temperature. The results are useful when the specific heat capacities for each freedom degree are estimated.

Another important conclusion is that the bodies in thermal contact change only a form of energy- kinetic, transposed and measurable by heat.

Two bodies with different internal energies, $U_1 \# U_2$, in thermal contact have same temperature and the same kinetic energy (KE) in average, k_B-Boltzmann constant
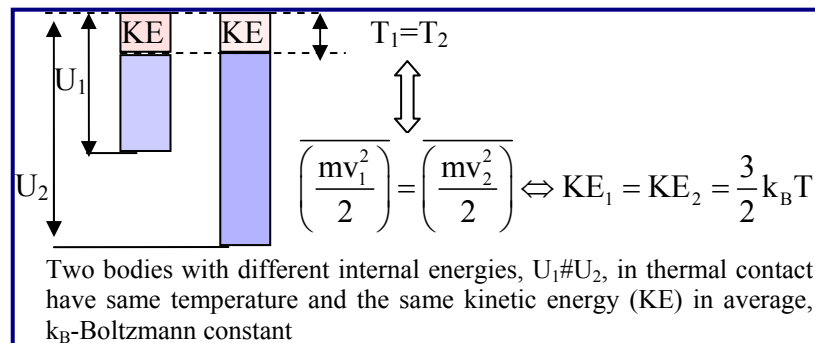
Resuming we can say:
- The heat transfer from hot to cold source takes place by translation kinetic energy (hot body= molecules with high speeds, cold body- molecule with low speeds)
- For each freedom degree there is an associated temperature (rotation T_r, vibration, T_v, translation, T). For a body in equilibrium state $T=T_v=T_r$
- One body with KE=0 can not supply thermal energy.
- There is a zero absolute (T=0) corresponding to KE=0

11.2 Temperature measurements

The fundamental scale of temperature is the thermodynamic scale, equation theoretically expressed by the second law of thermodynamics. Unfortunately, the second law not predicts a method how the temperature can be measured. Efforts to approximate the thermodynamic scale as closely as possible depend on relating measurements of temperature-dependent physical properties of systems to thermodynamic relations expressed by statistical thermodynamic equations, thus in general linking temperature to the average kinetic energy of the measured system.

The only base to make prediction how to invent a temperature scale is the zero law, where the thermometer body (device) is defined. Temperature-measuring devices, thermometers, are systems with properties that change with temperature in a simple, predictable, reproducible manner.

11.2.1 Absolute temperature scale

KELVIN SCALE

In 1874 William Thomson (Lord Kelvin), following Sadi Carnot' idea established the concept for absolute temperature in terms of the quantity of heat exchanged between two bodies. Kelvin designed an ideal body based on Carnot cycle who work at zero absolute without heat change. The Carnot cycle being ideal (no friction and other energy loss) also Kelvin scale is an ideal one. He shown the ratio Q/T =const for any reservoir involved in Carnot cycle and thus need a single experimental point to define 0 absolute using any temperature scale. Kelvin has selected a Carnot cycle working with water between T_H= 373 and T_C= 273 (ideal yield 0.268) and established the zero absolute at -273^{0}C.

The particular system water at triple point (liquid-vapour-ice in equilibrium) is defined to have a particular value of the absolute temperature: 273.16K. Any other un-

known temperature T_u is measuring by operating with a Carnot cycle between 273.16 and T_u:

$$T_u = 273.16 \ \ x \ \frac{Q_u}{Q_{273.16}} \ \ (K)$$

Notice:

- **Rankine Scale:** Rankine did same suppositions in parallel with Kelvin but he took in account Fahrenheit scale (water triple point being at 491.67[0]F) instead of Celsius.
- All absolute temperature scales have one single reference point: water triple point.

. There are other reference points used for thermometer calibration: Au- the solidification point, (1337.91 K,1948.57°F), Sulphur (717.85 K, 832.46°F), oxygen (90.18 K ,-297.35°F), helium (4.22 K , -452.07°F).

11.2.2 Zero Absolute

Absolute zero can be defined as the temperature at which a gas would exert no pressure. Temperature usually measured by ideal gas thermometers at constant volume is given by the following relationship:

$$T(K) = 273,16 \lim_{p \to 0} \frac{p(T)}{p(T_3)}$$

The laws of the ideal gas are applicable only if molecules do not in interact one with another and are not attracted by the walls of the container. Helium can be considered an ideal gas for thermometers. Using helium can measure temperatures of approximately 1K. By its definition the temperature assigned for a body require to define a mechanism for energy transfer. One can measure the Maxwell distribution of velocities to define temperature and estimate lower ones. However, this method has serious limitations. According to classical physics any motion will tend to absolute zero; quantum mechanics and the incertitude principle show

Gas thermometer needs only one reference point

that there exist a residual movement (absolute zero movement). Quantum mechanics and modern physical theories show that at absolute zero the motion of electrons and atoms inside molecules does not stop.

The Kelvin scale, obtained from measurements of efficiency for an ideal thermic machine operating between two heat sources at temperatures T_l and T_h , shows that for T_l=0K the efficiency reaches its maximum, which is 1.

All comparisons between the Kelvin thermodynamic scale and the gas thermometers scales show that they are equivalent.

Temperature can be defined using the Boltzmann distribution. If a ½ spins collection of magnetic ions is placed in a magnetic field then the occupation ratio of superior and inferior energy states is:
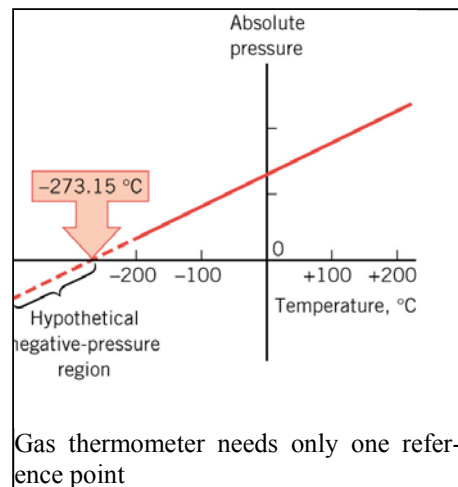
$$\frac{N_{\text{inf}}}{N_{\text{sup}}} = \exp\frac{|\Delta E|}{kT}$$

with the known notations, ΔE being the energy difference between the two energy states. Therefore, at high temperatures the two states are equally probable occupied, but as temperature decreases only low energy states will be occupied. By measuring the population of the two states one can determine the temperature of the system's spins.(Much more details in statistical physics).This relationship allows us to introduce the notion of negative temperatures that can be reached when the high energy state population exceeds the low energy state population. From the point of view of energy content, negative temperatures correspond to spin systems that have energies greater than the energy of a spin system at an infinite temperature or in other words spin systems which are hotter than ordinary temperatures.

The notion of negative temperature has no experimental support; but if we take into account the Third Law of thermodynamics (which states that absolute zero temperature cannot be reached in a finite number of steps) then the two issues (negative temperatures and absolute zero) are two cases which have to be explained in another theoretical context.

Presently, temperatures of tens of picokelvins (temperatures of nuclear spins) can be reached. The lowest temperature electrons have been cooled is 10 microkelvin in metallic systems where superconductivity and superfluidity phenomena are preponderant.

These phenomena are studied in low-temperature and superconductor physics.

11.3 Temperature scales

The standard scale assign temperature values of thermodynamic equilibrium fixed points. International body agrees this: the General Conference of Weights and Measures, which updates the scale about once every 20 years.

Thermometers for interpolating between fixed points and methods for realizing the fixed points are prescribed, providing a scheme for calibrating, thermometers used in science and industry.

The scale now in use is the International Temperature Scale of 1990 (ITS-90) with unit the kelvin, K, defined to be 1/273.16 of the thermodynamic temperature T of the triple point of water (the state in which the liquid, solid, and vapor phases coexist). The scale extends upward from 0.65 K.

For temperatures above 273.15 K, it is common to use International Celsius Temperatures, t_{90} (rather than International Kelvin Temperatures, T_{90}), having the unit degree Celsius, with symbol °C.

The degree Celsius has the same magnitude as the Kelvin

The ice point is the state in which the liquid and solid phases of water coexist at a pressure of 1 atm (101,325 pascals).

The Fahrenheit scale, with symbol °F, still in common use in the United States.

The ITS-90 is defined by 17 fixed points:

➡ Between 0.65 and 5.0 K, the ITS-90 is defined in terms of the vapor pressure of ^{3}He and ^{4}He;

➡ Between 3.0 and 24.5561 K, by interpolating constant-volume gas thermometry (using either ^{3}He or ^{4}He);

➡ Between 13.8033 K and 961.78°C, by platinum resistance thermometry;

- Above 961.78°C, by radiation thermometry. For radiation thermometry, based on Planck's radiation formula, the silver, gold, or copper melting point may be used as the reference temperature.

Below 0.65K, no internationally agreed upon scale exists. At present, temperatures below 0.65 K are determined by magnetic thermometry, nuclear orientation thermometry, and noise thermometry. In some cases, a ^{3}He melting-curve thermometer is used.

With above considerations the body thermometers (simple thermometer) are divided in:

Primary thermometers: devices which relate the thermodynamic temperature to statistical mechanical formulations incorporating the Boltzmann constant k_B or the Boltzmann factor exp(-Ei/k_BT), where E_i is the energy of the ith state of the system. However, the fixed points of at and below 419.527°C of the ITS-90 are all based on one or more types of gas thermometry, with those above 419.527°C being determined by spectral radiation pyrometry referenced to gas thermometry at a temperature near 460°C

Secundary Thermometry

These thermometers are used as reference standards in laboratories because primary thermometers are too difficult to be utilized. Secundary thermometers are calibrated using platinum resistance thermometers for the temperature interval 13.8933K – 961.78K and above this value spectroscopic methods and optical pyrometry. Calibrations between 0.3K and 35K are done using rhodium-iron resistance thermometers to cover platinum thermometers. The range 0.05 - 30 K is covered by germanium resistance thermometers and helium isotope thermometers.

Thermometers of Inferior Rank

These thermometers are of practical use if a high accuracy is needed. Usually, they are calibrated with regard to standard points maintained in specialized thermometry laboratories or in national metrological institutes. Thermometers from this class are of great constructivee variety, especially resistance thermometers (pure metals or semiconductors), thermometers using carbon or germanium, thermistors, thermoelectric thermometers (thermocouples), liquid thermometers, vapor pressure thermometers, magnetic thermometers, capacitive thermometers. The reproducibility must be identical with the one from calibration conditions.

Special conditions: good thermic contact with the probing body, low thermic inertia, low heat losses.

Temperature Indicators

It is often necessary to decide if a temperature has been reached or exceeded. This kind of qualitative information can be obtained from the use of either reversible or irreversible temperature indicators. Examples from this class are numerous, especially due to the explosion of micro and nanotechnologies producing advanced materials: pyrometric ceramic cones that can be built so they mellow or bend when they reach a fixed, metallic pellets or holed bars which when melting either they mellow or they melt. Examples of reversible indicators are several inks/dyes or crayons and liquid-crystals which change their colour very rapidly at a predetermined temperature (see liquid crystals).

11.4 Standard Temperature Points

Typical temperature scales take for reference the freezing point of water for 0 and the melting point of water at standard pressure for 100. However, there is a more precise method which uses standard points with predefined temperatures. Through international accord it has been settled the first standard point to be the triple point of water (at 273.16K). The freezing point of water at atmospheric pressure is 0.01 lower (that is 273.15K). The second standard point (boiling point) is usually obtained based on a measurement done with a gas thermometer. The boiling point is at 373,125K or 99,975^{0}C at standard pressure. These measurements are independent from the nature of the gas or substance and permit us to establish several reference points, which are used for secondary thermometers and temperature indicators calibration.

Reference points

Substance	State	Temperature K
Hydrogen	Triple Point	13.81
Hydrogen	Boiling Point	20.28
Neon	Boiling Point	27.102
Oxygen	Boiling Point	54.361
Argon	Triple Point	83.798
Oxygen	Boiling Point	90.188
Water	Triple Point	273.16
Water	Boiling Point	373.125
Tin	Melting Point	505.074
Zinc	Melting Point	692.664
Silver	Melting Point	1235.08
Gold	Melting Point	1337.58

11.5 Carbon Nanothermometer

Many applications have been found for carbon nanotubes, and we can now add one as a "nanothermometer" to this list (Nature, 415, 599, 2002). We describe how column of liquid gallium inside a carbon nanotube (up to about 10 micrometers long and about 75 nanometers in diameter) varies linearly and reproducibly in the temperature range 50 to 500^{0}C, with an expansion coefficient that is the same as for gallium in the macroscopic state. The world's smallest thermometer consisting of a single carbon nanotube filled with liquid gallium has been created by researchers in Japan. The instrument is so sensitive that it can measure the temperature change that occur when small groups of molecules react with each other.
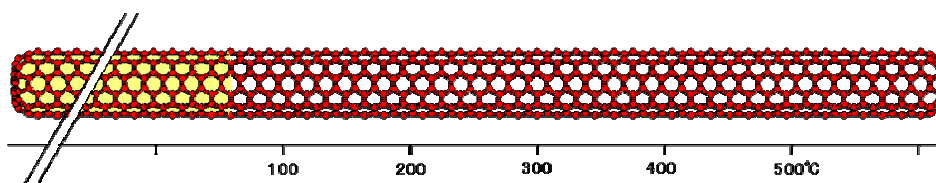
It length is about one tenth the width of a human hair.

The nanoscopic thermometer also has practical applications. It can reliably measure a broad range of temperatures when viewed using a high-powered electron microscope.

11.6 References

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Chapter 12

1st Law of thermodynamics

A brief philosophical excursion:
➡ Why can we just write down a postulate, let alone call it a law, and assume that it is somehow related to natural processes?
➡ This postulate like any scientific law is the essence of what has always been observed by many observers for any systems to which the law applies.
➡ But unlike mathematical laws that can often be proven without doubt by applying logic, laws in natural sciences are proven only to the extent that none has found a counterexample yet.
➡ Could this postulate, or other laws, be wrong?
➡ Could it be that it doesn't describe nature's mechanisms correctly?
Yes, it could be wrong or incomplete. But, again, none has found it to be wrong yet.

Therefore, we shall derive 1st law, phenomenological, for systems that can do mechanical work and exchange heat

12.1 Heat

The heat is a form to transfer energy to and from a system.

A system does not contain heat.

A system contains thermal energy stored in form of kinetic energy.

The kinetic energy is not dependent of direction and sense.

The dependence of the square speed involves a randomized movement of the molecules installed by randomizing collisions.

The Heat is a form of energy conversion of the system when a process takes place.

A process takes place when the system interacts with surrounding, environment, or with other system.

The heat is not temperature and the temperature is not heat but always the empirical established relationship:

$$Q = C\left(T_{final} - T_{initial}\right)$$

Energy transferred as heat

where C is heat capacity and T are temperatures for final and initial states of the systems in thermal contact. This relation is foundation for the chapter – calorimetry- where deals with methods to measure the heat capacity.
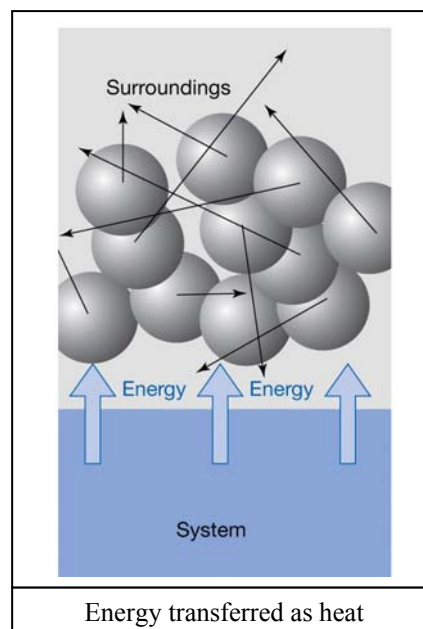
The relationship between temperature and heat is defined as:

$$\frac{\delta Q_V}{dT} = C_V$$

$$\frac{\delta Q_P}{dT} = C_P$$

In these equations, we have introduced the heat capacity of substances. Clearly, these equations are only appropriate for temperature changes that don't induce phase transitions, or chemical reactions ("sensible" heat capacity)

There are two equations for heat capacities, one with a subscript of *V*, the other with a subscript of *P*. The subscripts symbolize the parameter that is held constant: the first equation is for a process at constant volume, while the second one is for processes at constant pressure.

Most everyday processes occur at constant pressure, namely the atmospheric pressure, and in such cases the second should be used.

This brief introduction is sufficient for now; we shall later derive how heat capacities from changes of state functions such as the internal energy. In chapter "Calorimetry" the methods to measure the heat capacities are found.

Summarizing:

The process of attaining thermal equilibrium is described as a "flow of heat" from the "hot" object to the "cold" one. Heat is a quantity that flows across the boundary of the system during a change in state by virtue of a difference in temperature between the system and its surroundings.

Heat is an algebraic quantity, taken to be positive when it flows from the surrounds to the system (same convention as for work).

Thermodynamic heat is always measured in the surroundings, not in the system. A quantity of heat (Q) may be established, for example, by the amount of temperature increase it causes if transferred to a fixed amount of water (the "calorie" is defined as the amount of heat required to raise the temperature of 1 gram of water from 14.5 °C to 15.5 °C at a pressure of 1 atm).

As in the case of work, we find experimentally that the total heat flow for a cyclical process does not sum to zero:

$$\oint \delta Q \neq 0$$

The consequences of this for Q are the same as those given below for *L*. The question of how to define the positive direction of work or heat is arbitrary.

In modern thermodynamics, the usual convention is that heat is positive when absorbed by the system.

Recall that work was similarly defined to be positive when work is done on the system to the surroundings. (In older texts, the convention for work is often the opposite of this, so be careful)

Table 12.1 - Signs convention for Heat transfer				
System loses heat to the surroundings	System		Surroundings	
	Q < 0	System loses energy in the form of heat	Q > 0	Surroundings gains energy in the form of heat
System absorbs heat from the surroundings	Q > 0	System gains energy in the form of heat	Q<0	Surroundings loses energy in the form of heat

Exothermic and Endothermic Reactions/Processes

Exothermic: Releases heat
Endothermic: Absorbs heat

exothermic process	Q < 0	endothermic process	Q > 0
system releases heat to the surroundings		system absorbs heat from the surroundings	
T of system decreases, loses heat		T of system increases, gains heat	
T of surroundings increases, gains heat		T of surroundings decreases, loses heat	

System
Loses heat

Surroundings
Absorbs heat

Exothermic
$Q_{sys} < 0$

Surroundings
Loses heat

System
Absorbs heat

Endothermic
$Q_{sys} > 0$

12.2 Work

Work is the general concept. The work is familiar from elementary mechanics.

In thermodynamics work is defined as a quantity that flows across the boundary of a system during a change in state and which can be completely converted into the raising or lowering of a weight in the surroundings. Work is an algebraic quantity, taken to be positive by definition when it flows from the surroundings to the system. One never talks about work inside a system. Work is produced in the surroundings because of an unbalance of forces across a boundary. No transfer of matter is involved.

In principle, all kinds of work are completely convertible into each other. Because of its importance in thermodynamics, we will focus special attention on the work produced by varying the volume of a system (so-called "expansion work" or "compression work"),

How the work- works
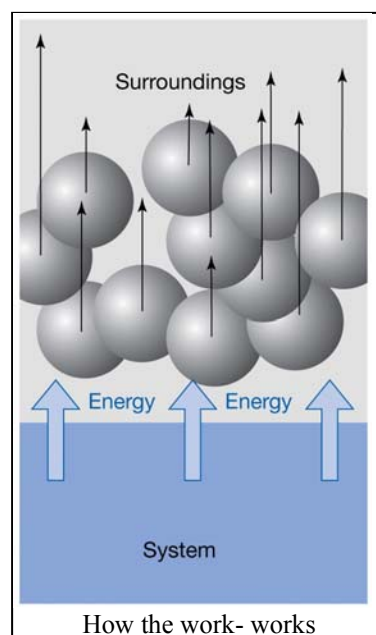
The work is a general phenomenon and refers to ordered motion of particles of systems. Many different forms of work exist; a few are listed below (Table 12.1)

12.2.1 Work in mechanics

➢ Work = Force × Distance: **$L = F\,\Delta x$**

➢ The unit for work is the Newton x meter which is also called a Joule.

The work produced by a force on a fluid is defined as **hydraulic work** or PV-work (figure 12.1).

$$L = F \cdot \Delta x = \frac{F}{S} \cdot S \cdot \Delta x$$

$$L = P \cdot \Delta V$$

Figure 12.1 gives a few examples with simple fluids (gases and liquids). In figure 12.1A, the Work is done when and object, e.g. a system's wall, moves against an opposing force. This is equivalent to an ordered motion done by the system on the surroundings or vice versa. In figure 12.1B represents the expansion against environment (external pressure. In figure 12.1C the pressure from a liquid pushes the piston (hydraulic work).
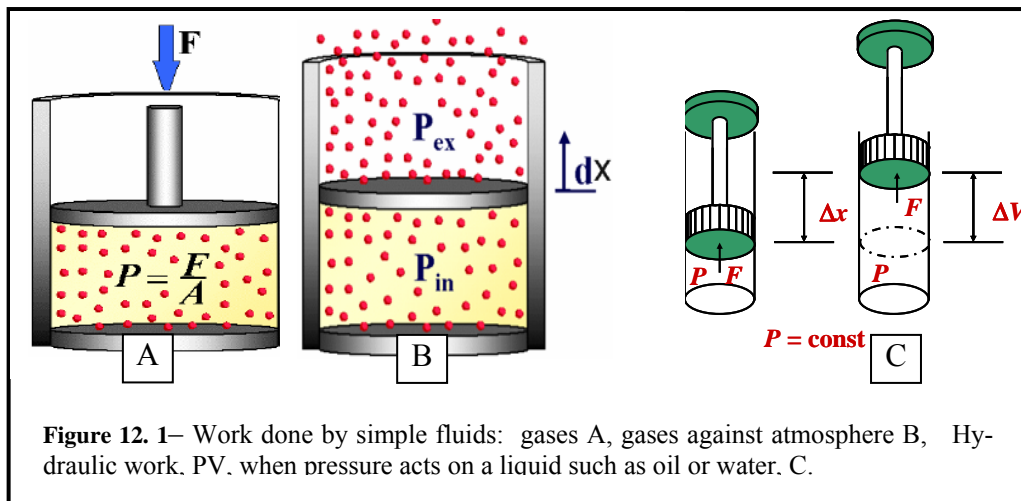
Figure 12. 1– Work done by simple fluids: gases A, gases against atmosphere B,   Hydraulic work, PV, when pressure acts on a liquid such as oil or water, C.

The work is an inexact differential. The work is not a state function.
The elemental work:

$$\delta L = -P_{ext} dV$$

and integral work:
$$L = - \int_{initial}^{final} P_{ext} dV$$

where P_{ext}, is the external pressure

Sign convention: Consider the system to have an energy-account. A negative sign means: Withdraw of energy (e.g., work done by the system). A positive sign means: deposit of energy (e.g., work done on the system).

Table 12.2 Other forms of work			
Type of work	dw	Comment	Units
Expansion	-Pex dV	Pex= external pressure V = volume	N/m^2 m^3
Surface expansion	$\gamma\, d\sigma$	γ= surface tension $d\sigma$= surface area	N/m m^2
Extension	f dl	f = tension dl = length	N/ m
Electrical potential	Φdq	Φ= electrical potential dq = charge	V C
Electrical dipole	Edp	E= electrical field dp= electric dipole moment	V/m mAs
Magnetic dipole	Bdm	B= magnetic field dm= magnetic dipole moment	$kg/s2$ A mAs
Chemical	μdN	μ= chemical potential dN = number of moles	J/mol mol

Table 12.3 – Signs convention for work				
System does work on the surroundings	System		Surroundings	
	L < 0	System loses energy in the form of work	L > 0	Surroundings gains energy in the form of work
Surroundings does work on the system	L> 0	System gains energy in the form of work	L < 0	Surroundings loses energy in the form of work

Inexact differentials: In thermodynamics differentials like heat and work are called imperfect (inexact) differentials and are symbolized by a bar through *d* or by δ.

While they represent infinitesimal changes, in this case of work, they cannot readily be computed without additional information. Integration can be carried out but the result of the integration is dependent on the integration path.

- ➡ As we saw the general concept of work is familiar from elementary mechanics. In thermodynamics work is defined as a quantity that flows across the boundary of a system during a change in state and which can be completely converted into the raising or lowering of a weight in the surroundings.
- ➡ Work is an algebraic quantity, taken to be positive by definition when it flows from the surroundings to the system.
- ➡ One never talks about work inside a system. Work is produced in the surroundings because of an unbalance of forces across a boundary.
- ➡ No transfer of matter is involved.

Properties of work. It is an experimental fact that the total work does not sum to zero for most processes that start and end in the same state (cyclical processes). I.e., in general:

$$\oint \delta L \neq 0$$

The consequences of this are:
A system in a specified state does not contain a definite fixed amount of work.

L is not a function of a set of independent state variables, such as L(P,T) for a pure substance in a single aggregation state.

δL is not an exact differential but simply an infinitesimal amount of work.

Generalized work

Work for a generalized force applied in the surroundings, F_{ext}^i and a generalized displacement dx_i in the variable x_i conjugate to it, $\delta L^i = -F_{ext}^i dx_i$ is the i^{th} kind of work. L^i is reversible only if $F_{ext}^i = F_{system}^i$

12.3 Reversible and Irreversible Processes

A reversible process is one that can be halted at any stage and reversed. In a reversible process the system is at equilibrium at every stage of the process. An irreversible process is one where these conditions are not fulfilled.

If $P_{int} > P_{ext}$ in an expansion process then the process is irreversible because the system does not remain at equilibrium at every stage of the process. (There will be turbulence and temperature gradients, for example.) For irreversible processes, PV work can be calculated using

$$\delta L = -P_{ext} dV$$

On the other hand, if $P_{int} = P_{ext}$ then the process can be carried out reversibly. In addition, there is then no need to distinguish between external pressure and internal pressure so that

$$P_{int} = P_{ext} = P$$

and there is only one pressure defined for the system. In this case, which will account for the majority of problems that we deal with, as $\delta L = -P_{ext} dV$.

Example: Expansion of gas

We assume that the outside pressure is always nearly equal to the inside pressure, a situation called *quasistatic*. In such a case, the motion of the movable wall separating the system from the surroundings is infinitely slow. Compression can easily be reversed by expansion; i.e. the process is *reversible*. If the pressure difference is larger the motion of this wall will not be slow any more and complicated effects, such as shock waves or turbulence, can occur. Such processes are certainly *irreversible*. Therefore, quasistatic processes are reversible. Then:

$$L = -\int_{path} P_{ext} dV = -\int_{path} P_{in} dV$$

Reversible heat transfer, e.g., refers to thermal contact between systems with infinitesimally small temperature difference.

In general, systems in equilibrium will never undergo changes of state. However, since we want to study interactions and the resulting changes of state, systems must be allowed to pass though non-equilibrium states. Unfortunately, non-equilibrium states are not well defined in thermodynamics. We, therefore, divide any process into infinitesimal steps with infinitesimally small changes, which then can be considered to be quasistatic. No real process is truly quasistatic, but we can design processes to be approximately quasistatic to almost any desired accuracy. We can then write

$$L = - \int_{path} PdV \quad \text{with } P_{ext} = P_{in}$$

Keep in mind, that "slow" and "quasistatic" is always judged relative to the relaxation time of the system. For instance, solids with good thermal conductivity will equilibrate heat faster then solids with low thermal conductivity.

12.4 Internal energy, The First Law of Thermodynamics, Conservation of Energy

> The internal energy **U** of a system can be defined as the capacity to do work.

The principle of the conservation of energy states that *energy can neither be created nor destroyed*. If a system undergoes a process by heat and work transfer, then the net heat supplied, **Q**, plus the net work input, **L**, is equal to the change of intrinsic energy of the working fluid, i.e.

$$\Delta U = U_2 - U_1 = Q + L$$

where **U₁** and **U₂** are intrinsic energy of the system at initial and final states, respectively. The special case of the equation applied to a steady-flow system is known as steady-flow energy equation. Applying this general principle to a thermodynamic cycle, when the system undergoes a complete cycle, i.e. **U₁ = U₂**, results in:

$$\sum Q + \sum L = 0$$

where:

$\sum Q$ = The algebraic sum of the heat supplied to (+) or rejected from (-) the system.

$\sum L$ = The algebraic sum of the work done by surroundings on the system (+) or by the system on surroundings (-).

Applying the rule to the power plant shown in figure below,
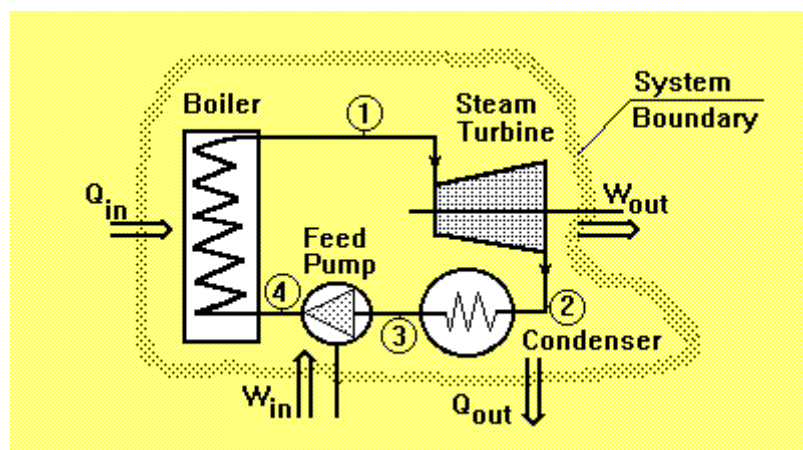
gives:

$$\left.\begin{array}{l} \sum Q = Q_{in} - Q_{out} \\ \sum L = L_{in} - L_{out} \end{array}\right\} \rightarrow Q_{in} + L_{in} - Q_{out} - L_{out} = 0$$

where,

Q_{in} = Heat supplied to the system through boiler;

W_{in} = Feed-pump work;

Q_{out} = Heat rejected from the system by condenser,

W_{out} = Turbine work.

Summarizing

When a system undergoes any cyclical process, the work given up from the surroundings is proportional to the heat withdrawn from the surroundings. The constant of proportionality (a negative number for the sign conventions we have adopted) depends only on the units in which heat and work are measured.

The Joule experiment permits one to relate units of work (joule) with units of heat (calorie).

The relationship is now established by defining the calorie in terms of the more fundamental unit, the Joule.

When the same units are used for L and Q:

$$\oint \delta L + \oint \delta Q = 0$$

for all cycles.

Definition of energy. In thermodynamics the energy U (sometimes called the internal energy) is defined by:

$$dU = \delta Q + \delta L. \qquad\qquad 12.1$$

Thus for every cyclic process:

$$\oint dU = 0$$

> The last two equations together constitute a complete mathematical statement of the first law.

Properties of the energy. The consequences of the statement Equations are:

➡ U is a state variable (a single-valued extensive property of the system) and is completely defined except for an additive constant;

➡ For unit mass of a pure substance in a single aggregation state, $U = U(V,T)$ and dU is the total differential of $U(V,T)$; dU is an exact differential;

➡ The increase in energy ΔU for any change in state is independent of the path, and depends only on the initial and final states:

$$\Delta U = U_2 - U_1 = \int_1^2 (\delta Q + \delta L)$$

Note that Q and L do depend on the path, but Q+L (=ΔU) does not. The symbol Δ will be used only for state variables such as U. ΔU represents the change in the energy content between state 2 and state 1, while Q or W represents the amount of heat or work which flows across the system's boundaries for a given process which takes the system

Figure 12.2 –a)1st law for adiabatic process: dU=δL; b) 1st Law
for diabatic process: dU= δQ+δL
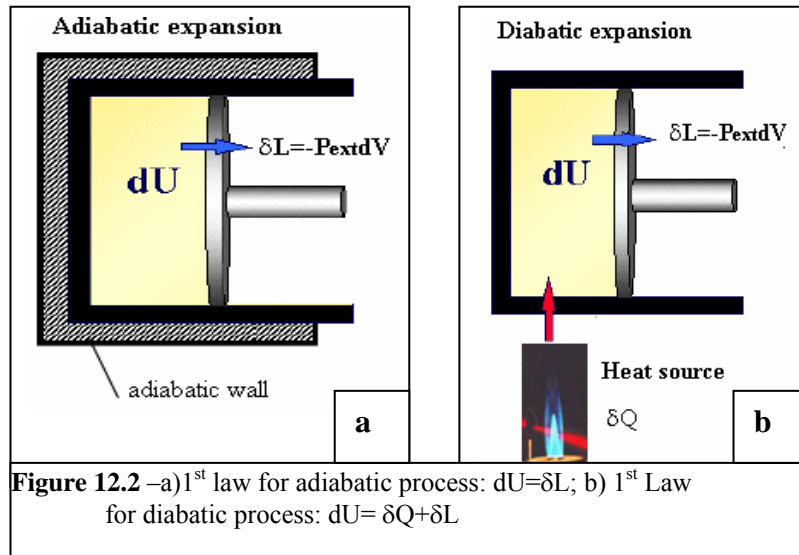
along a specified path from state 1 to state 2.

12.5 1st Law, axiomatic representation

We give a review regarding to the general efforts to put the first law in an axiomatic form

Poincare scheme: Poincare has taken as primitive concepts, heat transfer and temperature defining the exchange interaction for a complete cycle as:

$$\oint \delta Q = \oint \delta L$$

and the difference $\delta Q - \delta L$ called internal energy

Caratheodory scheme: here the primitive concepts have been taken- work interaction, and adiabatic boundary. The thermal interaction becomes a secondary property

$$dU = -\delta L_{adiabatic}$$

Keenan and Shapiro scheme. The primitive concepts are considered: temperature, rigid boundary and interaction by heat exchange. Thus:

$$dU = \delta Q_{when\ work=0}$$

and as derivative concept is : $\delta W = dU - \delta Q_{for\ work=0}$

12.6 1st Law and the Enthalpy, preliminaries

The first law, essentially states the conservation of energy being described with one of expressions above discussed. To measure a change in the internal energy of a process one might now be tempted to perform the process at constant volume, and measure the heat exchanged between the system and the surroundings under those conditions. For processes at constant volume, we have *dV = 0*, and therefore the volume work term is zero. One would obtain:

$$dU = \delta Q_V$$

and using the specific heat at constant volume definition

$$dU = mc_V dT$$

The equation states the direct correlation internal energy-temperature as a univocal dependence as stated in zero-th Law. That is, the internal energy for one typical system has an only one expression function of temperature.

Experimental the specific heat at constant volume encounter seriously difficulties in measurements. In addition, many practical situations where relevant processes need to be investigated take place at constant pressure (chemical reactions, phase changes, biological processes, etc).

The volume work those systems not supply any information with what happen in system. (We don't include other forms of work like surface work, tension work, and for now even, the chemical work). Being interested with the heat consumed or supplied to surroundings due to internal changes we need to define a new function more appropriate to many situations of Chemistry, Biology, and Physics, where the proposition to do a process at constant volume makes life difficult.

For instance, in many chemical reactions the density changes, and therefore the system change its volume unless very large pressures are applied. Reaction containers would need to have very thick walls made of stainless steel. Clearly, our theory so far does not relate well to real life physics and chemistry: one typically does not measure the heat of a process by keeping the volume constant. Rather, most processes are at constant pressure, under isobaric conditions. Since under such conditions *dP=0* it follows:

$$dU = \delta Q - PdV \xrightarrow{\ d(PV)=PdV+VdP\ } dU = \delta Q - d(PV) + VdP$$

$$dU + d(PV) = \delta Q + VdP \xrightarrow{\ P=ct\ } d(U+PV) = \delta Q_P$$

$$dH = \delta Q_P$$

where the quantity

$$H = U + PV \qquad\qquad\qquad 12.2$$

is called **Enthalpy.** It is a measure of the energy, just like U, but it is the appropriate one for processes at constant pressure. It turns out that because much of physics, chemistry and biological processes are at constant pressure, the enthalpy is a function with very much utility to us. Previously, enthalpy was referred to as total heat or heat content, but these terms are misleading and should be avoided

Summarizing:

Enthalpy is, from the viewpoint of mathematics, a point function or a state function, as contrasted with heat and work, which are path functions. (Remember the state functions or point functions depend only on the initial and final states of the system undergoing a change; they are independent of the paths or character of the change. Mathematically, the differential of a point function is a complete or perfect differential).

Experimental, recorded values of enthalpy are relative values measured above some convenient but arbitrarily chosen datum. Like the energy, also the enthalpy has no absolute value, because only the changes in enthalpy are measurable. So we need to define the standard states where the enthalpy is considered zero. There is limited utility for absolute enthalpies. It is instructive to examine the utility of the enthalpy function in terms of some simple but important thermodynamic processes:

➡ Joule-Thompson effect. The adiabatic, irreversible, steady flow of a stream of materials through a porous plug or a partially opened valve under circum-

stances where the change in kinetic energy of flow is negligible (a Joule-Thomson process) results in no change in enthalpy of the flowing stream. Although no change in enthalpy results from this process, there is a loss in the energy available for doing work as a result of the pressure drop across the plug or valve

➡ The heat balances on heat exchangers, furnaces, and similar industrial equipment that operate under steady flow conditions are really enthalpy balances.

➡ For a chemical reaction carried out at constant pressure and temperature with no work performed except that resulting from keeping the internal and external pressure equal to each other as the volume changes, the change in enthalpy of the system (the material taking part in the chemical reaction) is numerically equal to the heat that must be transferred to maintain the above-mentioned conditions. This heat is often loosely referred to as the heat of reaction. More properly, it is the enthalpy change for the reaction.

Examples:

1. Relationship ΔH and ΔU: 1 mol $CaCO_3$ transforms from phase calcite to aragonite (phase transformation) with internal energy change $+0,21kJ$. Find the difference ΔH and ΔU at pressure 1 atm if densities are , calcite 2,71 respective aragonite 2.93 g/cm^3.

$$\Delta H = H(aragonite) - H(calcite) = (U_a + pV_a) - (U_c + pV_a) = \Delta U + p\Delta V$$

Volume for 1 mol $CaCO_3$ (100g) aragonite:

$$V_a = \frac{M}{\rho_a} = \frac{100g}{2,93g\,/\,cm^3} = 34,13cm^3, \text{ and for calcite } V_c = 36,9cm^3$$

$$\Delta V = 34,13 - 36,9 = -2,77cm^3$$

$$p\Delta V = (1,01 \cdot 10^5\,Pa) \cdot (-2,77 \cdot 10^{-6})m^3 = -0,28J$$

$$\text{final}: \Delta H - \Delta U = -0,28J,$$

which is 0,1% of ΔU. Usually the difference for solid phases is small and H and U are comparable equals. At high pressures, $P\Delta V$ must be taken in account.

2. Tin has two phases corresponding the two allotropes with different colours, one grayish (densitaty 5.75 g/cm^3) and white (density 7.31 g/cm^3). At 10 bar the lower pressure phase transforms in the high pressure one. Find the difference in enthalpy and internal energy.

$$\Delta H - \Delta U = p\Delta V = pM\left(\frac{1}{\rho_{alb}} - \frac{1}{\rho_{cen}}\right) = 10 \cdot 1,01 \cdot 10^5 \left(\frac{1}{5.75} - \frac{1}{7.31}\right)10^{-6} \approx 0.03$$

3. Find that the enthalpy describes the isobaric process and dH=C_P dT. For any substance, heat capacity is dependent of temperature: C_P=a+bT+cT^2. Find the enthalpy change from 0K to T and give the significance of area under heat capacity curves, a and H_0, the enthalpy at 0K.

4. 1 mol ideal gas closed in a cylinder with a piston (mass m) is found in a space shuttle at room temperature. Find the volume change and the enthalpy when the gas is brought on earth.

5. 1 mol of water in droplets with radius r=10nm are closed in a bottle in space shuttle. The droplets form a cloudy atmosphere. When the bottle is brought on earth, you will find 1 mol liquid water. How much enthalpy change can be counted?. Take in discussion two cases with and without surface tension.

6. How much is the change in enthalpy when you heat 1 kg water from room temperature to boiling point in an open vessel and in a pressurized vessel.

7. In a melting/ crystallization process the naphthalene absorbs/ delivers heat. Evaluate the internal energy and enthalpy change using latent heat and densities for the two phases.

12.7 References

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Chapter 13

1st Law, Applications

13.1 The State of a System

We specify the state of a system - say, a sample of material - by specifying the values of all the variables describing the system. If the system is a sample of a pure substance this would mean specifying the values of the temperature, *T*, the pressure, *P*, the volume, *V*, and the number of moles of the substance, *n*.

> ➢ We must assume that the system is at equilibrium. That is, none of the variables is changing in time and they have the values they would have if we let time go to infinity. We will give a thermodynamic definition of equilibrium later, but this one will suffice for now.

> ➢ If the system is a mixture, you also have to specify the composition of the mixture as well as *T, P,* and *V*. This could be done by specifying the number of moles of each component, n_1, n_2, n_3, . . . , or by specifying the total number of moles of all the substances in the mixture and the mole fraction of each component, x_1, x_2, x_3, ... We will not deal with mixtures on this section.

13.2 Thermal coefficients

Definitions:

Isobaric expansion coefficient:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad 13.1$$

Isocoric coefficient:

$$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad 13.2$$

Isothermal compressibility and its modulus

$$\gamma = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \; ; \; K_T = -V\left(\frac{\partial P}{\partial V}\right)_T \qquad 13.3$$

For any set of independent variable for which an implicit state equation exists: *F(P,V, T)=0*, the Euler chain rule gives:

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T = -1 \Leftrightarrow \beta = \frac{\alpha K_T}{P} \qquad 13.4$$

13.3 The equations of state

Let's consider a sample of a pure substance, say *n* moles of the substance. It is an experimental fact that the variables, T, P, V, and n are not independent of each other.

That is, if we change one variable one (or more) of the other variables will change too. This means that there must be an equation connecting the variables. In other words, there is an equation that relates the variables to each other. This equation is called the "equation of state." The most general form for an equation of state is,

$$F(P,V,T,n) = 0 \qquad\qquad 13.5$$

This equation is not very useful because it does not tell us the detailed form of the function, F. However, it does tell us that we should be able to solve the equation of state for any one of the variables in terms of the other three. For example, we can, in principle, find:

$$P = P(T,V,n)$$

or $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 13.6$

$$V = V(T,P,n)$$

and so on. (These last two equations should be read as, "P is a function of V, T, and n" and "V is a function of P, T, and n."). If we do some more experiments we will notice that when we hold P and T constant we can't change n without changing V and vice versa. In fact, V is proportional to n. That is, if we double n, the volume, V, will also double, and so on. Because V is proportional to n these two variables must always appear in the equation of state as V/n (or n/V). This means that the most general form of the equation of state is simpler than that shown above. The most general form of the equation of state really has the form,

$$F(P,\frac{V}{n},T) = 0$$

which can be solved for P, V/n, or T in terms of the other two. For example,

$$P = P\left(T,\frac{V}{n}\right)$$

and so on.

All isotropic substances have, in principle, an equation of state, but we do not know the equation of state for any real substance. All we have is some approximate equations of state which are useful over a limited range of temperatures and pressures.

Some of the approximate equations of state are pretty good and some are not so good. Our best equations of state are for gases. There are no general equations of state for liquids and solids, isotropic or otherwise. On another section we will show how to obtain an approximate equation of state for isotropic liquids and solids which is acceptable for a limited range of temperatures around 25^0 C and for a limited range of pressures near one atmosphere.

13.3.1 The Ideal Gas Equation of State

The best-known equation of state for a gas is the "ideal gas equation of state." It is usually written in the form,

$$PV = nRT$$

This equation contains a constant, R, called the gas constant or, sometimes, the universal gas constant. We can write this equation in the forms shown above if we wish.

For example, the analog of above equation is, the implicit one

$$PV - nRT = 0$$

or explicit:

$$P = \frac{nRT}{V} \text{ or } V = \frac{nRT}{P}$$

and so on.

No real gas obeys the ideal gas equation of state for all temperatures and pressures. However, all gases obey the ideal gas equation of state in the limit as pressure

goes to zero (except possibly at very low temperatures). Another way to say this is to say that all gases become ideal in the limit of zero pressure. We will make use of this fact later when we deal with "fugacity" for example.

The ideal gas equation of state is the consequence of a model in which the molecules are point masses - that is, they have no size - and in which there are no attractive forces between the molecules.

13.3.2 The van der Waals Equation of State

The van der Waals equation of state is,

$$\left(P + a \frac{n^2}{V^2} \right)(V - nb) = nRT$$

13.7

(for n=1mol, we will denote $V = V_m$)

Notice that the van der Waals equation of state differs from the ideal gas by the addition of two adjustable parameters, a, and b (among other things). These parameters are intended to correct for the omission of molecular size and intermolecular attractive forces in the ideal gas equation of state. The parameter b corrects for the finite size of the molecules and the parameter, a, corrects for the attractive forces between the molecules.

The argument goes something like this: Assume that an Avogadro's number of molecules (i.e., a mole of the molecules) takes up a volume of space - just by their physical size - of b litres. Then any individual molecule doesn't have the whole (measured) volume, V, available to move around in. The space available to any one molecule is just the measured volume less the volume taken up by the molecules themselves, *nb*.

Therefore, the "effective" volume, which we shall call V_{eff}, is V - nb. The effective pressure, P_{eff}, is a little bit trickier. Consider a gas where the molecules attract each other. The molecules at the edge of the gas (near the container wall) are attracted to the interior molecules. The number of "edge" molecules is proportional to n/V and the number of interior molecules is proportional to n/V also. The number of pairs of interacting molecules is thus proportional to n^2/V^2 so that the forces attracting the edge molecules to the interior are proportional to n^2/V^2. These forces give an additional contribution to the pressure on the gas proportional to n^2/V^2. We will call the proportionality constant *a* so that the effective pressure becomes

$$P_{eff} = P + a \frac{n^2}{V^2}$$

13.8

We now guess that the gas would obey the ideal gas equation of state if only we used the effective volume and pressure instead of the measured volume and pressure.

That is,

$$P_{eff} V_{eff} = nRT$$

13.9

Inserting our forms for the effective pressure and volume we get, the first equation which **is** the van der Waals equation of state.

The van der Waals constants, a and b, for various gases must be obtained from experiment or from some more detailed theory. They are tabulated in handbooks and in most physical chemistry textbooks.

Remember:

1. Isotropic means that the properties of the material are independent of direction within the material. All gases and most liquids are isotropic, but crystals are not. The properties of the crystal may depend on which direction you are looking with respect to the crystal lattice. As we said above, most liquids are isotropic, but liquid crystals are not. That's why they are called liquid crystals. Amorphous solids and polycrystalline solids are usually isotropic.
2. The value of the gas constant, R, depends on the units being used. R = 8.314472 J/K mol = 0.08205746 L atm/K mol = 1.987207 cal/K mol = 0.08314472 L bar/K mol.

13.3.3 The Virial Expansion

The virial expansion, also called the virial equation of state, is the most interesting and versatile of the equations of state for gases. The virial expansion is a power series in powers of the variable, n/V, and has the form, (see Taylor and Mac Laurin series development in any math course)

$$\frac{PV}{nRT} = Z = 1 + B(T)\frac{n}{V} + C(T)\left(\frac{n}{V}\right)^2 + \dots\dots\infty \qquad 13.10$$

The coefficient, B(T), is a function of temperature and is called the "second virial coefficient. C(T) is called the third virial coefficient, and so on. The expansion is, in principle, an infinite series, and as such should be valid for all isotropic substances. In practice, however, terms above the third virial coefficient are rarely used in chemical thermodynamics.

Notice that we have set the quantity PV/nRT equal to Z. This quantity (Z) is called the "compression factor." It is a useful measure of the deviation of a real gas from an ideal gas. For an ideal gas the compression factor is equal to 1.

13.3.3.1 THE BOYLE TEMPERATURE

The second virial coefficient, B(T), is an increasing function of temperature throughout most of the useful temperature range. (It does decrease slightly at very high temperatures.) B is negative at low temperatures, passes through zero at the so-called "Boyle temperature," and then becomes positive. The temperature at which B(T) = 0 is called the Boyle temperature because the gas obeys Boyle's law to high accuracy at this temperature. We can see this by noting that at the Boyle temperature the virial expansion looks like,

$$\frac{PV}{nRT} = Z = 1 + 0 + C(T)\left(\frac{n}{V}\right)^2 + \dots\dots\infty \qquad 13.11$$

If the density is not too high the C term is very small so that the system obeys Boyle's law.

13.3.3.2 ALTERNATE FORM OF THE VIRIAL EXPANSION.

An equivalent form of the virial expansion is an infinite series in powers of the pressure.

$$\frac{PV}{nRT} = Z = 1 + B^{'}(T)P + C^{'}(T)P^2 + \dots\dots \qquad 13.12$$

The new virial coefficients, B', C', . . . , can be calculated from the original virial coefficients, B, C, ... To do this we equate the two virial expansions, then we solve the original virial expansion for P, and substitute this expression for P we get:

$$1+B(T)\frac{n}{V}+C(T)\left(\frac{n}{V}\right)^2+... = 1+B'\frac{nRT}{V}\left(1+B(T)\frac{n}{V}+C(T)\left(\frac{n}{V}\right)^2+...\right)+$$

$$+C'\left(\frac{nRT}{V}\right)^2\left(1+B(T)\frac{n}{V}+C(T)\left(\frac{n}{V}\right)^2+...\right)^2+.....$$

13.13

Both sides of the equation are power series in n/V. (We have omitted third and higher powers of n/V because the second power is as high as we are going here.) Since the two power series must be equal, the coefficients of each power of n/V must be the same on both sides. The coefficient of $(n/V)^0$ on each side is 1, which gives the reassuring but not very interesting result, 1 = 1. Equating the coefficient of (n/V) on each side gives B = B'RT and equating the coefficients of $(n/V)^2$ we find C$'$.

These equations are easily solved to give B' and C' in terms of B, C, and R.

Useful exercises would be:

➤ Extend the two virial expansions to the D and D' terms respectively and find the expression for D' in terms of B, C, and D.

➤ Find B' and C' in terms of the van der Waals a and b constants. (You were asked, in the homework to find the virial coefficients B and C in terms of a and b so you already have these.)

The word "virial" is related to the Latin word for force. Clausius named a certain function of the force between molecules "the virial of force." This name was subsequently taken over for the virial expansion because the terms in that expansion can be calculated from the forces between the molecules.

The virial expansion is important for several reasons, among them: In principle, it can be made as accurate as desired by keeping more terms. In addition, it has a sound theoretical basis. The virial coefficients can be calculated from a theoretical model of the intermolecular potential energy of the gas molecules.

13.4 Critical Phenomena

All real gases can be liquefied. Depending on the gas this might require compression and/or cooling. However, there exists for each gas a temperature above which the gas cannot be liquefied. This temperature, above which the gas cannot be liquefied, is called the **critical temperature** and it is usually symbolized by, T_C . In order to liquefy a real gas the temperature must be at, or below, its critical temperature.

There are gases, sometimes called the "permanent gases" which have critical temperatures below room temperature. These gases must be cooled to a temperature below their critical point, which means below room temperture, before they can be liquefied. Examples of "permanent gases" include, He, H_2, N_2, O_2, Ne, Ar, and so on.

Many substances have critical temperatures above room temperature. These substances exist as liquids (or even solids) at room temperature. Water, for example, has a critical temperature of 647.1 K, much higher than the 298.15 K standard room temperature. Water can be liquefied at any temperature below 647.1 K (although above 398.15 - the normal boiling point of water - we would have to apply a pressure higher than atmospheric temperature in order to keep it liquid.

It is convenient to think about liquefying substances and critical phenomena using a *P-V* diagram. This is a graph with pressure, P, plotted on the vertical axis and the vol-

ume, *V*, plotted along the horizontal axis. If we plot the pressure of a substance as a function of volume, holding temperature constant we get a series of curves, called isotherms. There is an example of such a plot in most physical and physical- chemistry texts. We already provided a example in section real gases.The isotherms below the critical temperature, for example, are peculiar to the van der Waals equation of state and are not physically realistic. Notice that when a substance is liquefied the isotherm becomes "flat," that is, the slope becomes zero. On the critical isotherm, the slope "just barely" becomes flat at one point on the graph. A point where a decreasing function becomes flat before continuing to decrease is called **inflection point**. The mathematical characteristic of an inflection point is that the first and second derivatives are zero at that point. For our critical isotherm on a P-V diagram we would write,

$$\left(\frac{\partial P}{\partial V}\right)_T = 0; \text{ and } \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0 \qquad\qquad 13.14$$

Equations constitute a set of two equations in two unknowns, *V*, and *T*. One can test to see if an approximate equation of state gives a critical point by calculating these two derivatives for the equation of state and trying to solve the pair of equations. If a solution exists (and P and V are neither zero nor infinity) then we say that the equation of state has a critical point.

Let's use this test to see if the ideal gas has a critical point. First, we have to solve the ideal gas equation of state. We can take the derivatives and set them (independently) equal to zero:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} = 0; \text{ and } \left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2nRT}{V^3} = 0 \qquad\qquad 13.15$$

It is easy to see that the only way these two equations can be satisfied is if *T* = 0, or *V* = ∞ . Neither of these solutions is physically reasonable so we conclude that the ideal gas does not have a critical point.

Good exercises would be for you to see if the approximate equation of state,

$$P(V - nb) = nRT$$

has a critical point.

13.4.1 Critical Constants of the van der Waals Gas

Let us to extend discussion of critical phenomena that the mathematical definition of the critical point to the Van der Waals gas

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3} = 0$$

$$P = \frac{RT}{V-nb} - a\frac{n^2}{V^2} \quad \rightarrow \qquad\qquad 13.16$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2nRT}{(V-nb)^3} - \frac{6an^2}{V^4} = 0$$

There are several ways to solve simultaneous equations. One way is to multiply the first with $2/(V-nb)$ and solving both, we obtain:

$$V = V_c = 3nb; \quad T = T_c = \frac{8a}{27bR} \text{ and } P_c = \frac{a}{27b^2} \hspace{2cm} 13.17$$

Our conclusion is that the van der Waals equation of state does give a critical point since the set of simultaneous equations has a unique solution. The van der Waals equation of state is still an approximate equation of state and does not represent any real gas exactly. However, it has some of the features of a real gas and is therefore useful as the next best approximation to a real gas. We will be deriving thermodynamic relationships (equations) using the ideal gas approximation. We can rederive some of these equations using the van der Walls equation of state in order to see how these relationships are affected by gas nonideality.

13.5 Solids and Liquids

There are approximate equations of state for gases which can give virtually any degree of accuracy desired. However, there are no analogous equations of state for solids and liquids. Fortunately the volumes of solids and liquids do not change very much with pressure as long as the pressure changes are not too large. This situation allows us to define parameters and form an approximate equation of state which is valid over a moderate range of temperatures and pressures.

We will restrict our attention to isotropic liquids and solids, which means that we are excluding liquid crystals and solid single crystals. Single crystals and liquid crystals are anisotropic. Their response to pressure and their expansion with temperature is different along different axes in the crystal. (Many solids, particularly metals and alloys are conglomerates of microscopic crystals with random orientations so that the bulk material behaves like an isotropic solid even though the individual microscopic crystals are anisotropic. We can apply our methods for isotropic substances to these materials even though, strictly speaking, they are crystalline.)

The volume of a sample of an isotropic material is known experimentally to be a function of temperature and pressure. Therefore, we can write

$$V = V(T,P) \rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = \alpha V dT - \gamma V dP$$

$$\frac{dV}{V} = \alpha dT - \gamma dP \hspace{2cm} 13.18$$

which can be integrated to give an approximate equation of state for isotropic liquids and solids:

$$V = V_0 \exp\left[-\gamma\left(P - P_0\right) + \alpha(T - T_0)\right] \hspace{2cm} 13.19$$

The quantity of interest which can be obtained from α and κ_T, namely

$$\left(\frac{\partial P}{\partial T}\right)_V = \alpha k_T$$

Gives us an important information then we rise a phase diagram in P-T coordinates.

For instance, we will apply to a mercury thermometer when the column reached the maximum height. Considering $\alpha = 1.82 \times 10^{-4} K^{-1}$ and $\gamma = 3.87 \times 10^{-5} atm^{-1}$ we obtain a value of 4.7 atm/grd which is high enough to break the glass.

13.6 Thermometers and the Ideal Gas Temperature Scale

Many of the thermometers we see and use are made of a thin glass tube containing a liquid. The temperature is measured by observing how far up the tube the liquid rises. However, we have already seen that α is not a constant so that liquid expansion is not uniform and the rise in the liquid is not linear with temperature. Worse, different liquids have different nonlinear expansions.

We could pick a standard substance and all agree to measure temperature by the expansion of this substance, but it is unsatisfactory to have our measuring devices tied to particular substances. It would be best if we had a temperature measuring device which was independent of any particular material.

The ideal gas thermometer is such a device and the temperature scale it defines is called the ideal gas temperature scale. The ideal gas temperature scale is based on the fact that all gases become ideal in the limit of zero pressure. Therefore, we can define the ideal gas temperature as,

$$T = \frac{1}{nR}\lim_{p\to 0}(pV).$$

13.20

This temperature scale is independent of the gas used. It has a natural zero since $P > 0$ and $V > 0$, so that PV is never negative. The value of R determines the size of the degree. If R is the gas constant, 0.082057459 Latm/Kmol, then the degree is the Kelvin degree. No one claims that the ideal gas thermometer is easy to use, but it does provide us with an unambiguous theoretical standard to establish a temperature scale.

13.7 Enthalpy vs Energy

13.7.1 Energy

We have agreed that work, potential energy, kinetic energy, and heat are all forms of energy. Historically, it was not obvious that heat belonged in this list. But beginning with the experiments of Count Rumford of the Holy Roman Empire, and later the experiments of Joule, it became clear that heat, too, was just another form (or manifestation) of energy. Recall that we defined the internal energy, U, as the total energy of the system. (Although the existence of atoms and molecules is not relevant to thermodynamics, we said that the internal energy is the sum of all the kinetic and potential energies of all the particles in the system. This statement is outside the realm of thermodynamics, but it is useful for us to gain an intuitive "feel" for what the internal energy is.) Recall also that energies are always measured relative to some origin of energy. The origin is irrelevant to thermodynamics because we will always calculate changes in U and not absolute values of U.

$$\Delta U = U_{fin} - U_{in}$$

In words, this equation reads, "the change in the internal energy is equal to the final internal energy minus the initial internal energy." This equation also reminds us that U is a "state function." That is, the change in U does not depend on how the change was done (in other words, on the path), but depends only on the initial and final states. Recall that the first law of thermodynamics in equation forms for a finite change is given by:

$$\Delta U = Q + L$$

This equation tells something else of importance. We know that U is a state function and that ΔU is independent of path. However, L is not a state function so that L

depends on path. Yet the sum of L and W is path independent. The only way this can happen is if Q is also path dependent. We now see that we are dealing with two path-dependent quantities, Q and L.

For a differential change, we write the first law in differential form,

$$\Delta U = \delta Q + \delta L$$

The L or the δL includes all types of work, work done in expansion and contraction, electrical work, work done in creating new surface area, and so on. Much of the work that we deal with in thermodynamics will be work done in expansion and contraction of the system, or PV work. Recall that the expression for PV work is, $\delta L = -PdV$. If we want to include both PV work and other types of work we can write the first law as:

$$dU = \delta Q - PdV + \delta L_{other}$$

If the system is confined due to PV work then we have the simple expression for first law and U is function only of the natural variables *T,V: U=U(T,V)*. Then *dU*:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad 13.21$$

For a process at V=const, dV=0 and :

$$dU_V = \delta Q_V = C_V dT \Rightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad 13.22$$

We shall regard this equation as the formal thermodynamic definition of the heat capacity at constant volume. This new definition is more satisfactory than our previous temporary definition. This equation is a better definition of the heat capacity because it is usually more satisfactory to define thermodynamics quantities in terms of state functions, like U, T, V, P, and so on, rather than on things like Q and L, which depend on path. One other comment, we can integrate the last equation at constant volume, to get,

$$\Delta U_V = Q_V \qquad 13.23$$

In words, for any process at constant volume the heat, Q, is the same as the change in the internal energy, ΔU.

13.7.2 Changes in state, Internal energy

Since P, V, and T are relate by an equation of state, one is free to choose any two of them to be independent variables. (It shall be assumed, in the following discussion, that n is held fixed at one mole). In the case of internal energy, the most useful choice of independent variables is V and T. Consider the total differential for *U=U(V,T),* defined by 13.21.

The first partial derivative is the heat capacity at constant volume and the second shall henceforth be represented by the symbol π_T.

$$dU = C_V dT + \pi_T dV \qquad 13.24$$

Because there are no interactions between molecules of an ideal gas (i.e., the energy does not depend on distance of separation), the internal energy depends only on temperature, $U = f(T)$. Therefore, $\pi_T = 0$ for an ideal gas. Later, it will be shown that a general expression for π_T:

$$\pi_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad 13.25$$

Exercise: determine π_T for a gas that obeys the van der Waals equation:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \rightarrow \pi_T = \frac{a}{V_m^2}$$

This is the "negative pressure" associated with attractive intermolecular forces discussed previously.

In summary, it may be concluded that the first term in the expression for the total differential dU represents the change in potential energy associated with change the average distance between molecules, while the second term represents the change in kinetic energy associated with changing the average speed of the molecules.

Joule devised an experiment to measure π_T, but it failed because this quantity is quite small. For example, π_T for NH_3 at 300K is only 8.40 J/m^3mol, but C_V= 27.32J/Kmol. Therefore when ΔT=2K and ΔV=-100cm^3 the π_T term is -0.084 J/mol and the C_V term is 55J/mol in contribution to internal energy variation.

Now let find an expression for $\left(\frac{\partial U}{\partial T}\right)_P$ start with equation 13.24

$$dU = C_V dT + \pi_T dV$$

divide with dT while keep P constant

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \pi_T \left(\frac{\partial V}{\partial T}\right)_P$$

Recall the definition of isobaric coefficient of expansion   13.26

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ therefore,}$$

$$\left(\frac{\partial U}{\partial T}\right)_P = C_V + \pi_T \alpha V$$

Note: The first law of thermodynamics is a law of observation. No one has ever observed a situation where energy is not conserved so we elevate this observation to the status of a law. The real justification of this comes when the things we derive using the first law turn out to be true - that is, verified by experiment. (Actually there are situations were energy is not conserved. We now know that in processes where the nuclear structure of matter is altered mass can be converted into energy and vice versa. This is a consequence of special relativity were it is found that matter has a "rest energy," mc^2, where m is the mass to be converted to energy and c is the speed of light. As a consequence of nuclear energy we should say that,

Energy + the energy equivalent of mass is conserved.

then the first law would be written,

$$\Delta U = Q + L + \Delta mc^2$$

For physical and chemical processes the change in energy due to changes in mass is negligible - though not zero - so we can ignore it.)

13.7.3 Enthalpy

It turns out that V not is the most convenient variable to work with or to hold constant. It is much easier to control the pressure, P, on a system than it is to control the volume of the system, especially if the system is a solid or a liquid. What we need is a new function, with units of energy, which contains all the information contained in U

but which can be controlled by controlling the pressure. Such a function can be defined (created) by a Legendre transformation. There are particular criteria which must be met in making a Legendre transformation, but in our case here these criteria are met. (A full discussion of the mathematical properties of Legendre transformations is beyond the scope of this discussion. There are more details given in the Analytical Mechanique-Aron Francisc, an excellent book.) In our case we will define a new quantity, H, called the **enthalpy**, which has units of energy, as follows, (already introduced in Chapter 12):

$$dU = \delta Q - PdV \xrightarrow{d(PV) = PdV + VdP} dU = \delta Q - d(PV) + VdP \rightarrow$$

$$\rightarrow d(U + PV) = \delta Q + VdP \qquad\qquad 13.27$$

or $\qquad$ H=U+PV

We can show that H is a natural function of P (in the same sense that U is a natural function of V) as follows

$$dH = dU + PdV + VdP = dQ + VdP \qquad\qquad 13.28$$

One of the great utilities of the enthalpy is that it allows us to use a state function, H, to describe the heat involved in processes at constant pressure rather than the heat, Q, which is not a state function. To see this, let's go through the same process with dH that we did with dU above. Let's regard H as a function of T and P (for now). Then we can write,

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial T}\right)_T dP \qquad\qquad 13.29$$

Consider a process at constant pressure (dP = 0). From above Equations we conclude that:

$$dH_P = \delta Q_P = C_P dT \Rightarrow C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad\qquad 13.30$$

We shall regard the equation as the formal thermodynamic definition of the heat capacity at constant pressure. Again, this definition is much more satisfactory than our temporary definition,

$$C_P = \left(\frac{\delta Q}{dT}\right)_P$$

since it defines the heat capacity in terms of the state function, H, rather than in terms of Q which is not a state function

Just as we integrated the equation for energy at constant volume, we can integrate the equation for enthalpy, at constant pressure, to get

$$\Delta H_P = Q_P \qquad\qquad 13.31$$

In words, for any process at constant pressure the heat, Q, is the same as the change in enthalpy, ΔH. This equation contains no approximations. It is valid for **all** process at constant pressure. This equation is vastly more useful than its counterpart at constant volume because we carry out our all chemistry, biological and thermal processes at constant pressure much more often than we do at constant volume.

People sometimes ask, "What is the meaning of H?" Unfortunately, there is no simple, intuitive physical description of enthalpy like there is for the internal energy. (Recall that the internal energy is the sum of all kinetic and potential energies of all the particles in the system). The nearest thing we can come to as a description of H is the

one above where ΔH is the heat (gain or loss) in a constant pressure process. For this reason the enthalpy is occasionally referred to as the "heat content."

*Reminde*r: Nuclear energy was unknown to the original formulators of thermodynamics. We now know that matter can be converted into energy and vice versa. The "energy equivalent of matter" is given by the famous Einstein formula, $E = mc^2$, where m is the mass of the matter and c is the velocity of light. Since the velocity of light is very large, about 3×10^8 m/s, a small amount of mass is equivalent to a very large amount of energy. Strictly speaking, the statement, "energy is conserved," should be replaced by the statement, "energy plus the energy equivalent of mass is conserved."

That is, energy + mc^2 is conserved. The conversion of mass to energy or energy to mass in chemical reactions is so small that it is virtually never observed in chemical problems. So, for thermodynamics, the simpler statement that energy is conserved is sufficient.

13.8 Heat Capacities review

Now we are in position to exploit the results stated in the first law. First we focus attention to Heat capacities at constant volume and pressure. Using the two state function, energy and enthalpy, the heat capacities are:

$$C_V = \frac{\delta Q_V}{dT} = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \frac{\delta Q_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

13.32

The energy U being a point function its natural variable are *V* and *T* i.e *U=U(T,V)*; for enthalpy *T* and *P* i.e *H=H(T,P)*. Their total differentials (recap 13.21, 13.29)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \rightarrow dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \rightarrow dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

13.33

For the heat changes :

$$\delta Q = dU - \delta L = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$$

or

13.34

$$\delta Q = dH - VdP = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

Dividing the first relation of 13.34 with dT and taking P=const we obtain:

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

13.35

which is the relationship between the heat capacities. Often we use a state equation to simplify by calculating $\left(\frac{\partial V}{\partial T}\right)_P$. For a particular case, the ideal gas:

$$C_P - C_V = nR$$

13.36

This is well-known Robert Mayer relation for heat capacities. For an ideal gas the internal energy is function only of temperature (review Joule's experiment). The kinetic theory shown the internal energy for an ideal gas is:

$$U = n\frac{3}{2}RT$$

and therefore

$$c_V = \frac{3}{2}R \, , \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Mayer' expression becomes:

$$c_P - c_V = R$$

With ratio between heat capacities (adiabatic exponent): $\gamma = \dfrac{c_P}{c_V} = \dfrac{5}{3}$

Another route: beginning with H=U+PV and using mathematical tools, combined with 13.26

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + \left(\frac{\partial PV}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + \alpha PV$$

$$= \left(\frac{\partial U}{\partial V}\right)_T \alpha V + C_V + \alpha PV \qquad\qquad 13.37$$

Therefore

$$C_P - C_V = \alpha V\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] = \alpha V\left(\pi_T + P\right)$$

Once again recall with

$$C_P - C_V = \alpha VT\left(\frac{\partial P}{\partial T}\right)_V \xrightarrow{\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{K_T}} C_P - C_V = \frac{\alpha^2 VT}{K_T} \qquad 13.38$$

Relationship general true for any system.

Comments: The heat capacities at constant pressure, which are experimental measurable, are small for solids and increase with molecule complexity. We note gases and solids have similar heat capacities. The liquids, especially those with many atoms per molecule, have particularly high heat capacity values. We can see in the figure 13.1 a few examples. Table 1 emphasize that the heat capacities relate to microscopic energy level structures in a very direct way: the more low lying states there are, the

Figure 13.1- heat capacities in STP for gases, solids and liquids

higher the heat capacity. These results were first time predicted in the kinetic theory of the gases in the law of energy equipartition: each freedom degree has the energy ~kT.

	U_{tr}	U_{vib}	U_{rot}	U_{total}	C_V	C_P	C_P/C_V
Table-13. 1- The energies for each type of movement in a complex molecules and their molar heat
capacity							
Monoatomic	3/2RT	-	-	3/2RT	3/2R	5/2R	5/3
Diatomic	3/2RT	RT	RT	7/2RT	7/2R	9/2R	9/7
Polyatomic	3/2RT	xRT	3/2RT	(3+x)RT	(3+x)R	(4+x)R	(4+x)/(3+x)
* x= 3N-6 for non linear polyatomic molecules and x=3N-5 for linear polyatomic molecules, N-number of atoms in molecule; x denote the number of freedom degree							

The Classical heat capacities, while being based on reasonable models, overestimate the heat capacities because the quantum mechanical nature of vibrations and rotations is ignored. Linear motions of particles can always be described classically, i.e. the distance between energy states for the linear motion is essentially zero. In contrast, distance between energy levels of rotation and vibrations are noticeable, i.e. they will not be populated unless a molecule receives certain minimum amounts of rotational or vibration energy. This can be see from the next table. In this table the distance between rotational and vibrational energy levels are shown. To put these quantities in perspective they are compared to the temperatures at which the energy of the 1st excited level is equal to kT. According to equation the theory developed in statistical physics this corresponds to a temperature at which 1/e = 36.8% of the molecules are in the 1st excited state.

13.9 Enthalpy change

When working with enthalpy, it is customary to choose P and T as independent variables; $H = H(P,T)$. The total differential is then (recall 13.29)

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

It is evident the first term contains C_P, but what is the significance of the quantity $\left(\frac{\partial H}{\partial P}\right)_T$ in the second term? This can be transformed into something more useful by employing the Euler chain relation to the variables H, P, and T;

$$\left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_H\left(\frac{\partial P}{\partial H}\right)_T = -1 \rightarrow \left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_H = -C_P\left(\frac{\partial T}{\partial P}\right)_H$$

since $\mu = \left(\frac{\partial T}{\partial P}\right)_H$ is Joule-Thompson coefficient $\rightarrow$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\mu C_P, \text{(Isothermal Joule-Thompson coefficient)} \qquad 13.39$$

and

$$dH = C_P dT - \mu C_P dP$$

Exercise: Derive an expression for $\left(\frac{\partial H}{\partial T}\right)_V$ from the above equation 13.39.

Divide both sides by dT while keeping V constant;

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P - \mu C_P \left(\frac{\partial P}{\partial T}\right)_V$$

using the Euler chain relation for set (V,T,P); $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{k_T}$

and hence:

$$\left(\frac{\partial H}{\partial T}\right)_V = C_P \left(1 - \mu \frac{\alpha}{k_T}\right)$$

13.10 The Joule Expansion

Much of the early progress in thermodynamics was made in the study of the properties of gases. One of the early questions was whether gases cool on expansion. Joule designed an experiment to find out whether or not gases cool on expansion and if so how much.

The Joule apparatus consisted of two glass bulbs connected by a stopcock. One bulb was filled with gas at some P and T. The other bulb was vacuumed. The entire apparatus was insulated so that $Q = 0$. That is, the experiment would be adiabatic.

The stopcock was opened to allow the gas to expand into the adjoining bulb. Since the gas was expanding against zero pressure no work was done, $L = 0$. With both $Q = 0$ and $L = 0$ it is clear that, $\Delta U = Q + L = 0$. The process is at constant internal energy. Clearly, $\Delta V \neq 0$, because the gas fill both bulbs by expanding. The question was, did T change? ΔT was measured to be zero, no temperature change. (It turns out that the Joule experiment was sufficiently crude that it could not detect the difference between an ideal gas and a real gas so that the conclusions we will draw from this experiments only apply to an ideal gas.)

In effect, Joule was trying to measure the derivative: $\left(\frac{\partial T}{\partial V}\right)_U$ and the result was

that, this derivative is zero. This particular derivative is not very instructive, with U being held constant. We can use our version of Euler's chain relation to obtain information that is more instructive:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial V}\right)_T} = \frac{\left(\frac{\partial U}{\partial V}\right)_T}{C_V} = 0 \tag{13.40}$$

We know that C_V for gases is neither zero nor infinity, so we must conclude that, $\left(\frac{\partial U}{\partial V}\right)_T = 0$. This is an important and useful result. It says that the internal energy of an ideal gas is not a function of T and V, but of T only. That is, in equation form, for an ideal gas $U = U(T)$.

For real gases, and most approximations to real gases, like the van der Waals equation of state, $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$. However, this quantity is quite small, even for real gases.

We will have occasion to calculate it for the van der Waals equation of state later on. This result extends to the enthalpy of an ideal gas. $H = U + pV = U(T) + nRT = H(T)$. Thus, for an ideal gas both U and H are functions of T only.

Then all of the following derivatives are zero:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0; \left(\frac{\partial U}{\partial P}\right)_T = 0; \left(\frac{\partial H}{\partial V}\right)_T = 0; \left(\frac{\partial H}{\partial PV}\right)_T = 0 \qquad (13.41)$$

We will now use some of these results to discuss that adiabatic expansion of an ideal gas.

13.11 Adiabatic Expansion of an Ideal Gas

The definition of an adiabatic expansion, for now, is $\delta Q = 0$. That is, no heat goes in or out of the system. However, $\delta L \neq 0$. As the gas expands it does work on the surroundings. Since the gas is cut off from any heat bath it can not draw heat from any source to convert into work. The work must come from the internal energy of the gas so that the internal energy decreases. Since the internal energy of an ideal gas in only dependent on T that means that the temperature of the gas must decrease. From the first law with only PV work we have : $dU=-PdV$. Regarding U as a function of T and V. That is, $U = U(T,V)$, we get $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT$, because of the definition of C_V and because our gas is an ideal gas so that the second derivative vanishes.

Then $-PdV=C_V dT$ and using the equation of state:

$$-\frac{nRT}{V}dV = C_V dT \rightarrow -\frac{dT}{T} = \frac{nR}{C_V}\frac{dV}{V}$$

By the same token, using enthalpy, we find $dH=\delta Q+VdP=VdP$, and $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT$ for which we deduce that:

$$\frac{dT}{T} = \frac{nR}{C_P}\frac{dP}{P}$$

Comparing Equations we see that:

$$\frac{dP}{P} = -\frac{C_P}{C_V}\frac{dV}{V} \rightarrow PV^\gamma = ct$$

or

$$P_1 V_1^\gamma = P_2 V_2^\gamma \qquad\qquad 13.42$$

where we have written $C_p/C_V = \gamma$. The last equation describes the adiabatic expansion/compression of an ideal gas.

Adiabatic Work - Ideal Gas

We can use Equation 13.42 as the equation for an adiabatic path on a PV diagram and calculate the work in adiabatic condition. It is easy to check:

$$L = -\int_{V_1}^{V_2} PdV = -P_1 \int_{V_1}^{V_2} \left(\frac{V_1}{V}\right)^\gamma dV = -\frac{const}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right]$$

13.12 Nonadiabatic behaviour of the ideal gas

In case when a ideal gas exchange heat $\delta Q = CdT$ 1st law help us to find a general equation of transformation as follow:

$$\delta Q = dU + PdV \rightarrow CdT = C_V dT + PdV \rightarrow (C - C_V)dT = PdV$$

$$\delta Q = dH - VdP \rightarrow CdT = C_P dT - VdP \rightarrow (C - C_P)dT = -VdP$$

and by dividing of the two expressions: 13.43

$$-\frac{C - C_P}{C - C_V}\frac{dV}{V} = \frac{dP}{P} \rightarrow PV^\lambda = const; \text{ where } \frac{C - C_P}{C - C_V} = \lambda$$

λ- being the polytrope index. This kind of behaviour comprises all types of processes:

if :

$C = 0 \rightarrow \lambda = \gamma,$ adiabatic

$\lambda = 1 \Leftrightarrow C_P = C_V;\ PV^\lambda = const \rightarrow PV = const,$ isotherm

$C = C_P \Leftrightarrow \lambda = 0 \rightarrow$ isobar

$C = C_V \Leftrightarrow \lambda = \infty \rightarrow$ isochor

A good exercise is to draw a graph those processes in P-V coordinates and estimate the work.

13.13 Joule-Thompson expansion

It soon became apparent that the result of the Joule expansion experiment was not valid for real gases. A more accurate experiment, slightly different, was carried out by Joule and J.J.Thompson to further elucidate the properties on real gases under expansion. Joule and Thompson devised an ingenious experiment to measure, the Joule- Thompson coefficient, by performing an adiabatic expansion under the constraint of constant enthalpy. Because this process can be used to heat or cool a gas, it has a number of important applications (e.g., re-

Figure 13.2, Effect discovered in 1852 by William Thomson (lord Kelvin) and James Prescott Joule, well known as "Joule-Thomson" a) Original experiment, Manometer with throttle and thermometer b) Functional diagram c) Theoretical description

frigerators and air conditioners). The basic components of a Joule-Thompson expansion apparatus are sketched in figure 13.2
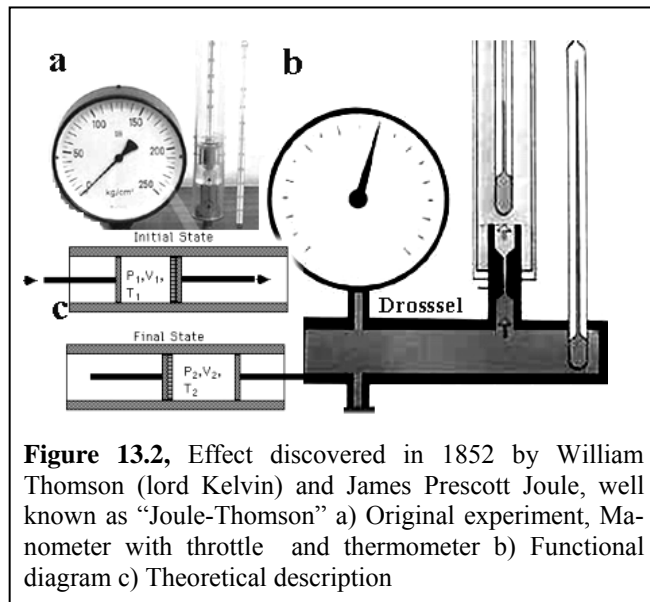
Air inside a flask of compressed air, under high pressure, flows through the fine opening in a throttle and expands in the process to the same pressure as the surrounding air. The throttle is isolated from heat exchange with its surroundings. The thermometers before and after the opening of the throttle show a large temperature difference. During expansion, the air has cooled. The amount of cooling increases in propor-

tion to the pressure difference at the throttle, and increases substantially when the starting temperature of the air is reduced. (Joule –Thomson)

Now referring to figure 13.2 C, an insulated cylinder containing two pistons is separated into two chambers by a throttle (partition with a small hole). A force is exerted on the downstream piston (left) forcing the gas to expand through the throttle from one constant pressure P_L to another P_R. The temperature is monitored on both sides of the throttle and, for a gas like nitrogen, it is found that the temperature is lower on the low-pressure side (right) than on the high-pressure side. In analyzing this process, it first should be noted that since the system is insulated, the process must be adiabatic (i.e., Q = 0). Let us take a look at what goes on in each chamber:

Left chamber: P_L = constant

$V_i = V_L$, $V_f = 0$, so $\Delta V = -V_L$ and work $L_L = P_L V_L$

Right chamber: P_R = constant

$V_i = 0$, $V_f = V_R$, so $\Delta V = V_R$ and work $L_R = -P_R V_R$ \qquad\qquad 13.44

Now, since Q = 0, $\Delta U = L_R + L_L = P_L V_L - P_R V_R$

Hence $(U_L + P_L V_L) - (U_R + P_R V_R) = 0$

or $\Delta H = 0 \iff H_L = H_R$

So the Joule -Thompson experiment is a process at constant enthalpy. In the experiment, they could select a value for ΔP, and then measure ΔT. The ratio of these two quantities approximates a derivative,

$$\frac{\Delta T}{\Delta P} \approx \left(\frac{\partial T}{\partial P}\right)_H = \mu$$

this is "coefficient of the Joule-Thompson effect". This coefficient is not zero for a real gas (or for realistic equations of state like the van der Waals equation of state), but we will now show that it *is* zero for an ideal gas. Applying the Euler chain rule we obtain:

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_P} = -\frac{\left(\frac{\partial H}{\partial P}\right)_T}{C_P}$$

Figure 13.3 Inversion temperatures (dashed line) and isenthalps for nitrogen. (From *Heat and Thermodynamics*, M. W. Zemansky and R.Dittman, McGraw-Hill, New York, 1981).

The numerator in equation is zero (see 13.41) for an ideal gas, but not necessarily zero for a real gas. The coefficient of the Joule-Thompson effect is important in the liquefaction of gases because it tells whether a gas cools or heats on expansion. It turns out that this coefficient is a decreasing function of temperature and it passes through zero at the Joule-Thompson inversion temperature, T_I. In an expansion $dP < 0$. Whether dT is positive or negative depends on the sign of μ. Looking at the definition of μ, we see that if μ is positive then dT is negative upon expansion so that the gas cools. On the other hand, if μ is negative, then dT is positive so that the gas warms upon expansion. Figure

13.3 are represented isoenthalps for nitrogen describing where μ is positive and negative. Here are few data for T_I measured for usual gases:

He	N₂	O₂	Ne
40 K	621 K	764 K	231 K

In order to liquefy a gas by a Joule-Thompson expansion the gas must first be cooled to below the J-T inversion temperature.

The inversion temperatures for nitrogen are shown by the dashed line in Fig. 13.3. The solid lines in this figure are **isenthalps** - lines of constant enthalpy.

Joule-Thompson expansion is the basic process that is used in household air conditioning systems and refrigerators. A schematic diagram of a typical refrigerator is shown in Fig. 13.4. A circulating gas (typically freon) is first compressed, then cooled below its inversion temperature (heat exchanger), and finally allowed to undergo Joule-Thompson expansion through a throttle. The expansion causes the gas to cool below its boiling temperature and liquefy. The liquid may then be used to cool a heat exchanger (such as the condenser in an air conditioning system).
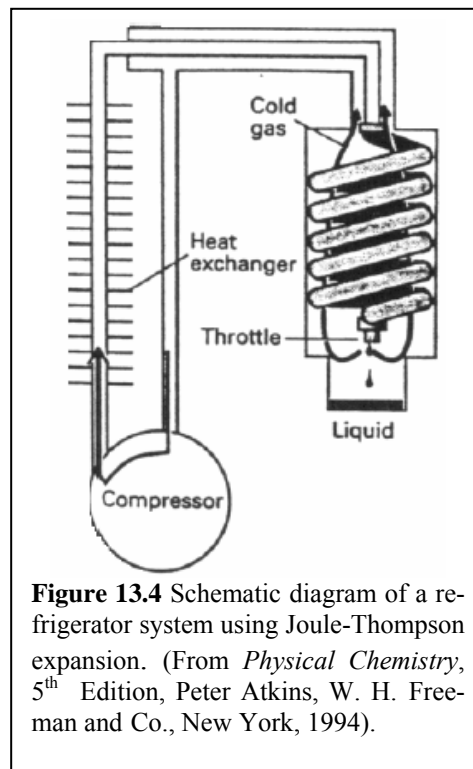
Figure 13.4 Schematic diagram of a refrigerator system using Joule-Thompson expansion. (From *Physical Chemistry*, 5th Edition, Peter Atkins, W. H. Freeman and Co., New York, 1994).

13.14 Heat Engines

13.14.1 Thermodynamic cycles and heat engines

This section is devoted to describing the basic fundamentals of how various heat engines work (e.g. a refrigerator, an IC-internal combustion engine, a jet).

We will also learn how to model these heat engines as thermodynamic cycles and how to apply the First Law of Thermodynamics to estimate thermal efficiency and work output as a function of pressures and temperatures at various points in the cycle. This is called **ideal cycle analysis**.

The estimates we obtain from the analysis represent the best achievable performance that may be obtained from a heat engine. In reality, the performance of these systems will be somewhat less than the estimates obtained from ideal cycle analysis.

We will deal with only "air-standard" thermodynamic cycles, where we ignore the changes in properties of the working fluid brought about by the addition of fuel or the presence of combustion products (we do of course account for the heat release that occurs due to the combustion of the fuel-air mixture).

In general this is a good assumption since in typical combustion applications the fuel accounts for only about 5% of the mass of the working fluid.

13.14.2 The Otto Cycle

The Otto cycle is an idealization of a set of processes used by spark ignition internal combustion engines (2-stroke or 4-stroke cycles). These engines a) ingest a mixture of fuel and air, b) compress it, c) cause it to react, thus effectively adding heat through converting chemical energy into thermal energy, d) expand the combustion products, and then e) eject the combustion products and replace them with a new charge of fuel and air. The various steps are illustrated on figure. A nice animation can be found in references. We model all of these happenings by a thermodynamic cycle consisting of a set of processes all acting on a fixed mass of air contained in a piston-cylinder arrangement.

The exhaust and intake processes are replaced by constant-volume cooling.
Fuel use ~ heat added ~ T_3 - T_2; efficiency ~ work out/fuel use.
Net work done by system = work of expansion + work of compression (-).
We analyze the cycle for a unit mass.

Both expansion and compression are adiabatic so: $\Delta L = (u_3 - u_4) - (u_2 - u_1)$. Assuming an ideal gas with constant c_v: $\Delta L = c_v[(T_3 - T_4) - (T_2 - T_1)]$. While the above expression is accurate, it is not very useful. We would like to put the expression in terms of the typical design parameters: the compression ratio ($r = V_1/V_2 = V_4/V_3$), and the heat added during combustion ($Q_{comb.} = c_v(T_3-T_2)$).

1'	2	3	4	1''
Ingest mixture of fuel and air	1'-2 Compress mixture quasi-statically and adiabatically	2-3 Ignite and burn mixture at constant volume (heat is added)	3-4 Expand mixture quasi-statically and adiabatically	4-1'' Cool mixture at constant volume
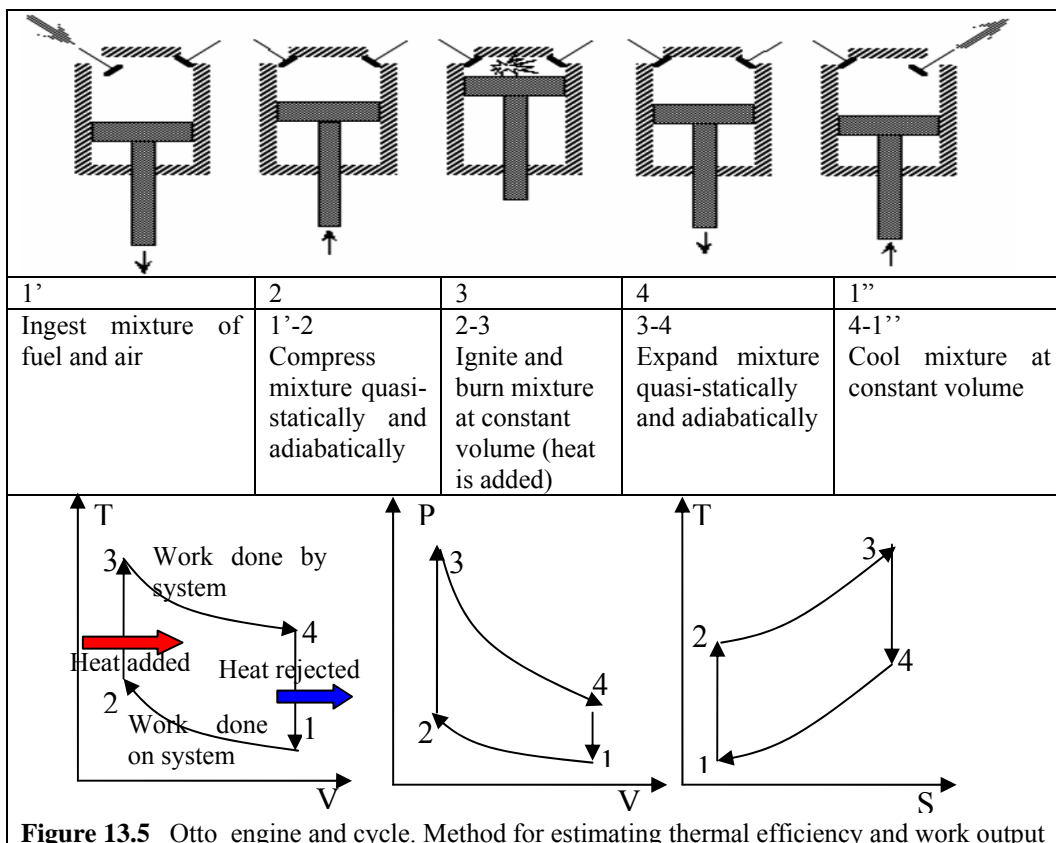
Figure 13.5 Otto engine and cycle. Method for estimating thermal efficiency and work output

For a quasi-static, adiabatic process: $\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{\gamma-1} = \dfrac{T_3}{T_4}$ so we can write the net

work as:

$$\Delta L = c_V T_1 \left(\frac{T_4}{T_1} - 1 \right) \left(r^{\gamma - 1} - 1 \right)$$

we also know that:

$$\frac{T_4}{T_1} - 1 = \frac{T_3}{T_2} - 1 = \frac{T_3 - T_2}{T_2} = \frac{T_3 - T_2}{T_1} \frac{1}{r^{\gamma - 1}}$$

and finally, the desired result in terms of typical design parameters:

$$\Delta L = L_{net} = Q_{comb} \frac{r^{\gamma - 1} - 1}{r^{\gamma - 1}}$$

The thermal efficiency of the cycle is :

$$\eta = \frac{\text{work net}}{\text{heat imput}} = \frac{L_{net}}{Q_{comb}} = 1 - \frac{1}{r^{\gamma - 1}} = 1 - \frac{T_1}{T_2}$$

showing that the efficiency of an Otto cycle depends only on the temperature ratio of the compression process.

Otto Cycle Efficiency
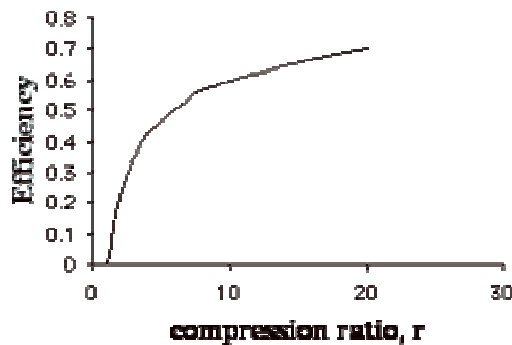
13.14.3 Brayton Cycle

The Brayton cycle is an idealization of a set of thermodynamic processes used in gas turbine engines, whether for jet propulsion or for generation of electrical power.

Nice illustrations and some of gas turbine engines are finding on NASA pages.

The thermodynamic cycle:

The cycle consists of four processes: a) quasi-static adiabatic compression in the inlet and compressor, b) constant pressure heat addition in the combustor, c) quasi-static adiabatic expansion in the turbine and exhaust nozzle, and finally d) constant pressure cooling to get the working fluid back to the initial condition.

Estimating the performance of the engine. Our objective with the Brayton cycle is the same as for the Otto cycle. First to derive expressions for the net work and the thermal efficiency of the cycle, and then to manipulate these expressions to put them in terms of typical design parameters so that they will be more useful.
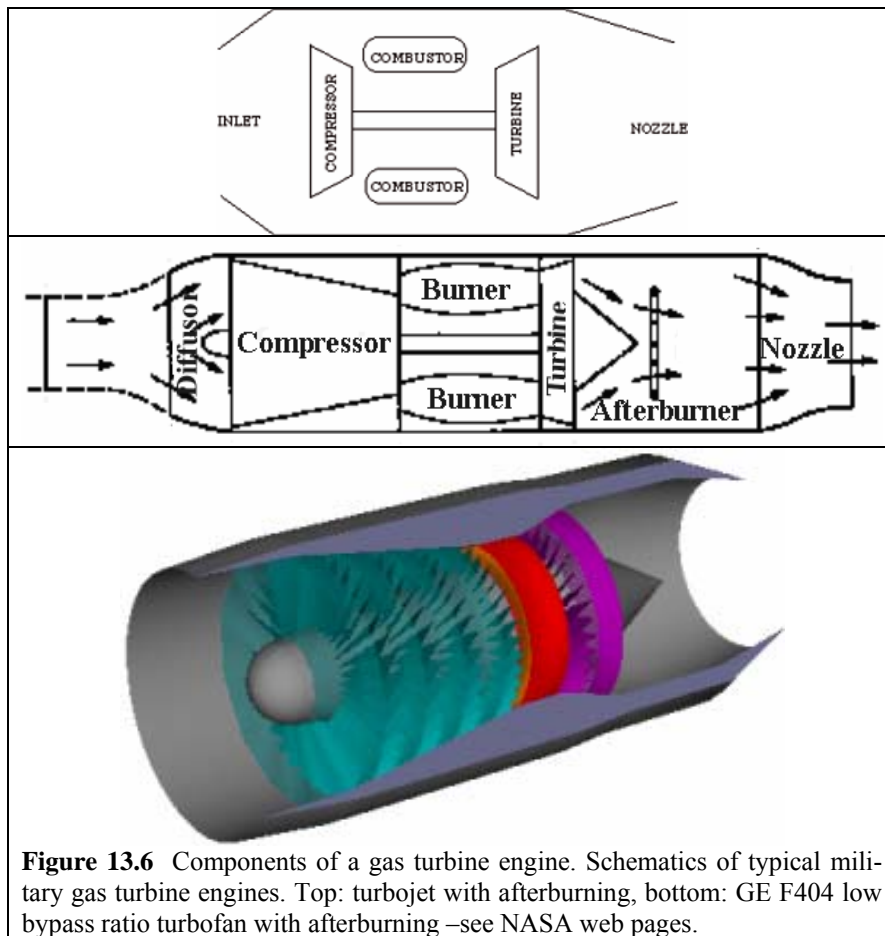
Figure 13.6 Components of a gas turbine engine. Schematics of typical military gas turbine engines. Top: turbojet with afterburning, bottom: GE F404 low bypass ratio turbofan with afterburning –see NASA web pages.
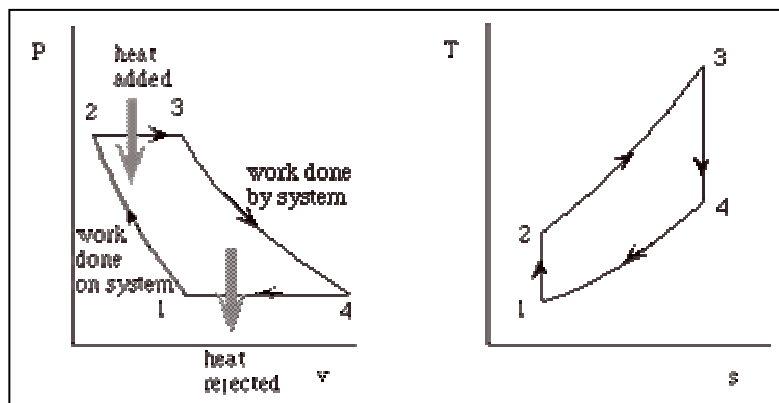
Figure 13.7- Brayton Cycle
1 - 2 Adiabatic, quasi-static compression in inlet and compressor
2 - 3 Combust fuel at constant pressure (*i.e.* add heat)
3 - 4 Adiabatic, quasi-static expansion in turbine
    a. take work out and use it to drive the compressor
    b. take remaining work out and use it to accelerate fluid for jet propulsion, or to turn a generator for electrical power generation.
4 - 1 Cool the air at constant pressure

From the First Law we can show that for any cyclic process heat and work transfers are numerically equal:

$$\Delta U = Q - L = 0 \Rightarrow Q = L \quad \text{or} \quad \oint \delta Q = \oint \delta L$$

This fact is often useful for solving thermodynamic cycles. For instance in this example, we would like to find the net work of the cycle and we could calculate this by taking the difference of the work done all the way around the cycle. Or, since $\Delta Q = \Delta L$, we could just as well consider the difference between the heat added to the cycle in process 2-3, and the heat rejected by the cycle in process 4-1.

Heat added between 2-3 (combustor):

First Law in terms of enthalpy for an ideal gas undergoing a quasi-static process:

$$\delta Q = dH - VdP = c_p dT \quad \text{at P=const}$$

$$Q_{added} = c_P \left(T_3 - T_2 \right)$$

Heat rejected between 4-1: similarly

$$Q_{rejected} = c_P \left(T_4 - T_1 \right)$$

Work done and thermal efficiency:

$$L = Q_{added} - Q_{rejected} = c_P \left[\left(T_3 - T_2 \right) - \left(T_4 - T_1 \right) \right]$$

And efficiency:

$$\eta_{Brayton} = \frac{Q_{added} - Q_{rejected}}{Q_{added}} = \frac{(T_3 - T_2) - (T_4 - T_1)}{T_3 - T_2}$$

Again, while these expressions are accurate, they are not all that useful. We need to manipulate them to put them in terms of typical design parameters for gas turbine engines. For gas turbine engines, the most useful design parameters to use for these equations are often the inlet temperature T_1, the compressor pressure ratio (P_2/P_1), and the maximum cycle temperature, the turbine inlet temperature T_3.

Rewriting equations in terms of design parameters:

$$L = c_P T_1 \left(\frac{T_3}{T_1} - \frac{T_2}{T_1} - \frac{T_4}{T_1} + 1 \right)$$

$$\frac{P_2}{P_1} = \frac{P_3}{P_4} = \left(\frac{T_2}{T_1} \right)^{\frac{\gamma}{\gamma-1}} = \left(\frac{T_3}{T_4} \right)^{\frac{\gamma}{\gamma-1}} \Rightarrow \frac{T_2}{T_1} = \frac{T_3}{T_4}$$

So

$$L = c_P T_1 \left[\frac{T_3}{T_1} - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - \frac{T_3}{T_2} + 1 \right] = c_P T_1 \left[\frac{T_3}{T_1} - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - \frac{T_3}{T_1} \left(\frac{P_2}{P_1} \right)^{-\frac{\gamma-1}{\gamma}} + 1 \right]$$

and for the efficiency

$$\eta = 1 - \frac{T_1}{T_2} \frac{\dfrac{T_4}{T_1} - 1}{\dfrac{T_3}{T_2} - 1} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{\left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}}$$

Performance plots

Brayton Cycle Work
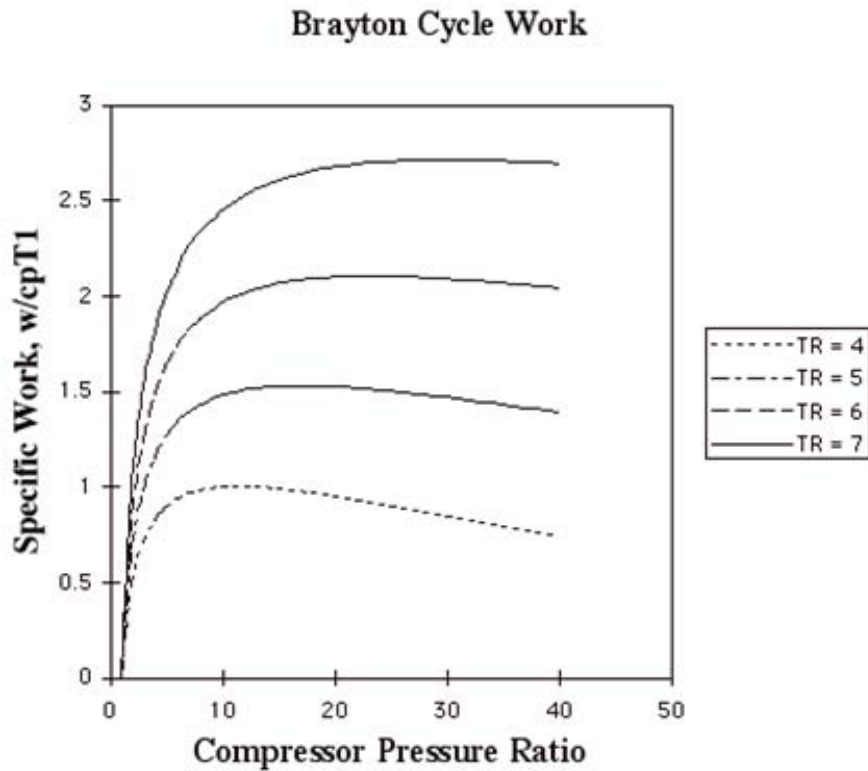
In the plot above, TR = T_3/T_1. Note that for a given turbine inlet temperature, T3, (which is set by material limits) there is a compressor pressure ratio that maximizes the work.

Brayton Cycle Efficiency
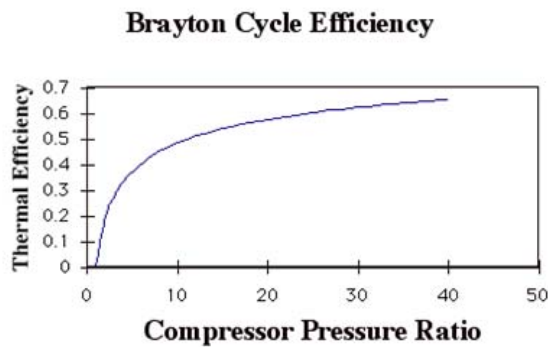
For more details: http://www.rolls-royce.com/education/default.jsp (click the link at lower left "Take a journey through a jet engine") and at http://www.pratt-whitney.com/how.htm; http://www.grc.nasa.gov/WWW/K-12/airplane/ngnsim.html

13.14.4 Generalized Representation of Thermodynamic Cycles
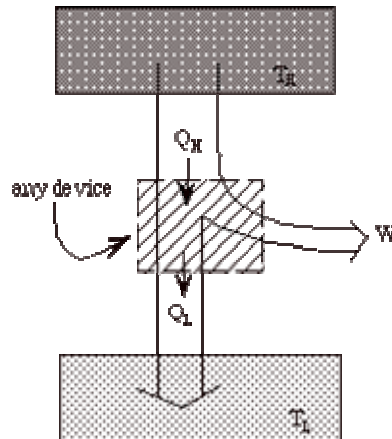
Note that heat engines can be represented generally as: a transfer of heat from a high temperature reservoir to a device + a rejection of heat from a device to a low temperature reservoir + net work done on surroundings. That is Carnot engines

13.14.5 Refrigeration Cycles

Refrigeration cycles take in work from the surroundings and transfer heat from a low temperature reservoir to a high temperature reservoir. Schematically, they look like the diagram given as in generalized thermal machine above sketched, but with the direction of the arrows reversed. They can also be recognized on thermodynamic diagrams as closed loops with a counter-clockwise direction of travel. A more detailed physical description is given below.
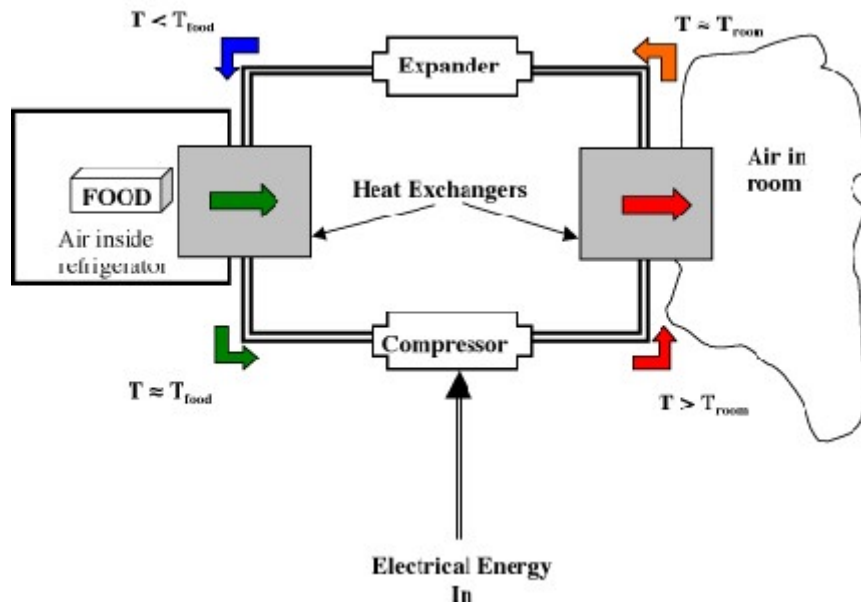
The objective of a refrigerator is to lower the internal energy of a body at low temperature (the food) and transfer that energy to the higher temperature surroundings (the room the refrigerator is in). It requires work (typically in the form of electrical energy) to do this. The medium for the energy exchange is a working fluid (a refrigerant) that circulates in a loop through a series of devices. These devices act to add and remove energy from the working fluid. Typically the working fluid in the loop is considered the thermodynamic system. Sometimes the fluid used alternates between gas-phase and liquid-phase, but this detail is not important for understanding the basic process.

A simplified schematic is shown above. As the refrigerant circulates around the loop, its internal energy (and temperature) is alternately raised and lowered by a series of devices. In this manner, the working fluid so that it is colder than the refrigerator air at one point and hotter than the air in the room at another point. Thus heat will flow in the appropriate direction as shown by the two arrows in the heat exchangers. Starting in the upper right hand corner of the diagram, first the internal energy is lowered either by passing through a small turbine or through an expansion valve. In these devices, work is done by the refrigerant so its internal energy is lowered. The internal energy is lowered to a point where the temperature of the refrigerant is lower than that of the air in the refrigerator. A heat exchanger is used to transfer energy from the air (and food) in the refrigerator to the cold refrigerant (energy transferred by virtue of a temperature difference only = heat). This lowers the internal energy of the air/food and raises the internal energy of the refrigerant. Then a pump or compressor is used to do work on the refrigerant adding additional energy to it and thus further raising its internal energy. Electrical energy is used to drive the pump or compressor. The internal energy of the refrigerant is raised to a point where its temperature is hotter than the temperature of the room. The refrigerant is then passed through a heat exchanger (the coils at the back of the refrigerator) so that energy is transferred from the refrigerant to the surroundings. As a result, the internal energy of the refrigerant is reduced and the internal energy of the surroundings is increased. It is at this point where the internal energy of the food and the energy used to drive the compressor or pump are transferred to the surroundings. The refrigerant then continues on to the turbine, repeating the cycle.

13.15 Steady Flow Energy Equation

13.15.1 First Law for a Control Volume

Frequently (especially for flow processes) it is most useful to express the First Law as a statement about <u>rates</u> of heat and work, for a control volume.

Conservation of mass

$$\frac{dm}{dt} = \dot{m} = \dot{m}_{in} - \dot{m}_{out} \Leftrightarrow \left\{ \begin{matrix} \text{rate of change} \\ \text{of mass in c.v} \end{matrix} \right\} = \left\{ \text{mass flow in} \right\} - \left\{ \text{mass flow out} \right\}$$

For steady state : $\dfrac{dm}{dt} = 0$ and therefore $\dot{m}_{in} = \dot{m}_{out} = \dot{m}$
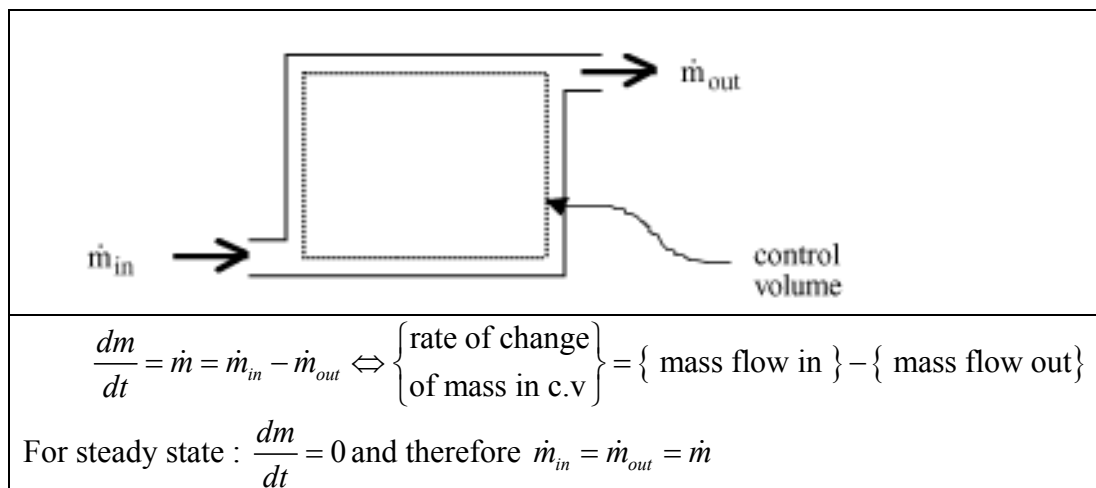
Conservation of Energy

Recall first law we can apply same considerations for the control volume:

$$\frac{dU}{dt} = \dot{Q}_{cv} - \dot{L}_{cv} + \dot{m}_{in}h_{in} - \dot{m}_{out}h_{out} \Leftrightarrow$$

$$\begin{Bmatrix} \text{rate of change} \\ \text{of energy in c.v} \end{Bmatrix} = \begin{Bmatrix} \text{rate of heat} \\ \text{added in c.v} \end{Bmatrix} - \begin{Bmatrix} \text{rate of work} \\ \text{done} \end{Bmatrix} + \begin{Bmatrix} \text{rate of energy} \\ \text{flow in c.v} \end{Bmatrix} - \begin{Bmatrix} \text{rate of energy} \\ \text{flow out c.v} \end{Bmatrix}$$

where:

$$\dot{Q} = \lim_{dt \to 0} \frac{\delta Q}{dt}, \text{ rate of energy transfer o te system as heat}$$

$$\dot{L} = \lim_{dt \to 0} \frac{\delta L}{dt}, \text{ rate of work done by system}$$

For steady-state (work and heat area algebraically counted)

$$\dot{Q} - \dot{L} = \dot{m}(h_{out} - h_{in})$$

h- being specific enthalpy (enthalpy per unit mass). All units are in J/s.
or if we take in account IE- internal energy (U), KE-kinetic energy, PE-potential energy, CE-chemical energy: all here

$$\dot{Q} - \dot{L} = \dot{m}\left[\left(IE + KE + PE + CE\right)_{out} - \left(IE + KE + PE + CE\right)_{in}\right]$$

Neglecting potential and chemical energy (PE and CE):

$$\dot{Q} - \dot{L} = \dot{m}\left[\left(u + \frac{c^2}{2}\right)_{out} - \left(u + \frac{c^2}{2}\right)_{in}\right]$$

Where c is the speed of the fluid, and $c^2/2$ is the kinetic energy of the fluid per unit mass relative to some coordinate system. If we divide through by the mass flow and set the inlet of the control volume as 1, and the outlet as 2, then

$$q_{1-2} - w_{1-2} = u_2 - u_1 + \frac{c_2^2}{2} - \frac{c_1^2}{2}$$

where q and w are respectively, Q and L per unit mass. In case when the flow wok is considered then:

$$q_{1-2} - w_{1-2} = \left(u_2 + P_2 v_2\right) - \left(u_1 + P_1 v_1\right) + \frac{c_2^2}{2} - \frac{c_1^2}{2} = h_2 - h_1 + \frac{c_2^2}{2} - \frac{c_1^2}{2}$$

being more convenient to divide the work into two terms: 1) the flow work done by the system which is $P_2 v_2 - P_1 v_1$, and 2) any additional work which we will term external work or shaft work; v- specific volume, h- specific enthalpy.

For an ideal gas $dh = c_p dT$ and :

$$q_{1-2} - w_{1-2} = \left(c_P T_2 + \frac{c_2^2}{2}\right) - \left(c_P T_1 + \frac{c_1^2}{2}\right)$$

Flow work and external work

Enthalpy is most useful for separating flow work from external work (as might be produced by a shaft crossing the control volume boundary for instance). In the figure shown below. Heat is added, a compressor is doing work on the system, the flow entering the system does work on the system (work = $-P_1 V_1$), and work is done by the system through pushing out the flow (work = $+P_2 V_2$). The first law relates the change in energy between states 1 and 2 to the difference between the heat added and the work done by the system.
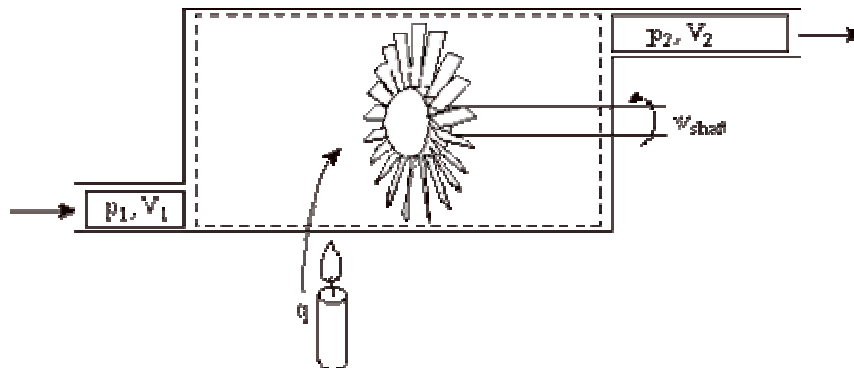
Frequently, however, we are interested only in the work that crosses the system boundary, not the volumetric or flow work. In this case it is most convenient to work with enthalpy.

This also leads to a direct physical interpretation for enthalpy. In an open flow system, enthalpy is the amount of energy that is transferred across a system boundary by a moving flow. This energy is composed of two parts: the internal energy of the fluid (u) and the flow work (PV) associated with pushing the mass of fluid across the system boundary.

Note that both of the following cases are also frequently encountered. Heat addition, with no external work only flow work:
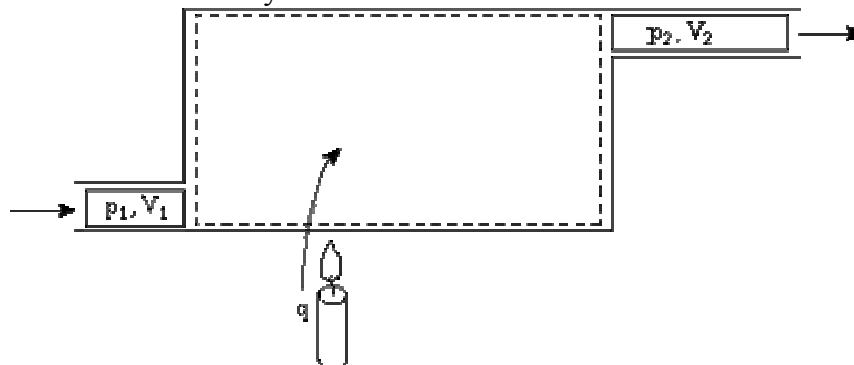
No heat addition, with external work and flow work:
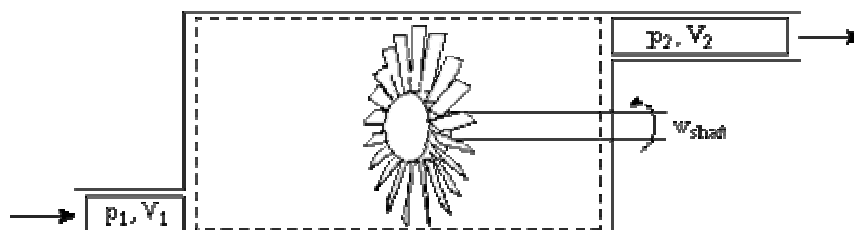
Stagnation Temperature and Stagnation Enthalpy

Suppose that our steady flow control volume is a set of streamlines describing the flow up to the nose of a blunt object.
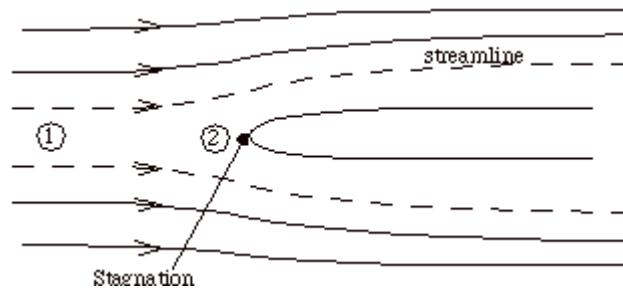
The streamlines are stationary in space, so there is no external work done on the fluid as it flows. If there is also no heat transferred to the flow (adiabatic), then the steady flow energy equation becomes:

$$c_P T_1 + \frac{c_1^2}{2} = c_P T_2 + \frac{c_2^2}{2}$$

The quantity that is conserved is called the stagnation temperature:

$$T_T = T + \frac{c^2}{2c_P} \text{ , or } \frac{T_T}{T} = 1 + \frac{\gamma - 1}{2} M^2, \text{ with sound speed } c_s = \sqrt{\gamma RT}$$

The stagnation temperature is the temperature that the fluid would reach if it were brought to zero speed by a steady, adiabatic process with no external work. Note that for any steady, adiabatic flow with no external work, the stagnation temperature is constant. (The Mach number, M, is the ratio of the flow speed, c, to the speed of sound, c_s. we will learn more about these quantities in fluids, but it is interesting to see that M^2 measures the ratio of the kinetic energy of the gas to its thermal energy.)

It is also convenient to define the **stagnation enthalpy, h_T:**

$$h_T = c_P T + \frac{c^2}{2}$$

So we can write the Steady Flow Energy Equation in a convenient form as:

$$q_{1-2} - w_{s,1-2} = h_{T2} - h_{T1}$$

Note that for a quasi-static adiabatic process

Using the adiabatic process:

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2} \right)^{\frac{\gamma - 1}{\gamma}} \rightarrow \frac{T_T}{T} = \left(\frac{P_T}{P} \right)^{\frac{\gamma - 1}{\gamma}}$$

so we can write and define the relationship between stagnation pressure and static pressure as :

$$\frac{P_T}{P} = \left(1 + \frac{\gamma - 1}{2} M^2 \right)^{\frac{\gamma - 1}{\gamma}}$$

where, the stagnation pressure is the pressure that the fluid would reach if it were brought to zero speed, via a steady, adiabatic, quasi-static process with no external work.

Frame dependence of stagnation quantities

An area of common confusion is the frame dependence of stagnation quantities.

The stagnation temperature and stagnation pressure are the conditions the fluid would reach if it were brought to zero speed relative to some reference frame, via a steady, adiabatic process with no external work (add quasi-static for stagnation pres-

sure). What if the body or reference frame is moving? We know from looking at re-entry vehicles, that the skin temperature is much hotter than the atmospheric temperature. If the atmosphere is assumed still, and we stagnate a fluid particle on the nose of a high speed vehicle (carrying it along with the vehicle and thus essentially giving it kinetic energy) its stagnation temperature is given by

$$T_T = T + \frac{c^2}{2c_P}$$

where c is the vehicle speed. The temperature the skin reaches (to first approximation) is the stagnation temperature. The atmospheric temperature, T, is not frame dependent. The confusion comes about because T is usually referred to as the static temperature and in common language this has a similar meaning as "stagnation". In fluid mechanics and thermodynamics static is commonly used to label the thermodynamic properties of the gas P, T, etc.–these are not frame dependent. Stagnation quantities are those the flow would arrive at if brought to zero speed relative to some reference frame, via a steady, adiabatic process with no external work (add quasi-static for stagnation pressure). Stagnation quantities depend on the frame of reference. Thus for a re-entry vehicle, the stagnation temperature (vehicle frame) is hotter than the atmospheric (static) temperature. And in a still atmosphere, the static temperature is the same as the stagnation temperature (atmospheric frame).

Example:

For the case shown below, a jet engine is sitting motionless on the ground prior to take-off. Air is entrained into the engine by the compressor. The inlet can be assumed to be frictionless and adiabatic.
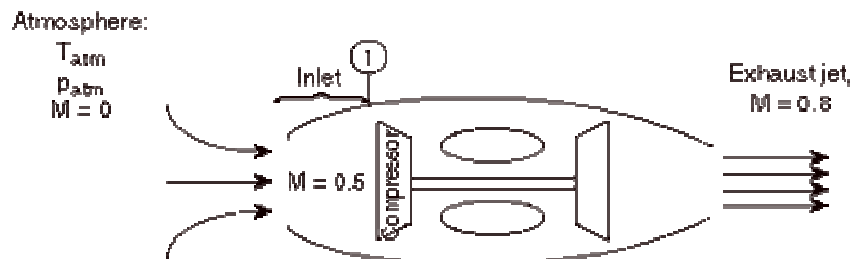
Considering the state of the gas within the inlet, prior to passage into the compressor, as state (1), and working in the reference frame of the motionless airplane:

a) Is T_{T1} greater than, less than, or equal to T_{atm}?

The stagnation temperature of the atmosphere, T_{Tatm}, is equal to T_{atm} since it is moving the same speed as the reference frame (the motionless airplane). The steady flow energy equation tells us that if there is no heat or shaft work (the case for our adiabatic inlet) the stagnation enthalpy (and thus stagnation temperature for constant c_P) remains unchanged. Thus $T_{T1} = T_{Tatm} = T_{atm}$

b) Is T_1 greater than, less than, or equal to T_{atm}?

If $T_{T1} = T_{atm}$ then $T_1 < T_{atm}$ since the flow is moving at station 1 and therefore some of the total energy is composed of kinetic energy (at the expense of internal energy, thus lowering T_1)

c) Is P_{T1} greater than, less than, or equal to P_{atm}?

Equal, by the same argument as a).

d) Is P_1 greater than, less than, or equal to Patm?

Less than, by the same argument as b).

Example: Applications of the Steady Flow Energy Equation

Flow through a rocket nozzle

A liquid bi-propellant rocket consists of a thrust chamber and nozzle and some means for forcing the liquid propellants into the chamber were they react, converting chemical energy to thermal energy.
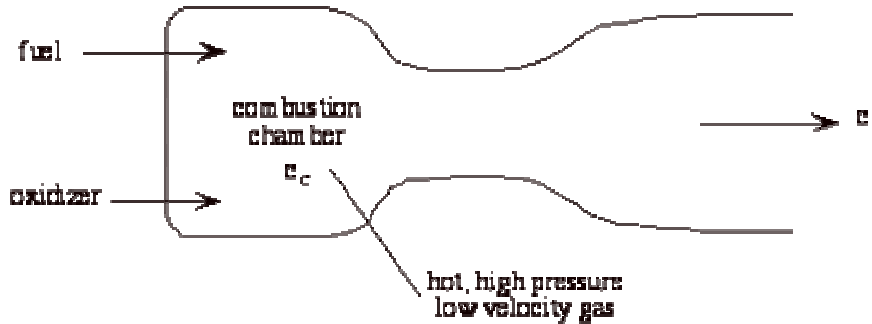
Once the rocket is operating we can assume that all of the flow processes are steady, so it is appropriate to use the steady flow energy equation. Also, for now we will assume that the gas behaves as an ideal gas, though in general this is a poor approximation. There is no external work, and we assume that the flow is adiabatic. Then we can write the First Law as:

$$q_{1-2} - w_{s,1-2} = h_{T2} - h_{T1} \xrightarrow{h_{T2}=h_{T1}} c_P T_c + \frac{c_c^2}{2} = c_P T_e + \frac{c_e^2}{2} \rightarrow c_e = \sqrt{c_P \left(T_c - T_e\right)}$$

If we assume quasi-static, adiabatic expansion then:

$$c_e = \sqrt{2c_P T_e \left(1 - \left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right)}$$

where T_c and P_c are conditions in the combustion chamber (set by propellants), and P_e is the external static pressure.

Power to drive a gas turbine compressor

Consider for example the PW4084 pictured below. The engine is designed to produce about 84,000 lbs (how much in SI?) of thrust at takeoff.
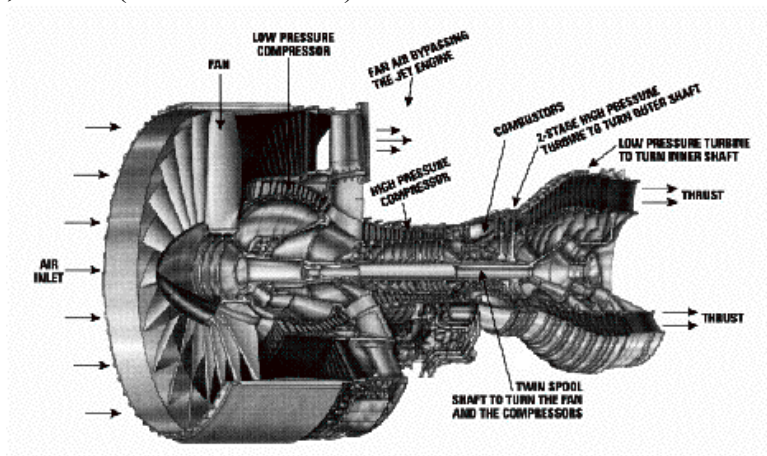
(one nice Pratt and Whitney engine)

The engine is a two-spool design. The fan and low pressure compressor are driven by the low pressure turbine. The high pressure compressor is driven by the high pressure turbine.

πf = *total pressure ratio across the fan = 1.4*

πc = *total pressure ratio across the fan + compressor = 45*

$\dot{m}_f = 650 Kg/s$; $\dot{m}_{core} = 120 Kg/s$

Tinlet = 300K

Heat transfer from the gas streams is negligible so we write the First Law (steady flow energy equation) as:

$$\dot{Q} - \dot{L} = \dot{m}(h_{T2} - h_{T1})$$

For this problem we must consider two streams, the fan stream and the core stream, so

$$-\dot{L}_s = \dot{m}_f \Delta h_{Tf} + \dot{m}_c \Delta h_{Tc} = \dot{m}_f c_P \Delta T_{Tf} + \dot{m}_c c_P \Delta T_{Tc}$$

We obtain the temperature change by assuming that the compression process is quasi-static and adiabatic. So

$$\left.\left(\frac{T_{T2}}{T_{T1}}\right)\right|_{fan} = \left(\pi_f\right)^{\frac{\gamma-1}{\gamma}} = 1.1 \rightarrow \Delta T_{Tfan} = 30K \left.\begin{array}{c} \\ \\ \end{array}\right\}$$

$$\left.\left(\frac{T_{T2}}{T_{T1}}\right)\right|_{core} = \left(\pi_{core}\right)^{\frac{\gamma-1}{\gamma}} = 3.0 \rightarrow \Delta T_{Tcore} = 600K \left.\begin{array}{c} \\ \\ \end{array}\right\} \rightarrow$$

$$\rightarrow -\dot{L}_s = 610\frac{kg}{s}30K1008\frac{J}{KgK} + 120\frac{kg}{s}600K1008\frac{J}{KgK} = 91\times10^6 J/s$$

Negative sign implies work done on fluid. Note if 1Hp=745 Watts and one car has 110Hp then our turbo engine is equivalent to 1110 automobiles.

13.16 Speed of sound

$Cs = sqrt (\gamma\ R\ T)$

Bell
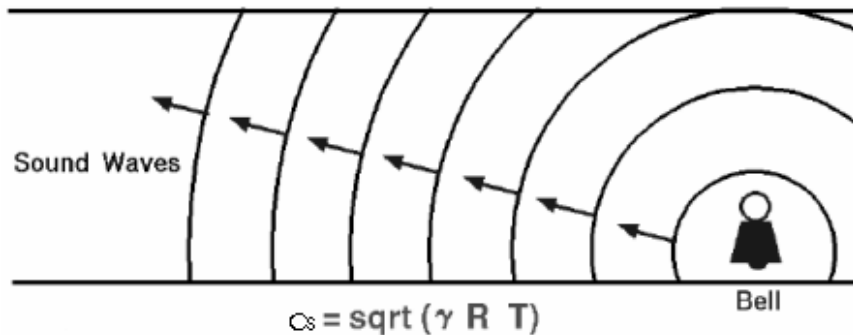
Air is a gas, and a very important property of any gas is the **speed of sound** through the gas. Why are we interested in the speed of sound? The **speed of "sound"** is actually the speed of transmission of a small disturbance through a medium. (**Sound** itself is a sensation created in the human brain in response to sensory inputs from the inner ear. We won't comment on the old "tree falling in a forest" discussion!). **The transmission of a small disturbance through a gas is an isentropic process**. The conditions in the gas are the same before and after the disturbance passes through. *The speed of sound depends on the state of the gas*; more specifically, the square root of the

temperature of the gas. The speed of sound (c_s) is equal to the square root of the ratio of specific heats (γ) times the gas constant (R) times the absolute temperature (T).

$$c_s = \sqrt{\gamma RT}$$

Notice that the temperature must be specified on an absolute scale (Kelvin or Rankine). The speed of sound depends on the temperature and temperature changes with altitude in a very complex way.

The derivation of this equation

The speed of sound is that speed which a small amplitude perturbation travels trough a medium (small perturbation is weak if the local variation of the pressure in fluid is negligible in rapport with total pressure). Consider a tube containing a compressible fluid and the small perturbation is induced by a piston displaced on a short distance with speed dw. The gas being compressible will not move at all.
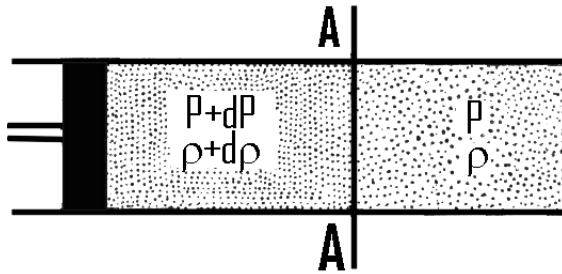
The first "layer" of gas in contact with piston will take the momentum. The momentum transfer is fast and the gas compression can be considered adiabatic. The pressure increases in value up to *P+dP* and the density $\rho+d\rho$. The neighborhood layer separated by section AA (figure) is at rest with *P* and ρ at equilibrium values. For a time dt the section AA which divide the two regions, perturbed and respectively unperturbed, moves for a distance $c_s\, dt$ and the elemental mass displaced is:

$$dM_{unp} = \rho\, s\, adt, \ s - area\ of\ AA$$

The mass of perturbed gas will fill the space leaved by AA:

$$dM_p = (\rho + d\rho)\, s\, (c_s\text{-dw})$$

and of the continuity condition: $dM_p = dM_{unp}$:

$$\rho a = (\rho + d\rho)(c_s - dw)$$

The section AA moves under the force action:

$$dP\, sdt = dM_{unp}dw = \rho s\, c_s dt\ dw$$

or

$$dP = \rho c_s dw$$

Combining the equations we get:

$$dP = c_s^2 d\rho$$

equation which defines the relationship between the speed of sound and the gas parameters:

$$c_S = \sqrt{\left(\frac{\partial P}{\partial \rho}\right)_S}$$ e.g the speed of sound in a fluid.

Taking in account the compressibility modulus:

$$c_S = \sqrt{\frac{K_s}{\rho}}$$ with K_s- the isentropic compressibility modulus

or:

$$c_S = \sqrt{\frac{KP}{\rho}} \quad k = -\left(\frac{\partial \ln P}{\partial \ln v}\right)_S , \quad v = \frac{1}{\rho}, \text{ specific volume}$$

13.16.1 Flow in convergent tube

This is a subject important involved in phenomena such as: plasma technology, aerodynamics, rocket propulsion, gas transport, etc

For study, it is considered a fluid with parameters P_1, v_1(specific volume), T_1 in a reservoir and P_2, pressure at outlet trough an opened orifice. The gas speed is w. Note with w_1, speed at entrance in tube and with w_2, at outlet. Using the first law of thermodynamics for fluids in motion and considering the process adiabatic:

$$0 = (h_2 - h_1) + \frac{c_2^2}{2} - \frac{c_1^2}{2} \rightarrow c_2 = \sqrt{c_1^2 - 2(h_2 - h_1)}$$

where h- specific enthalpy.

$$dq = dh - vdP \rightarrow dh = vdP$$
$$h_2 - h_1 = v(P_2 - P_1), \text{ for incompressible fluids}$$
$$c_2 = \sqrt{c_1 + 2v(P_1 - P_2)}$$
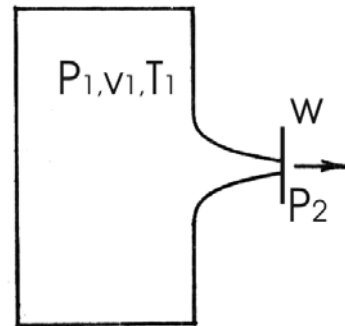
considered *here v≠f(P)*

For an perfect gas the adiabatic flow

$$P_1 v_1^\gamma = P v^\gamma \rightarrow v = \frac{P_1^{\frac{1}{\gamma}}}{P^{\frac{1}{\gamma}}} v_1 \Rightarrow h_2 - h_1 = \int_{P_1}^{P_2} vdP = P_1^{\frac{1}{\gamma}} v_1 \int_{P_1}^{P_2} \frac{dP}{P^{\frac{1}{\gamma}}} =$$

$$= -\frac{\gamma}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right] P_1 v_1$$

and

$$c_2 = \sqrt{2\frac{\gamma}{\gamma - 1} P_1 v_1 \left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right] + c_1^2}$$

If $c_1 = 0$ the equation takes a simple form. The speed at outlet is dependent only by pressures rapport

To find the flow gas through tube remembers some definitions:

mass flow : $\dot{M} = \rho \dot{V}$ and volume flow: $\dot{V} = Sc$

$$\dot{M} = \frac{Sc}{v_2} \quad v_2 - \text{ specific volume}$$

and

$$\frac{1}{v_2} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}} \frac{1}{v_1}$$

results

$$\dot{M} = \frac{Sc}{v_1}\left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}, \text{ mass flow for a fluid in adiabatic conditions}$$

In final, we have:

$$\dot{M} = S\sqrt{2\frac{\gamma}{\gamma-1}\frac{P_1}{v_1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{2}{\gamma}} - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma+1}{\gamma}}\right]}$$

equation which describes the mass flow of perfect gas in adiabatic reversible conditions. If we note with *ψ=P₂/P₁*, the rapport of the final and initial pressures and plot the mass flow. The mass flow is null then ψ=0 or 1, and have a maximum for

$$\psi_{cr} = \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}}; \quad \dot{M}_{max} = S\sqrt{2\frac{\gamma}{\gamma+1}\frac{P_1}{v_1}\left(\frac{2}{\gamma+1}\right)^{\frac{2}{\gamma-1}}}$$

and maximum speed

$$w_{2\,max} = \sqrt{2\frac{\gamma}{\gamma+1}P_1v_1}$$

Now recall the speed of sound and replacing the pressure at critical value:

$$a^2 = \left(\frac{\partial P}{\partial \rho}\right)_s; \quad Pv^\gamma = ct; \quad \frac{1}{\rho} = v; \quad \left(\frac{\partial P}{\partial \rho}\right)_s = -v^2\left(\frac{\partial P}{\partial v}\right)_s$$

$$\left(\frac{\partial P}{\partial v}\right)_s = -\gamma\frac{P}{v} \Rightarrow a^2 = \gamma Pv \text{ and for outlet section: } a^2 = \gamma P_2 v_2$$

Expressing P₂ and v₂ using critical value

$$a^2 = \gamma P_2 v_2 = \gamma\frac{P_2 v_2}{P_1 v_1}P_1 v_1; \quad \frac{P_2}{P_1} = \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma}{\gamma-1}} \rightarrow \frac{v_2}{v_1} = \left(\frac{2}{\gamma+1}\right)^{\frac{1}{\gamma-1}} \rightarrow \frac{P_2 v_2}{P_1 v_1} = \frac{2}{\gamma+1}$$

$$a^2 = \frac{2\gamma}{\gamma+1}P_1 v_1 \Rightarrow w_{2crit} = a, speed \text{ of sound}$$

In conclusion, the maximum speed of a fluid is speed of sound.

13.17 References

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Chapter 14

Enthalpy, applications

The Standard State

Before we go on, we have to establish some standard condition at which enthalpies are measured. One could choose any set of parameters, but it is important that all chemists, physicists, biologists, engineers refer to the same conditions. The standard conditions that have been chosen are: *Pressure: 1 bar = 10^5 N/m^2, Temperature: depends on process; 298 K if possible.*

First law give us through the two state functions U and H a deeply introspection in what happen in system when a process takes place. At the first sight the relationship U, Q and L in the first law describes the global effects and changes observable in surrounding. If any changes in U are produced in system then we can measure them by Heat and Work as global effect. U contains all types of energies at microscopic scale (kinetic and potential). Then any thermal effect is a consequence in modifications of the potential and kinetic energy. Therefore measuring the thermal effects, we can find information about system at microscale level. This is not so important for technical thermodynamics where we deal with heat engines and heat exchangers. For physics, chemistry and biology the thermal effects correlated with microstructural changes in system are basics to find out more about transformations. Historical this chapter in thermodynamics is thermochemistry.

Since with advances in nanomaterial science where size dependent effects in systems at nanometric scale are strongly evidenced we should revisit this field in a new concept.

Few examples will convince us:

1. Nucleation and growth by freezing, (water-ice; vapour-liquid, liquid-solid); crystallization of the solute in a binary solution (NaCl in water) by controlled evaporation of solvent or by freezing. The phenomenon consists of the formation in first stage of small critical nuclei (droplets in vapour-liquid respectively, solid phase as small crystallites). Their dimension reaches a critical value for given thermodynamic conditions then they continue to growth. The global effect in transformation is measurable by latent heat. At microscale level we can consider atoms are associate in small clusters forming new bonds with heat releasing:

$$A_1 + A_1 \rightarrow A_2; \ \Delta h_2 = h_2 - 2h_1$$
$$A_2 + A_1 \rightarrow A_3; \ \Delta h_3 = h_3 - h_2 - h_1$$

......

$$A_i + A_1 \rightarrow A_{i+1}; \ \Delta h_{i+1} = h_{i+1} - h_i - h_1$$
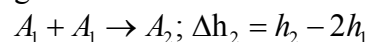
when each step is considered to add only one atom to a cluster of A_i atoms; h_i is specific enthalpy. The global heat can be measured as latent heat released by system: $= \sum_i \Delta h_i$

2. In case when atoms interact with the new compounds forming then we say a chemical reaction has taken place. If we notice a number of atoms A interact with b number of atoms B and output is c number of atoms C and d number of atoms D then the mass conservation give us a general equation:

$$aA + bB \rightarrow cC + dD$$
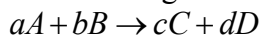
That is a chemical reaction as usual chemists work. The thermal effect at constant pressure is easy counted as reaction heat $= ch_C + dh_D - ah_A - bh_B$ with the same significance as above example.

The latest example is classical for chapter thermochemistry where the reaction heat is measured in standard conditions. In fact reactions as above defined we find everywhere in physics and chemistry where changing in interatomic bonding and reorganizing of matter by phase transformation.

14.1 Thermal effects for any changes in system

Without loosing in generality we consider a hypothetical transformation with species: *A, B, C, D*

$$aA + bB \rightarrow cC + dD \qquad\qquad 14.1$$

defined as chemical reaction and it deals with the heats involved. A typical chemical reaction might have a form similar to the following hypothetical chemical reaction:
(In equation, the upper case letters stand for elements or compounds and the lower case letters stand for small whole numbers, which balance the reaction. We would read this as saying, "*a* moles of A reacts with *b* moles of B to give *c* moles of C and *d* moles of D.")

A chemical reaction is a process just like any other thermodynamic process. It has an initial state (the reactants) and a final state (the products). We can calculate the changes in internal energy, enthalpy, and so on for the reaction. For example,

$$\Delta U = U_{products} - U_{reactants} \qquad\qquad 14.2$$

and

$$\Delta H = H_{products} - H_{reactants} \qquad\qquad 14.3$$

One thing is sometimes not made very clear. "Reactants" and "products" in these equations mean that the reactants and products are separated, isolated, and pure. Furthermore, the reactants and products are all at the same temperature and pressure. So, for example, the *ΔH* above is the enthalpy of *c* moles of C (isolated and pure in its own container at temperature, *T*, and pressure, P) plus the enthalpy of *d* moles of D (isolated and pure in its own container at temperature, *T*, and pressure, *P*) minus the enthalpy of *a* moles of A (isolated and pure in its own container at temperature, *T*, and pressure,*P*) minus the enthalpy of *b* moles of B (isolated and pure in its own container at temperature, *T*, and pressure, P).

From time to time, we will add a superscript ^{o} to *H* or *U* to indicate that reactants and products are in their "standard states." That is, they are in their most stable state at *T* and *P*. For example, the standard state of water at 25^oC and 1 atm pressure is liquid water.

If our reaction takes place at constant *V*, as in a bomb calorimeter, $dV = 0$ and:

$$\Delta U_V = Q_V \qquad\qquad 14.4$$

If the reaction takes place at constant *P*, as in open to atmospheric pressure, $dP = 0$ and:

$$\Delta H_P = Q_P$$

14.5

If $\Delta H_P < 0$ we say that the reaction is exothermic. That is, the system gave heat to the surroundings. On the other hand, if $\Delta H_P > 0$ we say that the reaction is endothermic. The system absorbed heat from the surroundings. From the definition of enthalpy, we find that:

$$\Delta H = \Delta U + \Delta (pV),$$

where

$$\Delta (pV) = (pV)_{products} - (pV)_{reactants}$$

14.6

For liquids and solids $\Delta(PV)$ is quite small. $\Delta(PV)$ is not necessarily small for gases, but we can get a reasonable estimate for this quantity by approximating the gases as ideal. Then:

$$\Delta (PV)_{gas} = (PV)_{gas\ products} - (pV)_{gas\ reactants} =$$
$$= n_{gas\ products} RT - n_{gas\ reactants} RT = RT \Delta n_{gas}$$

14.7

where Δn_{gas} is the difference in the number of moles of gaseous products and reactants. Using this approximation, we get:

$$\Delta H = \Delta U + RT\Delta n_{gas}$$

14.8

However, we have to be careful how we understand this equation because the conditions of the reaction must be the same on both sides of the equation. Since ΔH is the heat we measure if the reaction is run and constant pressure ($\Delta H_P = Q_P$) and ΔU is the heat we measure if the reaction is run at constant volume ($\Delta U_V = Q_V$), it is tempting (and common) to write equation $Q_P = Q_V + RT\Delta n_{gas}$. However, this equation cannot be rigorously true since the Q's refer to different conditions, one at constant P and one at constant *V*. We can get an indication whether or not equation is a good approximation with the following example:

Consider the reaction:

$$2\,C(s) + O_2(g) \rightarrow 2\,CO(g)$$

14.9
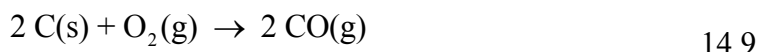
run at $dV = 0$. $\Delta (PV) \approx \Delta (PV)_{gas} \approx RT\Delta n_{gas} = RT$. The heat measured is Q_V. Now let us find a way to measure Q_p. Consider the following two steps :

$$2\,C(s) + O_2(g) \rightarrow \ 2\,CO(g) \rightarrow \ \ 2\,CO(g)$$
$$\underline{P_1, V_1, T}, \rightarrow \ Q_V \rightarrow \underline{P_2, V_1, T} \rightarrow \ \Delta H_2 \rightarrow \underline{P_1, V_2, T}.$$

14.10
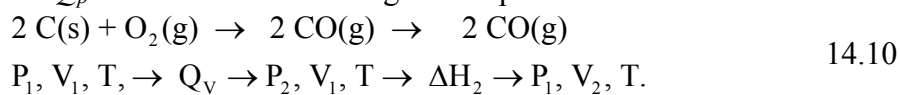
The first step is the constant volume reaction we had before with $\Delta U_V = Q_V$. Notice that the pressure increases. The second step takes the product of the constant volume reaction and reduces the pressure back to the original pressure. We call the heat for this step ΔH_2. So it is rigorously true that $\Delta H_P = \Delta H_V + \Delta H_2 = Q_V + RT + \Delta H_2$. However, the ΔH_2 term is the enthalpy for the expansion of a gas at constant temperature. If the gas is ideal this term is zero. For real gases this term would be very small, so we make a negligible error is neglecting it. So to pretty good approximation we can use the equation, $Q_P = Q_V + RT\Delta n_{gas.}$

14.2 Hess's law

Hess' law states that if we add or subtract chemical reaction equations we can (must) add or subtract their corresponding ΔH's or ΔU's to get ΔH or ΔU for the overall reaction. For example, if we add the reaction:

$$a\,A\,+\,b\,B\,\rightarrow\,c\,C\,+\,d\,D \qquad \Delta H_1,\ \Delta U_1$$

14.11

to the reaction

$$e\,E\,+\,f\,F\,\rightarrow\,g\,G\,+\,h\,H \qquad \Delta H_2,\ \Delta U_2$$

14.12

to get

$$a\,A\,+\,b\,B\,+\,e\,E\,+\,f\,F\,\rightarrow\,c\,C\,+\,d\,D\,+\,g\,G\,+\,h\,H$$

14.13
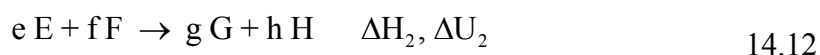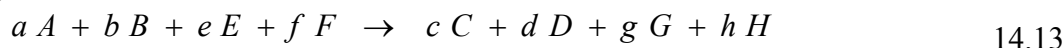
Then, for the overall reaction: $\Delta H = \Delta H_1 + \Delta H_2$ and $\Delta U = \Delta U_1 + \Delta U_2$. The great utility of Hess' law is that we do not have to tabulate ΔH for every possible reaction. We can get ΔH , for a particular reaction by adding and subtracting ΔH's , for a much smaller set of reactions, called formation reactions.

> We define $\Delta_f H\,^o$ for a compound to be the enthalpy of the reaction: pure, isolated elements, in their standard (most stable) states $\rightarrow$ one mole of compound in its standard state.

For example, the heat of formation of liquid water is defined as ΔH^o for the reaction, $H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$. By definition, then, the heat of formation for an element in its most stable state is zero. To obtain ΔH^o for the hypothetical reaction, Equation 14.11, we add and subtract the appropriate heats of formations, $\Delta_r H^o = c\Delta_f H_C^o + d\ \Delta_f H_D^o - a\ \Delta_f H_A^o - b\ \Delta_f H_B^o$.

For example, ΔH^o for the reaction,

$$CH_4(g)\,+\,2\,O_2(g)\,\rightarrow\,CO_2(g)\,+\,2\,H_2O(l)$$

14.14

is given by:

$$\Delta H_r^0 = \Delta_f H_{CO_2(g)}^0 + 2\Delta_f H_{H_2O(l)}^0 - \Delta_f H_{CH_4(g)}^0 =$$
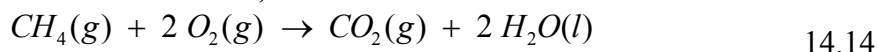
$$= 1\text{mol}(-393.51)\frac{\text{kJ}}{\text{mol}} + 2\text{mol}(-285.3)\frac{\text{kJ}}{\text{mol}} - 1\text{mol}(-74.81)\frac{\text{kJ}}{\text{mol}} =$$

$$= -890.36\text{kJ}$$

As we see $\Delta_r H^o$ for O_2 has been considered 0, being in the most stable state. (We don't always write out explicitly that the coefficients which balance the reaction have units, but we have done so here to make it clear that these numbers have units.)

> Hess's Law: if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps the overall enthalpy change for the process is independent of the number of steps or the particular nature of the path by which the reaction is carried out.

Thus, we can use information tabulated for a relatively small number of reactions to calculate ΔH for a large number of different reactions.

Determining ΔH for the reaction:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)\ \Delta H = -393\text{kJ}$$

14.15
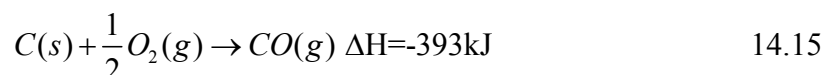
is difficult because some CO_2 is also typically produced. However, complete oxidation of either C or CO to yield CO_2 is experimentally easy to do.

We can invert reaction making it ***endothermic*** and have CO(g) as a ***product.*** (This describes the decomposition of CO_2 to produce CO and O_2)

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \quad \Delta H = +283.0 \text{ kJ}$$

14.16
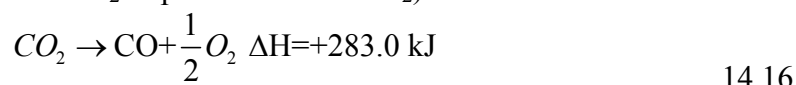
Thus, we now have two equations with known enthalpies of reaction: the first describes the combustion of carbon and oxygen to produce CO_2 and the second describes how CO_2 can be decomposed to produce carbon monoxide (and oxygen). We can combine these together to describe the production of carbon monoxide from the combustion of carbon and oxygen:

$$C(s) + O_2 \xrightarrow{\Delta H = -393.5 kJ} CO_2 \xrightarrow{\Delta H = +283 kJ} CO + \frac{1}{2}O_2$$

14.17
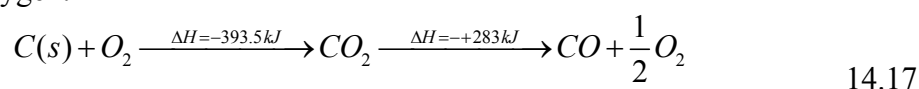
The overall reaction, going from left-hand side reactant(s) to the right-hand side product(s) would be:

$$C(s) + O_2 \rightarrow CO + \frac{1}{2}O_2$$
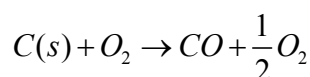
We can algebraically subtract the one-half O_2 from both sides to yield the following equation with the associated overall enthalpy:

$$C(s) + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -110.5 \text{ kJ}$$

14.18
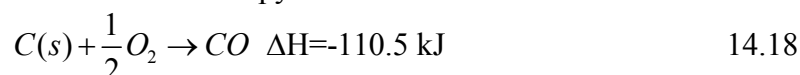
Another way to look at the method of combining reactions would be as follows:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -393.5 kJ$$

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \quad \Delta H = +283.0 kJ$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$C + O_2 + CO_2 \rightarrow CO_2 + CO + \frac{1}{2}O_2 \text{ simplifying } CO_2 \text{ and } O_2 \Rightarrow$$

14.19

$$\Rightarrow C + \frac{1}{2}O_2 \rightarrow CO \text{ with } \Delta H = -110.5 \text{ kJ}$$
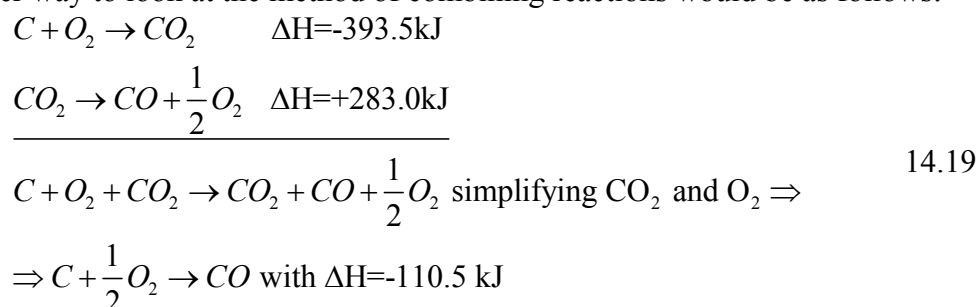
Carbon occurs in two forms: graphite and diamond. The enthalpy of combustion of graphite is -393.5 kJ, and that of diamond is -395.4 kJ

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

$$C(\text{diamond}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -395.4 \text{ kJ}$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

or

$$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$$

$$CO_2(g) \rightarrow C(\text{diamond}) + O_2(g) \quad \Delta H = +395.4 \text{ kJ}$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$C(\text{graphite}) \xrightarrow{sp^2 \rightarrow sp^3} C(\text{diamond}) \Leftrightarrow \Delta H = 1.9 kJ$$

14.20
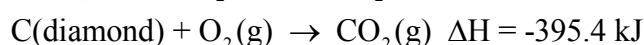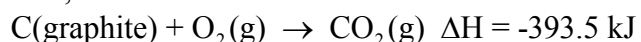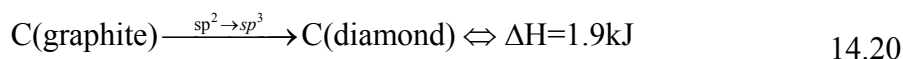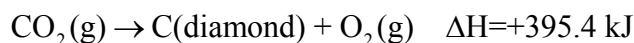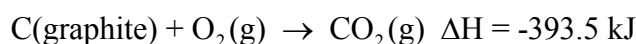
That is, graphite can be converted in its allotrope spending a small quantity of energy. In reality, that is not truth. The conversion of the graphite lattice in diamond needs much more energy. *This is an example where thermodynamics says the transformation is possible but from kinetics point of view there is need much more activation energy (kinetic hindered).*

We can never expect to obtain more or less energy from a chemical reaction by changing the method of carrying out the reaction ("conservation of energy"). Another

way of saying this is that the particular pathway chosen to arrive at the same reactants yields the same *ΔH* for the overall reaction. Consider the previous example of the combustion of methane (14.14) to produce gaseous H_2O and then the condensation of the gaseous H_2O to the liquid state. How is this represented in an Enthalpy Diagram? (Figure 14.1).

The key features:

1. Each line represents a set of reactants or products for a balanced chemical reaction. When going from one line to another, the atoms must balance. For example, if we were to ask what is the enthalpy associated with the condensation of water we would have (from the above data):

$$CO_2 + 2H_2O(g) \rightarrow CO_2 + 2H_2O(l) \ \Delta H\text{=-88kJ}$$
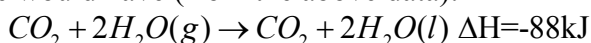
The CO2(g) on both sides will cancel to yield

$$H_2O(g) \rightarrow H_2O(l) \text{ with } \Delta H\text{=-88kJ}$$
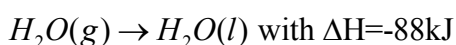
14.21

2. The relative distance of each line must reflect the relative enthalpy difference (ΔH) between the reactants/products. If the enthalpy change in going from reactants to products is negative, then the line for the products must be below the reactants. Furthermore, the length of the distance must be proportional. For example, the distance reflecting the enthalpy associated with the condensation of water (ΔH = -88 kJ) is only about 10% as long as the distance between the reactants and products for the combustion of methane to CO_2 and liquid water (ΔH = -890 kJ)
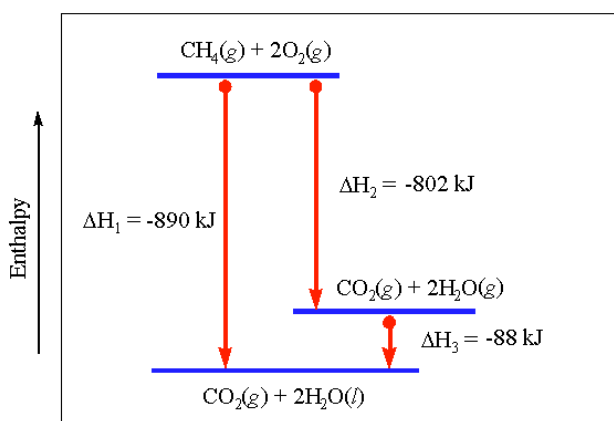
Figure 14.1 Enthalpy diagram, in an energetic representation

14.3 Hess law and Haber-Born cycle

The above representation (Figure 14.1) is usefully to count the lattice energy for each crystal or any kind of molecular structure. Figure 14.2 gives one example how to count lattice energy for NaCl crystal. *For an ionic compound the lattice enthalpy is the heat energy released when one mole of solid in its standard state is formed from its ions in the gaseous state*. This value cannot be determined directly and so we make use of changes for which data are available and link them together with an enthalpy cycle.

This enthalpy cycle is based on the formation of the compound from its elements in their standard states. Figures 14.2 a,b,c describe a cycle, invented by Haber and Born, which gives us a simple method to evaluate the energy content in any body. In particular, we give case study on NaCl lattice.

Figure 14.2 a- Haber-Born cyle, The lattice energy for NaCl starting with standard states for Na(s) and Cl$_2$(g), atomisaton Na and Cl, ionization stage, electron capture by Cl (affinity energy)
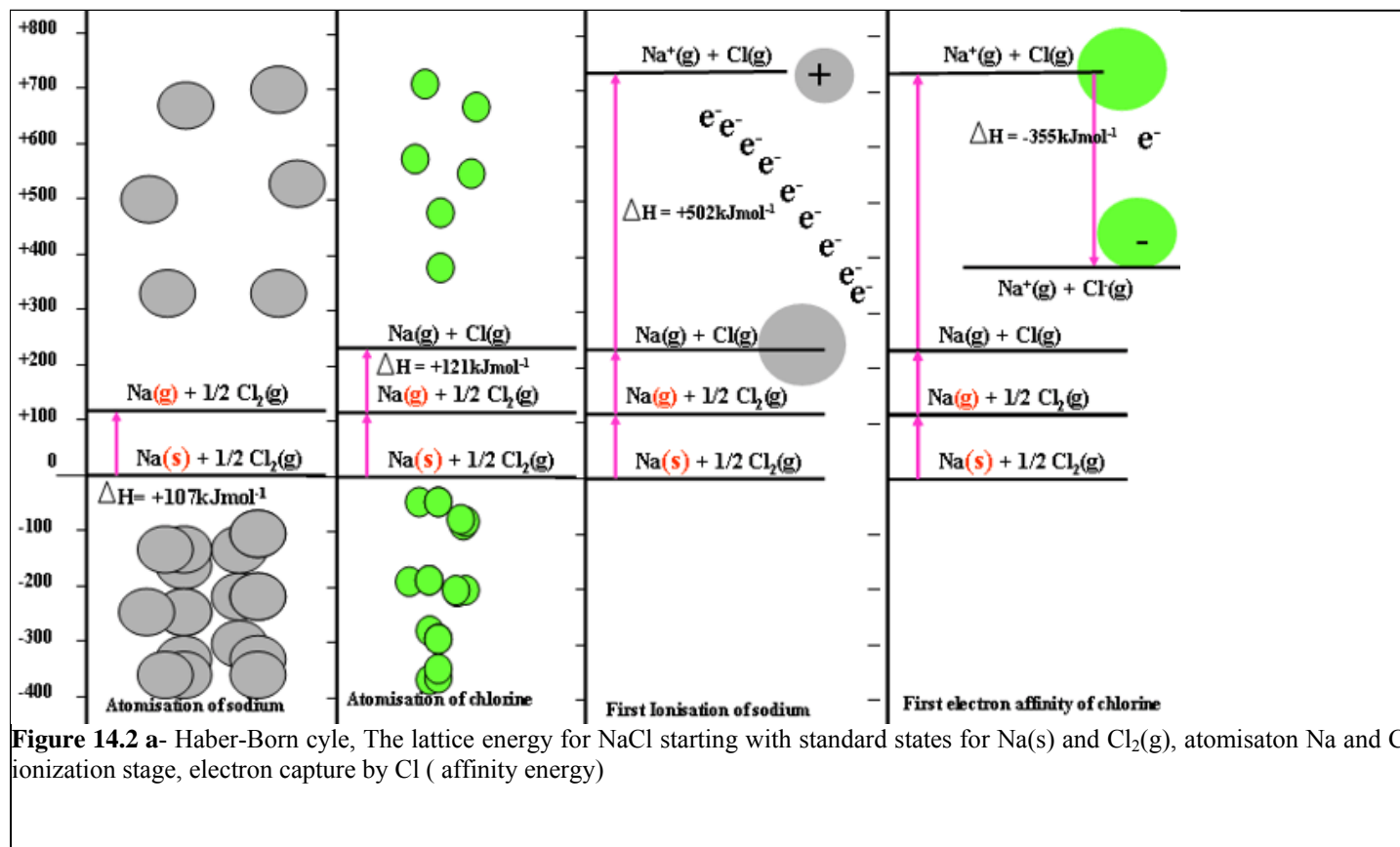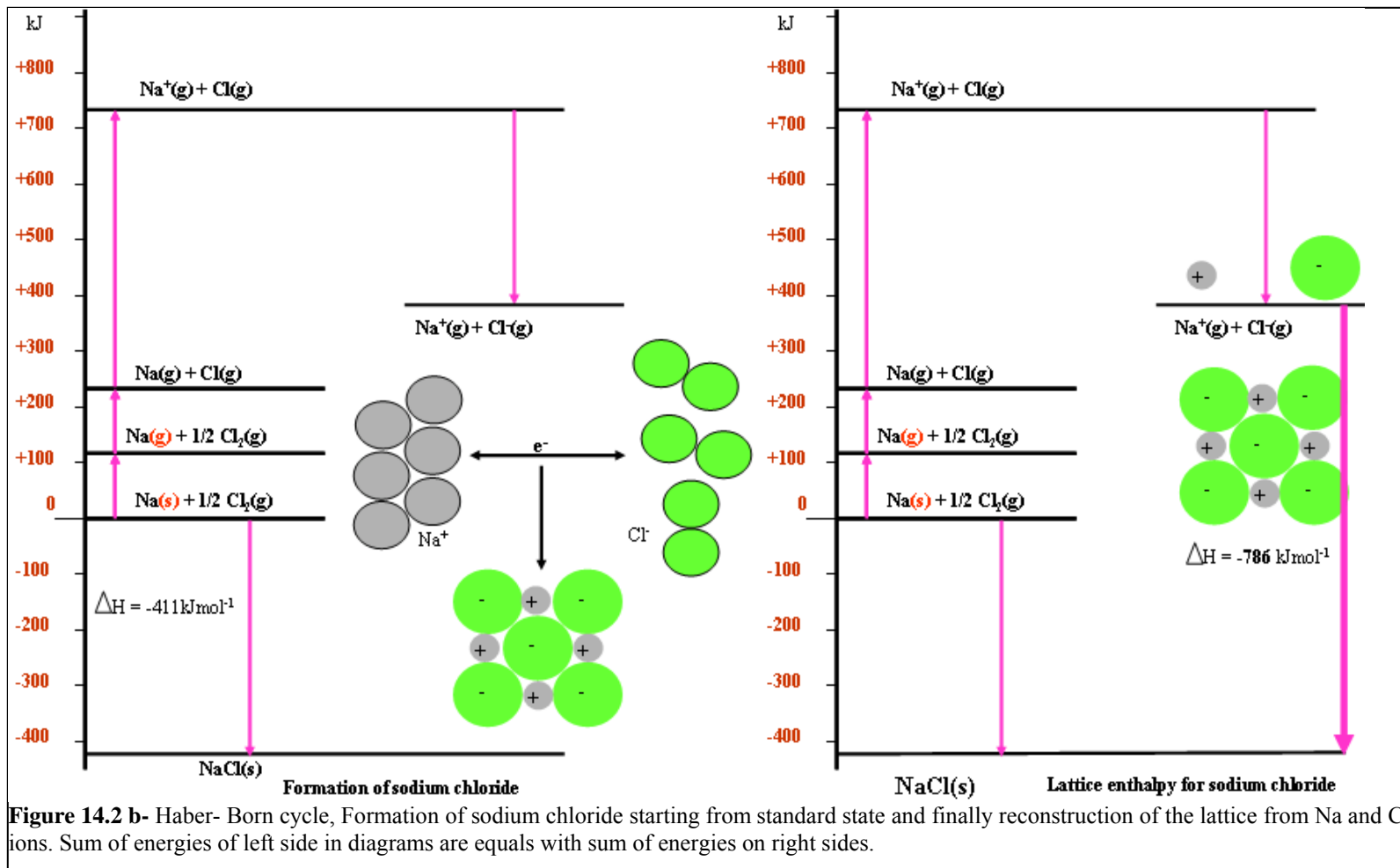
Figure 14.2 b- Haber- Born cycle, Formation of sodium chloride starting from standard state and finally reconstruction of the lattice from Na and Cl ions. Sum of energies of left side in diagrams are equals with sum of energies on right sides.

14.4 ΔH for various processes:

14.4.1 Heats of formation

The cycle Haber-Born gives us useful basics in finding other types of energies

The heat of formation is defined as:

$$\Delta H_f = E_{elect} + E_{nuc} - E_{isol} + E_{atom}$$

where E_{elect} is the electronic energy, E_{nuc} is the nuclear-nuclear repulsion energy, $-E_{isol}$ is the energy required to strip all the valence electrons off all the atoms in the system, and E_{atom} is the total heat of atomization of all the atoms in the system.

(For a single atom, there is no nuclear term, therefore:

$$\Delta H_f = E_{elect} - E_{isol} + E_{atom}$$

But $E_{elect} = E_{isol}$ for an isolated atom, therefore

$$\Delta H_f = E_{atom}$$

Heat of formation for any compound from its elements is a measure of the bond energies in compound and the bond energies in the simple substances. For simple molecules such as H_2, F_2, Cl_2, etc the binding energies have been measured by spectroscopic methods and they represent the formation enthalpy $(-\Delta H^0)$. Here are few examples:

$$2H(g) \rightarrow H_2(g) + 436 \; kJ/mol$$

$$2F(g) \rightarrow F_2(g) + 158 \; kJ/mol$$

$$2Cl(g) \rightarrow Cl_2(g) + 243 \; kJ/mol$$

$$2Br(g) \rightarrow Br_2(g) + 193 \; kJ/mol$$

$$2I(g) \rightarrow I_2(g) + 151 \; kJ/mol$$
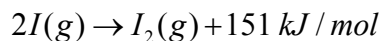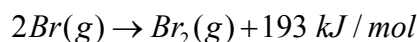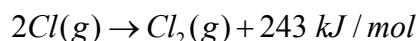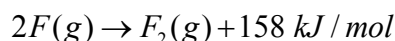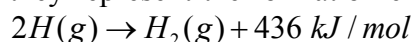
The energy for bond breaking H-H and F-F is 4326+158 = 594k J/mol, and the bonding energy for HF is :

$$H(g) + F(g) \rightarrow HF(g) + 563kJ/mol$$

or

$$2H(g) + 2F(g) \rightarrow 2HF(g) + 1126kJ/mol$$

We see for two bonds H-F formation need 1126kJ/mol and for breaking H-H and F-F need 594 kJ/mol. The difference 1126-594= 532kJ/mol shows that the two bonds H-F are stronger than bonds in hydrogen and fluorine with 266 kJ/mole. This value is the bond formation enthalpy for HF of hydrogen and fluorine.

14.4.2 Bondlengths and Bond Energies

Distances between centers of bonded atoms are called **bondlengths**, or **bond distances**. Bondlengths vary depending on many factors, but in general, they are very consistent. Of course, the bond orders affect bondlength, but bondlengths of the same order for the same pair of atoms in various molecules are very consistent. Thus, there are tables of **interatomic distances** or bondlengths in some standard handbooks. Bondlengths are determined by X-ray diffraction of solids, by electron diffraction, and by spectroscopic methods (study the light absorbed or emitted by molecules).

The bondlengths ranges from the shortest of 74 pm for H-H to some 200 pm for large atoms, and the bond energies depends on bond order and lengths. Half of the bondlength of a single bond of two similar atoms is called covalent radius. The sum of two covalent radii of two atoms is usually the single bondlength. For example, the covalent radii of H and C are 37 and 77 pm respectively. The C-H bond is thus (37+77)= 114

pm. Note that 77 pm = 154/2 pm. The bond order is the number of electron pairs shared between two atoms in the formation of the bond. Bond order for C=C and O=O is 2.

The amount of energy required to break a bond is called bond dissociation energy or simply bond energy. Since bondlengths are consistent, bond energies of similar bonds are also consistent. Thus, tables of bond energies are also of common occurrence in handbooks. Some typical bondlengths in picometers (1 pm = 10^{-12} and bond energies in kJ/mol are given here to illustrate a general trend so that we are familiar with these quantities.

The bond energy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. For the methane molecule, C(-H)$_4$, 435 kJ is required to break a single C-H bond for a mole of methane, but breaking all four C-H bonds for a mole requires 1662 kJ. Thus the average bond energy is (1662/4) 416 (not 436) kJ/mol.

Bond energy is a measure of the strength of a chemical bond. The larger the bond energy, the stronger the bond.

14.4.3 Covalent Bonds

Bonds between the same type of atom are **covalent bonds**, and bonds between atoms when their electronegativity differs by a little (say 0.7) are predominant covalent in character. There is also some covalent character between ions of what we usually call ionic solids.

Bondlength (pm) and bond energy (kJ/mol)					
Bond	Length	Energy	Bond	Length	Energy
H--H	74	436	H--C	109	413
C--C	154	348	H--N	101	391
N--N	145	170	H--O	96	366
O--O	148	145	H--F	92	568
F--F	142	158	H--Cl	127	432
Cl-Cl	199	243	H--Br	141	366
Br-Br	228	193	H--I	161	298
I--I	267	151			
			C--C	154	348
C--C	154	348	C=C	134	614
C--N	147	308	C≡C	120	839
C--O	143	360			
C--S	182	272	O--O	148	145
C--F	135	488	O=O	121	498
C--Cl	177	330			
C--Br	194	288	N--N	145	170
C--I	214	216	N≡N	110	945

For example, bonds in the following substances are predominantly covalent:

- Elements: H2, Li2, B2, C2, N2, O2, F2, Cl2, S8, P4, I2, diamond, graphite, silicon etc
- Covalent compounds: H2O, NH2, CH4, H3C-CH3, H2C=CH2, SiO2, CO2, N2O4, NO2, SO2, SO2 etc.

Theoretically, even ionic bonds have some covalent character. Thus, the boundary between ionic and covalent bonds is a vague one.

For covalent bonds, bond energies and bondlengths depend on many factors: electron affinities (as defined in figure 14.2), sizes of atoms involved in the bond, differences in their electronegativity (energy spend by atom to attract an electron), and the overall structure of the molecule. There is a general trend in that the shorter the bondlength, the higher the bond energy. However, there is no formula to show this relationship, because the variation is widespread. From a table of values, we can not grasp the trend easily. The best method to see the trend is to plot the data on a graph. The relation between bonds electronegativity and bond energy is 100 $(x_A - x_B)^2$ kJ/mol (Linus Pauling) where x is electronegativity for each element.

In a discussion of bond energies in 14.4.1 and 14.4.2 has shown how energy varies as bond. For two H atoms approach each other in the formation of a H-H covalent bond we can imagine as a superposition of two effects one is the repulsive potential en-

ergy among charges and another is the attractive potential energy. Figure 14.3 shows the four situation
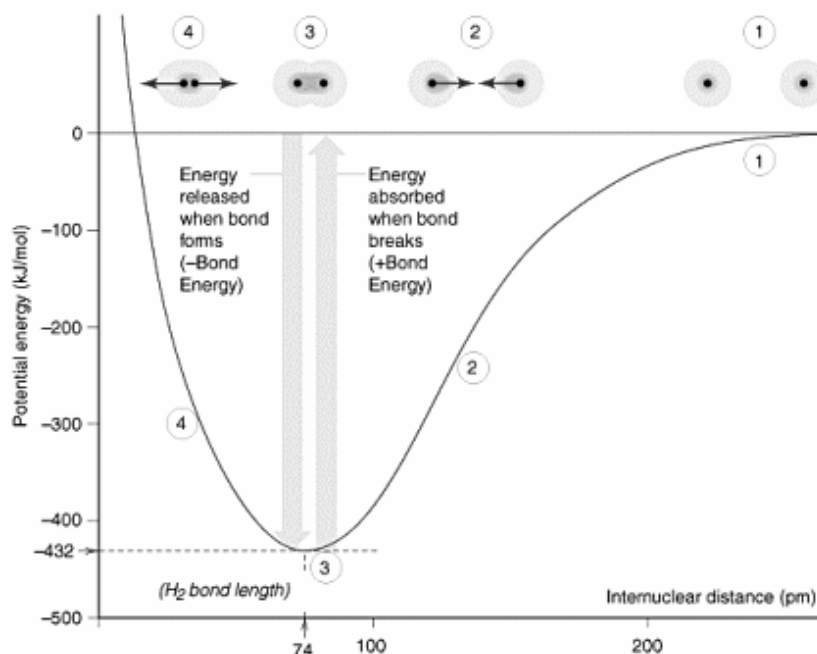
Figure 14.3 – Potential energy for H-H bonding/breaking

Covalent bonds such as H-Cl, H-I etc are *polar*, because the bonding electrons are attracted to the more electronegative atoms, Cl and I in these cases. In general, the higher the electronegativity difference, the more polar are the bonds. In particular, H-F, and H-O bonds are very polar.

Example 1.

Use the table of bond energies to find the ΔH^o for the reaction:

$$H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$$
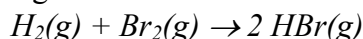
Solution

From the Table of bondlength and bond energy given above,

Changes	$\Delta H^0 (kJ/mol)$
$H - H \rightarrow H + H$	436
$Br\text{-}Br \rightarrow Br + Br$	193

$H\text{-}H + Br\text{-}Br \rightarrow 2Br\text{-}H(=-2\times 366), -732$

overall (add up)

$H - H + Br\text{-}Br \rightarrow 2Br\text{-}H \Rightarrow \Delta H^0 = -732 + 436 + 193 = -103$

Discussion

Another approach is shown below. Write the bond energy below the formula, and then apply the principle of conservation of energy:

Bond broken	Bond formed
H-H , Br-Br	2Br-H
ΔH^0 : 436 , 193	-2×366 (energy released)

$$\Delta H^0 = 436 + 193 - 2 \times 366 = -103$$
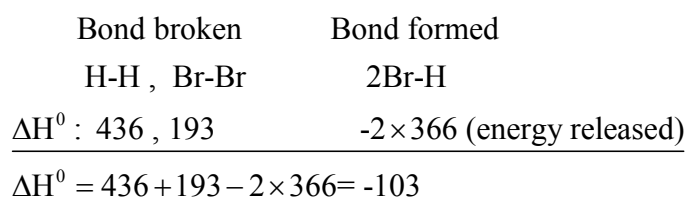
Exercise

1. Evaluate the energy changes for the following reactions

ans: -127kJ
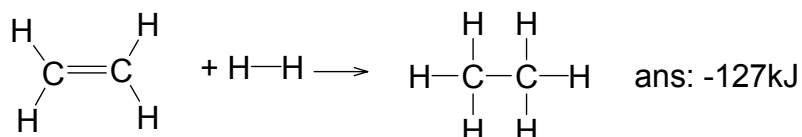
2. Which bond in the list has the highest bond energy, H-H, H-O, H-F, H-I or I-I?

14.4.4 Strengths of Covalent Bonds

The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together. How do we measure the strength of a covalent bond? = Bond-dissociation energy (i.e. "bond energy") :

Bond energy is the enthalpy change (ΔH, heat input) required to break a bond (in 1 mole of a gaseous substance).

Here is one example:
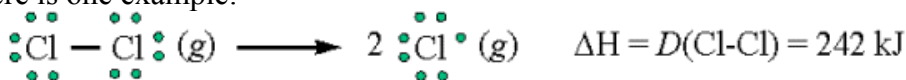
where "D(Cl-Cl)" represents the bond dissociation energy for the Cl-Cl bond

What about when we have a compound, which is not a diatomic molecule? Consider the dissociation of ***methane***:
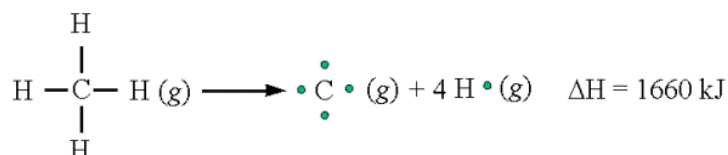
There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$D(\text{C-H}) = (1660/4) \text{ kJ/mol} = 415 \text{ kJ/mol}$$

Note:

1. The bond energy for a given bond is influenced by the rest of the molecule.
2. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms).
3. Thus, *the bond energy for most bonds varies little from the average bonding energy for that type of bond*

Bond energy is always a positive value - *it takes energy to break a covalent bond* (conversely, *energy is released* during bond formation)

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction

14.4.5 Bond Energies and the Enthalpy of Reactions

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we don't know the enthalpies of formation ($\Delta H_f°$)for the reactants and products:

$$\Delta H = \Sigma(\text{bond energies of broken bonds}) - \Sigma(\text{bond energies of formed bonds})$$

Example 1: The reaction between 1 mol of chlorine and 1 mol methane
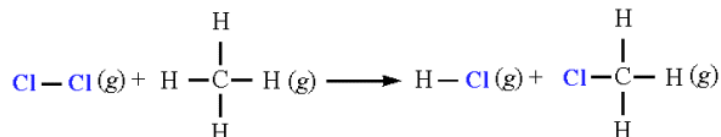
Bonds broken: 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
Bonds formed: 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

$$\Delta H = [D(Cl\text{-}Cl) + D(C\text{-}H)] - [D(H\text{-}Cl)+D(C\text{-}Cl)]$$
$$[242 \ kJ + 413 \ kJ] - [431 \ kJ + 328 \ kJ]=-104 \ kJ$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example2: The combustion of 1 mol of ethane

$$C_2H_6(g) + {}^7/_2O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$$
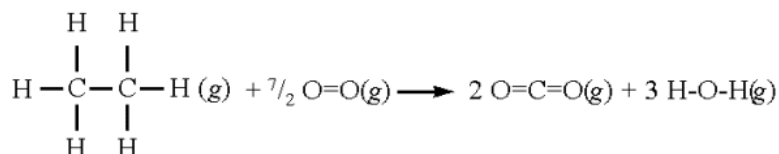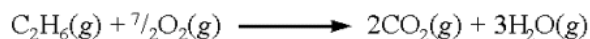
bonds broken: 6 moles C-H bonds, 1 mol C-C bonds, $^7/_2$ moles of O=O bonds
bonds formed: 4 moles C=O bonds, 6 moles O-H bonds

$$\Delta H = [(6*413) + (348) + (^7/_2*495)] - [(4*799) + (6*463)]$$
$$= 4558 - 5974$$
$$= -1416 \ kJ \text{ (the reaction is exothermic)}$$

As the number of bonds between two atoms increases, the bond grows shorter and stronger

14.4.6 Enthalpies of bond formation

The modern techniques (fast FT-IR/UV spectroscopy, flash-pyrolysis, differential scanning calorimetry, thermal analysis, mass spectroscopy) make possible to study the fragmentation of molecules, and measure the energy required to break individual chemical bonds. Such studies have to be conducted in the gas phase, so as to avoid solvent effects. The energy required to break a bond is called bond enthalpy. Example:

$$CH_4(g) \rightarrow CH_3(g)+H(g) \quad \Delta H^0 = 416 kJ/mol$$
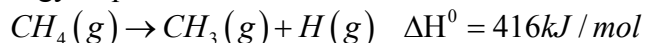
The enthalpy of the reaction is a direct measure of the energy of the bond between the carbon and the hydrogen. It turns out that many chemically similar bonds have similar bond enthalpies. One conveniently takes the average over a number of representative molecules to assemble tables. Bond enthalpies are of course directly related to quantum mechanical bond energy of molecules. Compare the bond enthalpies to the table of binding energies.

Comparison bond energy- bond enthalpy (kJ/mol)						
	C-C	F-F	H-Cl	H-H	O-O	N-N
DH0(A-B)		155	431	436	497	945
DE0(A-B)		154	427.7	432.1	494	941.7
DH0, DE0- dissociation enthalpy and energy which are equal in value with the bond energy						

There is a slight difference between the bond enthalpies and the bond energies; the difference arises from the fact that the macroscopic measurement contains other small energy terms relating to the pressure of the gas; as apparent, these terms are small compared to most bond enthalpies. We can estimate these differences the following way:

If a gas reaction involves a change of Δn moles of gases in the system, then we can write for an ideal gas:

$$\Delta P \cdot V = \Delta n \cdot RT \xrightarrow{\text{H=U+PV}} \Delta H = U + \Delta P \cdot V \rightarrow \Delta H = U + \Delta n \times RT$$

$$RT = 2.5 kJ/mol \text{ at } 298K$$

Therefore, the bond enthalpies should be approximately the bond energies plus 2.5 kJ/mol.

14.4.7 ΔH as Making and Breaking Chemical Bonds

Breaking a chemical bond is an endothermic process. That is, you must put energy into the system to break the bond. Forming a chemical bond is an exothermic process. The energy released in forming the bond goes into the surroundings. We can make an estimate of the ΔH for a chemical reaction by adding the bond energies of all the bonds broken and subtracting the bond energies of all the bonds formed.

$$\Delta H \approx BE_{\text{bonds broken}} - BE_{\text{bonds formed}}.$$

Let's try it on the gas phase reaction,

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3.$$
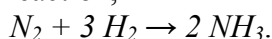
(There are tables of bond energies in physical chemistry texts and in data handbooks. From the tables we find the following bond energies: N−N , 945 kJ; H−H ,436 kJ ;N−H 388 kJ).

In the reaction we break 1 N−N bond and 3 H−H bonds. We form 6 N− H bonds. The approximate ΔH is then, $\Delta H \approx 1 \times 945 + 3 \times 436 - 6 \times 388 = -75$ kJ.

This can be compared to the actual value of -92 kJ. The method is not super accurate, but it gives a ball-park answer and might be useful in cases where other data are not available. Further, however it demonstrates graphically that the heat of a reaction is related to the making and breaking of chemical bonds.

14.4.8 Heats of Formation of Ions in Water Solution

When we look in a table of heats of formation we find values listed for ions in water solutions. That is, you will find an entry for species such as $Na^+(aq)$. It is fair to ask where these numbers come from. We know that in equilibrium chemistry it is impossible to prepare $Na^+(aq)$ ions in solution all by themselves. It is possible to prepare a solution that has both $Na^+(aq)$ and Cl− (aq) ions, but not a solution that has only ions of one charge.

The heats of formation of solutions of soluble ionic compounds can be measured.

That is, we can measure the heat of formation of HCl(aq). The heat of formation of HCl(aq) is defined as ΔH° for the reaction,

$$1/2\ H_2(g) + 1/2\ Cl_2(g) \rightarrow HCl(aq)$$

Since ionic compounds in solution are completely dissociated, it must be true that

$$\Delta_f H^0_{HCl(aq)} = \Delta_f H^0_{H^+(aq)} + \Delta_f H^0_{Cl^-(aq)}$$

We cannot know the heat of formation of either of the ions in solution, but we do know their sum. By convention we arbitrarily set the heat of formation of the $H^+(aq)$ ion equal to zero. That is, $\Delta_f H^0_{H^+(aq)} \equiv 0$. Then the heats of formation of all other aqueous

ions can be determined relative to the heat of formation of the $H^+(aq)$ ion. As a start, we see that :

$$\Delta_f H^0_{Cl^-(aq)} = \Delta_f H^0_{HCl(aq)} - \Delta_f H^0_{H^+(aq)} = \Delta_f H^0_{HCl(aq)}$$

This convention allows us to build up a table of heats of formation of aqueous ions. For example, from the measured value of the heat of formation of NaCl(aq) and the knowledge that :

$$\Delta_f H^0_{NaCl(aq)} = \Delta_f H^0_{Na^+(aq)} + \Delta_f H^0_{Cl^-(aq)}$$

we find that:

$$\Delta_f H^0_{Na^+(aq)} = \Delta_f H^0_{NaCl(aq)} - \Delta_f H^0_{Cl^-(aq)} = \Delta_f H^0_{NaCl(aq)} - \Delta_f H^0_{HCl(aq)}$$

Continuing these procedures we can define the heats of formations of other aqueous ions,

$$\Delta_f H^0_{Br^-(aq)} = \Delta_f H^0_{BrH(aq)} - \Delta_f H^0_{H^+(aq)} \left(\equiv 0\right) = \Delta_f H^0_{BrH(aq)}$$

We now have enough data in our table to calculate the heat of formation of aqueous NaBr without measuring it.,

$$\Delta_f H^\circ_{NaBr(aq)} = \Delta_f H^\circ_{Na^+(aq)} + \Delta_f H^\circ_{Br^-(aq)}$$

$$= \Delta_f H^\circ_{NaCl(aq)} - \Delta_f H^\circ_{HCl(aq)} + \Delta_f H^\circ_{HBr(aq)}.$$

If the heat of formation of $H^+(aq)$ were set to some value other than zero, it would have cancelled out of Equation where we imposed $\Delta_f H^0_{H^+(aq)} \equiv 0$. In this manner an entire table of heats of formation of aqueous ions can be built with all values relative to the heat of formation of the $H^+(aq)$ ion.

14.5 Enthalpies of phase transitions

Phase transitions are processes in which a substance changes from one state to another. Examples include the melting of a solid, the vaporization of a liquid, and the sublimation of a solid. There are also examples of phase transitions between solid states with different forms. More details about phase transitions in vol II(review chapter **systems).** Phase transitions are always connected with an enthalpy change. For example, to melt ice to liquid water one must provide an amount of energy equal to the enthalpy of melting:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H^0_m(273K) = 6kJ/mol$$

The enthalpy is the energy that is required to melt one mole of ice at 273 K to liquid water, also at 273 K. (This is an example for a process that we cannot measure at 298 K!)

14.6 ΔH at other Temperatures

Tables of heats of formation usually give data for reactions at 25°C. We frequently need to know the heat of a reaction at a temperature other than 25°C. If we know the heat capacities at constant pressure we can calculate the heat of reaction at a temperature other than 25°C. We use the following chain of reasoning. We know that,

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \xrightarrow{then} \left(\frac{\partial H^0}{\partial T}\right)_P = C_P^0 \xrightarrow{and} \left(\frac{\partial \Delta H^0}{\partial T}\right)_P = \Delta C_P^0$$

where ΔC_P^0 is defined for our hypothetical chemical reaction, described in introduction of this chapter:

$$\Delta C_P^0 = dC_{PD}^0 + cC_{PC}^0 - aC_{PA}^0 - bC_{PB}^0$$

Prepare Equation for integration as : $d\Delta H^0 = \Delta C_P^0 dT$ and integrate,

$$\Delta H^0(T_2) = \Delta H^0(T_1) + \int_{T_1}^{T_2} \Delta C_P^0 dT$$

For very accurate work we will have to use the temperature dependent heat capacities.

As an example, let's calculate the heat of reaction for the reaction of methane oxidation at 95°C. ΔC_P^0 for the reaction is given by,

$$\Delta_r C_P^0 = C_{PCO_2(g)}^0 + 2C_{PH_2O(l)}^0 - C_{PCH_4(g)}^0 - 2C_{PO_2(g)}^0$$

$$= 1\,\text{mol} \times 37.11 \frac{J}{Kmol} + 2\,\text{mol} \times 75.291 \frac{J}{Kmol} -$$

$$\text{-}1\,\text{mol} \times 35.31 \frac{J}{Kmol} - 2\,\text{mol} \times 29.355 \frac{J}{Kmol} = 93.67 \frac{J}{K}$$

Then, Equation for ΔH^0 gives,

$$\Delta H^0(95^0 C) = \Delta H^0(25^0 C) + \int_{298.15}^{368.15} \Delta C_P^0 dT = -890.36 kJ + 93.67 \frac{J}{K}(368.15 - 298.15) =$$

$$= \text{-}883.80 \text{ kJ}$$

Note: There is another way to do this problem. Calculate ΔH^o for cooling the reactants down to 25°C, calculate ΔH^o for the reaction at 25°C, calculate ΔH^o for heating the products back up to 95°C, and then add them up. Since H is a state function ΔH is independent of path. This method will also work if one of the components of the reaction has a phase change somewhere in the temperature range.

For example, if we let the new temperature be over 100°C we would have to account for the vaporization of the liquid water product. This is not hard to do, but requires some extra steps, including also the use of the heat capacity of water vapor. If the upper temperature in this problem is above 100°C we carry out the reaction in several steps:

    Step 1 - Cool the reactants from the upper temperature to 25°C

    Step 2 - Run the reaction at 25°C,

    Step 3 - Heat the product CO_2 from 25°C to the upper temperature,

    Step 4 - Heat the liquid water from 25°C to 100°C,

    Step 5 - Vaporize the water at 100°C,

    Step 6 - Heat the water vapor from 100°C to the upper temperature.

The heat of reaction at the upper temperature is the sum of the ΔH's for all six steps. Again we have taken advantage of the fact that ΔH is independent of path.

HEAT & CALORIMETRY

Heat
Q

Heat transfer change the thermal state

Changes in internal energy

Changes in temperature of the body

Q produces work but not in equal quantitiy

Q = ΔU +L

Thermal an specific heat
Q=cmΔT
Latent heat

Changes in thermal state and the heat transferred = heat received is foundation for **Calorimetry**

Thermoconduction, radiation, convection , etc

THERMAL ANALYSIS

Cool   Hot
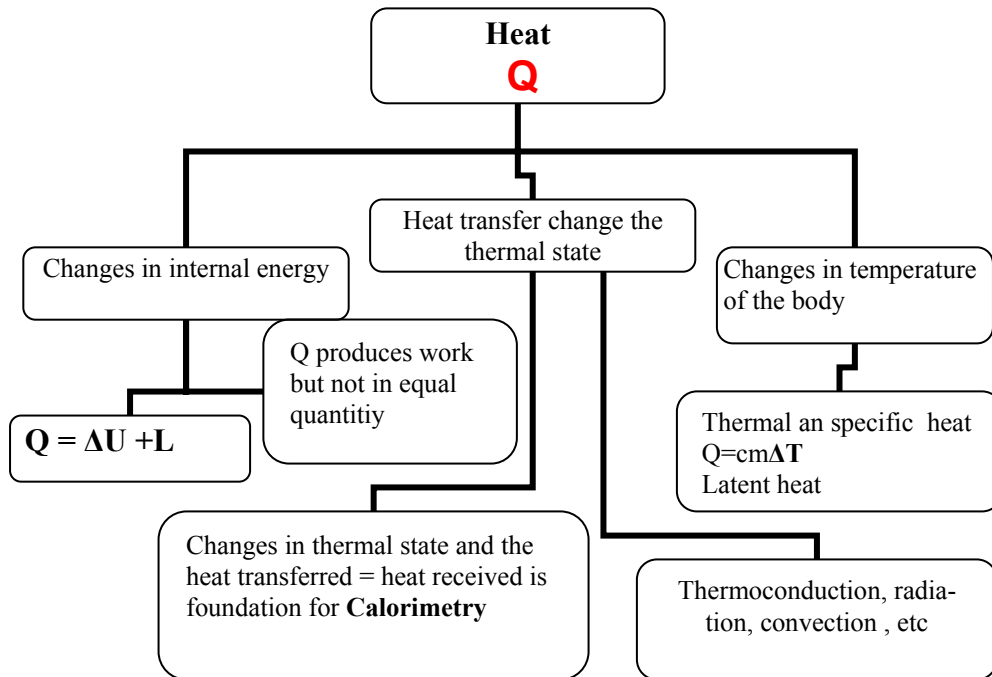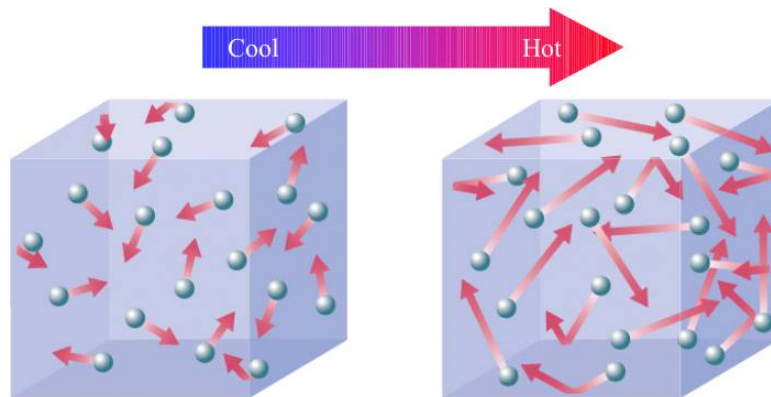
Longer arrows mean higher average speed.

15.1 Introductory part

Thermodynamics is the study of energy and its transformations by the two components: heat and work. Thermodynamics not have any tools to give information about structural properties and the relationship with the physical properties. The interest is the relationship between heat and work with temperature-thermal properties. The answers are given in a branch of thermodynamics, the calorimetry. The calorimetry is a fundamental tool in thermochemistry and in thermal physics, branches of thermodynamics. The Calorimetry is the measurement of heat flow. The relationship between the heat (Q) that is transferred and the change in temperature (ΔT) is:

$$Q = C \cdot \Delta T = C \cdot \left(T_f - T_i \right)$$

the fundamental relationship of the calorimetry.

The proportionality constant in this equation is called the **heat capacity** (C). The heat capacity is the amount of heat required to raise the temperature of an object or substance with one degree. The temperature change is the difference between the final temperature (T_f) and the initial temperature (T_i).

Quantity	Symbol	Unit	Meaning
Heat	Q	joule (J)	Energy transfer that produces or results from a difference in temperature
Temperature	T	^{o}C or K	Measure of the kinetic energy of molecular motion
Temperature change	ΔT	^{o}C or K	Difference between the final and initial temperatures for a process
Heat capacity	C	J ^{o}C^{-1} or J K^{-1}	Heat required to change the temperature of a substance one degree

The calorimetry laws:

1. The heat flow from hot body to cool body when the two bodies with different temperatures are in contact
2. The heat flow ceases when the two bodies reach same temperature.
3. In thermal contact the two bodies exchange heat, until they reach an equilibrium state, in equal portions

Expressions for sensible and latent heats

Two type of heat can be defined: **sensible heat** and **latent heat**

Sensible heat: the heat transferred to body induces the temperature changes. The body changes the thermal state with no any phase transformation takes place. The sensible heat is characterized by the physical property: heat capacity (C), specific heat capacity (c), molar specific heat (C_μ)

$$C = \frac{Q}{\Delta T} \rightarrow Q = C\Delta T$$

$$\left. \begin{array}{l} c = \frac{1}{m}\frac{Q}{\Delta T} \rightarrow Q = mc\Delta T \\[2mm] C_\mu = \frac{1}{n}\frac{Q}{\Delta T} \rightarrow Q = nC_\mu\Delta T \end{array} \right\} \rightarrow C_\mu = \mu c$$

If the body is in different constraints (such as volume or pressure constant) and the heat exchanges are infinitesimal (very small quantity), then we have the most used expressions:

$$c_V = \left(\frac{\delta Q}{dT}\right)_V \Leftrightarrow \text{specific heat when V is constant}$$

$$c_P = \left(\frac{\delta Q}{dT}\right)_P \Leftrightarrow \text{specific heat when P is constant}$$

for m=1 Kg

units:

$$[c_V]_{SI} = [c_P]_{SI} = \frac{J}{Kg \cdot grd}$$

δQ- is the infinitesimal heat changed between body with other body or environment. The heat is a not a state function, is a process variable then is not a exact differential

Latent heat: When phase changes take place in a body and the temperature is constant then we deal with latent heat (melting, sublimation, vaporization, etc). The latent heat is defined:

$$\lambda_V = \left(\frac{\delta Q_V}{dV}\right)_T \rightarrow \text{latent heat for isochore condition, T=const}$$

$$\lambda_P = \left(\frac{\delta Q_P}{dP}\right)_T \rightarrow \text{latent heat for isobar condition, T=const}$$

15.2 Calorimeters

They are experimental devices in which a physical process or chemical reaction takes place. The calorimeter is well insulated so that, ideally, no heat enters or leaves the calorimeter walls. For this reason, any heat liberated by the reaction or process being studied must be picked up by the calorimeter and other substances in the calorimeter.

A thermometer is typically inserted in the calorimeter to measure the change in temperature that results from the reaction or physical process. A stirrer is employed to keep the contents of the calorimeter well mixed and to ensure uniform heating. The
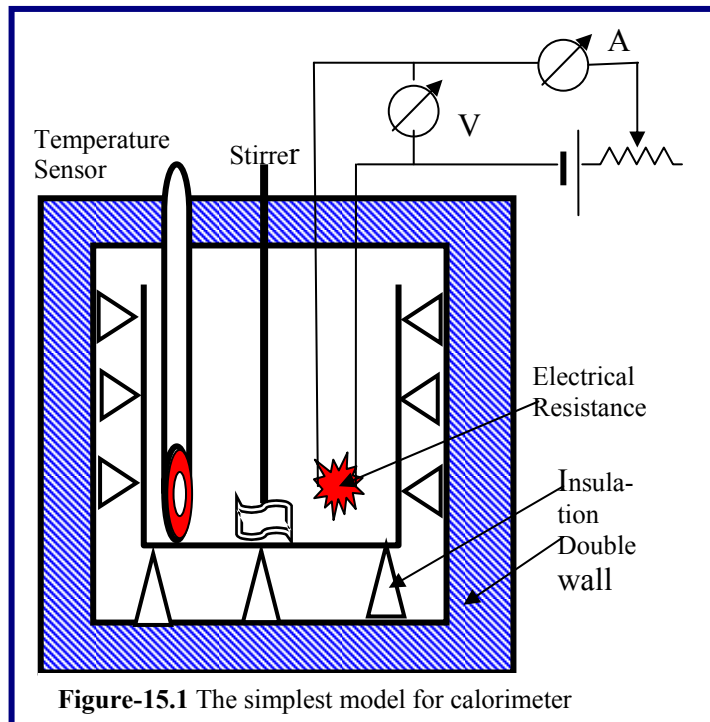
Figure-15.1 The simplest model for calorimeter

calorimeter shown in figure 15.1 contains some water and is equipped with a thermometer, a stirrer, and a heating element. When activated, an electric current is passed through the heating element to generate heat, which is transferred to the calorimeter. A typical calorimeter to measure the reaction heat, combustion, etc is the adiabatic calorimeter bomb (figure 15.2). In a pressurized vessel (bomb) with oxygen the sample is completely burnt and the resulted heat is measured by water heating. Today modern adiabatic calorimeters are designed for precise measurements such as melting points, the purity of the substances, etc.
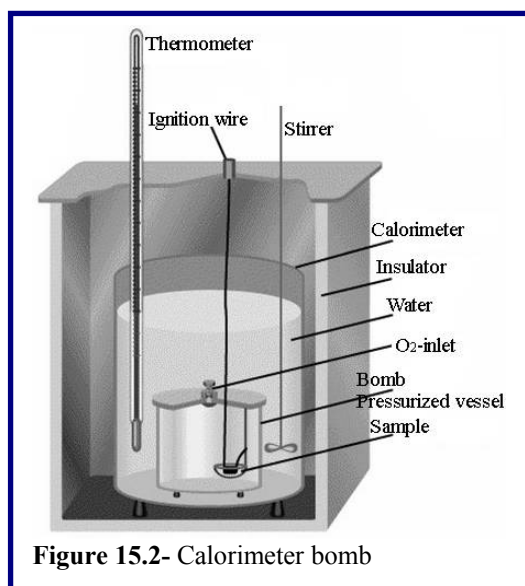
Figure 15.2- Calorimeter bomb

In figure 15.3 is shown a modern adiabatic calorimeter with multiple shielding and internal heater to study melting /freezing dependence for materials with impurities.

In the next sections are presented few experiments with calorimeters

15.2.1 Heat capacity of the calorimeter

Objective:

- Determine the heat capacity of the entire calorimeter system (calorimeter and water).

Approach:

- Use the heating element to transfer a known amount of heat to the calorimeter system.
- Observe the temperature of the system before and after the heating process.

Figure 15.3- Thermal design for adiabatic calorimeter to study melting /freezeing behaviour of the materials

- Calculate the change in temperature for the system.
- Calculate the heat capacity of the entire calorimeter system.

In this part of the experiment, the heating element is set to operate for 5-20 seconds, during which time the heating element will transfer a total of $R*I^2*time$ kJ of heat to the calorimeter.

Theoretical description

In calorimetry it is often desirable to know the heat capacity of the calorimeter itself rather than the heat capacity of the entire calorimeter system (calorimeter and water). The heat Q released by a reaction or process is absorbed by the calorimeter and any substances in the calorimeter. If the only other substance in the calorimeter is water, the following energy balance exists:

$$Q = Q_{cal} + Q_w$$

where Q_{cal} is the heat flow for the calorimeter and Q_w is the heat flow for the water.

Both of these individual heat flows can be related to the heat capacity and temperature change for the substance.

$$Q_{cal} = C_{cal} \, \Delta T$$

$$Q_w = C_w \, \Delta T$$

where C_{cal} is the heat capacity of the calorimeter and C_w is the heat capacity of the water. Because the water and calorimeter are in thermal equilibrium, they both have the same temperature and thus ΔT is the same for both. The consequence is that the heat capacity of the entire system (C) is the sum of the heat capacities for the individual components.

$$C = C_{cal} + C_w$$

The heat capacity is an extensive property; that is, the heat capacity depends upon the amount of substance present.

The calorimeter exists as a fixed unit, thus its heat capacity is a fixed value. The amount of water in the calorimeter, however, can vary, and thus the heat capacity of the water can vary. When dealing with variable amounts of material, one often prefers to use an intensive measure of the heat capacity.

One common intensive version of the heat capacity is the specific heat capacity, c, which is the heat capacity of one Kg of a substance.

Because the mass of water (m_w) and the specific heat capacity of water are both known, one can readily calculate the heat capacity of the water. The specific heat capacity of water (c_w) is

$$c_w = 4.184 \text{ J } {}^{\circ}C^{-1} \, g^{-1}$$

Overall one can write

$$C = C_{cal} + c_w \, m_w$$

15.2.2 Specific Heat Capacity of Copper

Calorimeters are designed to be well-insulated, so no heat is gained from or lost to the surroundings. If no heating element is used to introduce heat in the system, the total heat transferred (Q) for the entire calorimeter system must equal zero. The total heat can be split into heats for each component in the system. Imagine an experiment in which a hot copper ball is dropped into a calorimeter containing water at room temperature. The copper ball will lose heat, which will be absorbed by the calorimeter and water. Because no heat enters or leaves the system from the calorimeter, the heat balance for this experiment is

$$0 = Q = Q_{Cu} + Q_{cal} + Q_w$$

In this case $Q_{Cu} < 0$, because the copper ball will lose heat to the calorimeter and water. Similarly $Q_{cal} > 0$ and $Q_w > 0$, because both the calorimeter and the water will gain heat.

The basic strategy in calorimetry is to use a temperature change and a heat capacity to determine a heat. In this experiment, all substances have the same final temperature (T_f), but not all substances have the same initial temperature. The copper ball is initially at temperature T_{Cu} while the calorimeter and water are initially at temperature T_i.

$$Q_{Cu} = m_{Cu} \, c_{Cu} \, (T_f - T_{Cu})$$

$$Q_{cal} = C_{cal} \, (T_f - T_i)$$

$$Q_w = m_w \, c_w \, (T_f - T_i)$$

The heat capacity of the calorimeter must be obtained from a separate calibration experiment (for example, a heating element can be used to introduce a known amount of heat). The specific heat capacity of water is know (4.184 J $^{\circ}C^{-1}gram^{-1}$), and the temperatures T_{Cu}, T_i, and T_f can be measured experimentally. The masses of the copper and water (m_{Cu} and m_w) can also be measured experimentally. The only unknown property in the above equations is the specific heat capacity of the copper.

$$c_{Cu} = -\frac{\left(C_{cal} + m_w c_w\right)\left(T_f - T_i\right)}{m_{Cu}\left(T_f - T_{Cu}\right)}$$

In this experiment the **objective** is the specific heat capacity of copper and **approaches:** Determine the heat capacity of the calorimeter using a metal of known specific heat capacity, Determine the specific heat capacity of copper.

15.2.3 Specific Heat Capacity of Ethanol

Remenber: The heat capacity of the entire calorimeter system (C) is the sum of the heat capacities of the calorimeter (C_{cal}) and all of the substances in the calorimeter.

Although water is the most frequently used liquid, it is possible to employ a liquid other than water in the calorimeter. In this example, suppose the calorimeter contains ethanol. The heat capacity of the entire calorimeter system is thus

$$C = C_{cal} + C_{EtOH}$$

The heat capacity of the ethanol (C_{EtOH}) depends upon how much ethanol is in the system. It is therefore more convenient to replace C_{EtOH} with the specific heat capacity of ethanol (c_{EtOH}) and the mass of ethanol (m_{EtOH}).

$$C = C_{cal} + c_{EtOH}\, m_{EtOH}$$

Experimentally one knows the mass of ethanol used in the experiment, and one can measure the heat capacity of the entire calorimeter system. This leaves two unknowns, C_{cal} and c_{EtOH}, in the above equation.

One approach to determining these values is to perform two experiments using two different masses of ethanol. Two equations involving C_{cal} and c_{EtOH} may then be written.

The simultaneous solution of these two equations yields values for C_{cal} and c_{EtOH}.

A superior strategy for determining C_{cal} and c_{EtOH} is to make a series of measurements of C at varying values of m_{EtOH}. A plot of *C* vs m_{EtOH} will yield of straight line with a slope of c_{EtOH} and an intercept of C_{cal}. This approach has the advantage of using multiple measurements to obtain "average" values of C_{cal} and c_{EtOH} to reduce the experimental error. In addition, the linearity of the plot is a good diagnostic tool for checking the integrity of both the data and the theory used to generate the working equation.

15.2.4 Heat of Neutralization

Large concentrations of hydrogen ion and hydroxide ion cannot coexist in solution, because the neutralization reaction

$$H^+ (aq) + OH^- (aq) = H_2O (l)$$
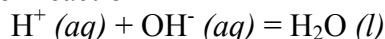
strongly favors the product (water). In this experiment, an aqueous hydrochloric acid solution will be added to an aqueous sodium hydroxide solution. The neutralization reaction will occur until either H^+ or OH^- is entirely consumed. The reactant which is consumed first is called the limiting reactant. The molar enthalpy of neutralization is defined as:

$$\Delta H_{neut} = Q_{neut}/n$$

where Q_{neut} is the heat of neutralization, measured calorimetrically, and n is the moles of the limiting reactant. One typical experiment consists of:

- Add a known volume of 3.00 M aqueous HCl to a known volume of 1.00 M aqueous NaOH.
- Observe the temperature of the system before and after the neutralization reaction occurs.
- Calculate the change in temperature for the system.
- Use the temperature change and heat capacities for the calorimeter and aqueous solution to calculate the heat of neutralization.
- Divide the heat of neutralization by the moles of the limiting reactant to determine the molar enthalpy of neutralization

15.2.5 Heat of Solution of Ammonium Nitrate

Imagine a reaction in which solid ammonium nitrate (a component in some fertilizers and an explosive) is dissolved in water to produce an aqueous ammonium nitrate solution:

$$NH_4NO_3\ (s) = NH_4^+\ (aq) + NO_3^-\ (aq)$$
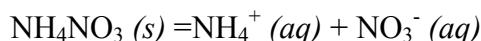
The heat (Q_{rxn}) for this reaction is called the heat of solution for ammonium nitrate. When the reaction is finished, the system contains two substances, the calorimeter itself and the aqueous solution, and there is a heat associated with each component. The heat balance for this experiment is thus

$$0 = Q = Q_{rxn} + Q_{cal} + Q_{soln}$$

The basic strategy in calorimetry is to use a temperature change and a heat capacity to determine a heat. In this experiment all substances start at the same initial and final temperatures:

$$Q_{cal} = C_{cal}\ \Delta T = C_{cal}\ (\ T_f - T_i\ )$$

$$Q_{soln} = C_{soln}\ \Delta T = m_{soln}\ c_{soln}\ (\ T_f - T_i\ )$$

One typically determines the heat capacity of the aqueous solution (C_{soln}) from the mass of the solution (m_{soln}) and the specific heat capacity of the solution (c_{soln}). The mass of the solution is the sum of the masses of the water and ammonium nitrate originally placed in the calorimeter. The specific heat capacity of the aqueous solution is usually close to that of pure water (4.184 J $^oC^{-1}$ g^{-1}).

The objective of this experiment is to determine the heat of reaction (in this case a heat of solution). The above equations can be combined and rearranged to yield a working equation:

$$Q_{rxn} = - Q_{cal} - Q_{soln} = - (\ C_{cal} + m_{soln}\ c_{soln}\ )(\ T_f - T_i\ )$$

Just as the heat capacity of a substance is an extensive property, so the heat of solution is an extensive property.

It is generally more convenient to report intensive properties, thus the heat capacity of a substance is usually reported as a specific heat capacity, that is, the heat capacity per gram of substance. Similarly, one can report a specific heat of solution, which is the heat a solution per gram of solute. More commonly, though, the molar heat of solution is reported.

The molar enthalpy of solution (ΔH_{soln}) is the heat of solution (Q_{rxn}) per mole of solute (n). In this experiment the reaction is performed under conditions of constant

pressure and the only work is "PV-work"; under these conditions the heat flow for the process equals the enthalpy change for the process:

$$\Delta H_{soln} = Q_{rxn} / \text{n}$$

One typical experiment consists of:
- Dissolve a known mass of ammonium nitrate in a known mass of water in a calorimeter: the calorimeter is filled with 60.0 g of water. A small sealed glass bulb containing 5.00 g of pure NH_4NO_3 is placed in the calorimeter
- Observe the temperature of the system before and after the dissolution reaction occurs.
- Calculate the change in temperature for the system.
- Use the temperature change and heat capacities for the calorimeter and aqueous solution to calculate the heat of solution.
- Divide the heat of solution by the moles of ammonium nitrate to obtain the molar heat of solution of Nitrate.
- The heat capacity of the calorimeter must be determined. The formula weight of NH_4NO_3 is 80.04

15.2.6 Heat of Solution of Sulfuric Acid

The objective of this experiment is to determine the heat of solution of sulfuric acid.

$$H_2SO_4 \, (l) = H^+ \, (aq) + HSO_4^- \, (aq)$$
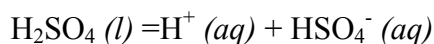
The procedure for this experiment is similar to that for determining the heat of solution of ammonium nitrate. A small glass bulb containing pure sulfuric acid is placed in a calorimeter containing water. When the bulb is broken, the sulfuric acid dissolves in the water, and the heat from the reaction is released to the water and the calorimeter.

This experiment adds a degree of realism to the experimental procedure. To this point, it has been assumed that the calorimeter is perfectly insulated and no heat enters or leaves the system from the surroundings. In practice, the insulation is not perfect and there is some heat loss or gain.

If the system is at room temperature initially, the initial temperature of the system will be stable. The final temperature, however, typically will not be at room temperature. If the reaction is exothermic, the final temperature will be above room temperature, and heat will slowly be lost from the calorimeter to the surroundings. Instead of being constant, the final temperature will slowly drift downward. The converse is true for an endothermic reaction.

To compensate for this heat loss/gain, the temperature is measured as a function of time. Prior to the initiation of the chemical reaction, the temperature vs time plot can be used to establish the initial baseline. When the reaction is complete, the temperature vs time plot can be used to establish the final baseline. These baselines are typically linear, especially if the calorimeter is well-insulated, which makes the heat loss/gain relatively small. The baselines represent the temperature changes attributable to heat exchange from the surroundings.

To determine T_i and T_f, imagine that the reaction took place instantaneously and the heat from the reaction is instantly distributed evenly throughout the system. In this hypothetical case, the temperature would instantaneously jump from T_i to T_f at the time the reaction was initiated. These temperatures cannot be measured directly, but they can

be inferred by extrapolating the baselines to obtain the temperatures on the initial and final baselines at the time the reaction was initiated.

- Dissolve sulphuric acid in water in a calorimeter.
- Monitor the variation of the temperature with time
- Determine baselines for the times before the reaction started and after the reaction finished.
- Extrapolate the baselines to the reaction time to obtain the initial and final temperatures.
- Calculate the heat of solution of sulphuric acid.

15.2.7 Heat of Solution of Calcium Hydroxide

Calcium hydroxide is commonly known as slaked lime and is spread on soil to raise the pH of the soil (if the soil is too acidic).

In determining the heat of solution of ammonium nitrate and sulphuric acid, it was possible to directly dissolve the analyte in pure water and measure the heat for this process. Unlike ammonium nitrate and sulfuric acid, however, calcium hydroxide has a very low solubility and does not dissolve to any great extent when treated with water.

Consequently, it is not possible to directly measure the heat of solution of calcium hydroxide.

Bases like $Ca(OH)_2$ are very soluble in acids owing to the neutralization reaction, which removes hydroxide ion from the system.

$$Ca(OH)_2 \ (s) = Ca^{2+} \ (aq) + 2 \ OH^- \ (aq)$$
$$H^+ \ (aq) + OH^- \ (aq) = H_2O \ (l)$$
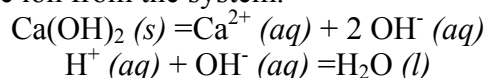
In performing a calorimetry experiment in which calcium hydroxide is dissolved in an acidic aqueous solution, one must account for both the heat of the solubility reaction (Q_{soln}) and the heat of the neutralization reaction (Q_{neut}). The heat balance equation is

$$0 = Q_{cal} + Q_{water} + Q_{soln} + Q_{neut}$$

Approach: Determine the molar enthalpy of neutralization using the Heat of Neutralization experiment.

Using calorimetry, determine the molar enthalpy of solution by dissolving calcium hydroxide in an aqueous HCl solution and accounting for the heat of neutralization in the calculations. (The calorimeter is initially filled with 100.0 mL of 6 M aqueous HCl. Enter the value for the mass of calcium hydroxide (FMW 74.093) to use in this experiment.

During the course of the calorimetry experiment, the temperature is sampled at 0.5 sec intervals and automatically plotted on the graph. The temperature vs time data is listed. You will need to perform extrapolations to the initiation time for the reaction (5.00 sec) to determine the initial and final temperatures for the experiment, just as was performed in the Heat of Solution of Sulfuric Acid experiment.

The specific heat capacity of the aqueous solution should be determened.

Perform the Heat of Neutralization experiment to determine the molar enthalpy of neutralization.

Use the data from this experiment and the molar enthalpy of neutralization to calculate the molar enthalpy of solution for calcium hydroxide.

15.2.8 Heat of Combustion of Methane

The combustion reaction for methane is:

$$CH_4 \ (g) + 2 \ O_2 \ (g) = CO_2 \ (g) + 2 \ H_2O \ (l)$$
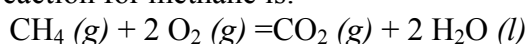
The enthalpy change for this reaction is measured by pressurizing a strong metal reaction vessel (called a bomb) with a mixture of methane and oxygen gas. The bomb is immersed in a calorimeter filled with water. An electrical current is passed through ignition wire (a fine iron wire), which ignites the wire and the gas mixture (see figure 15.2)

The heat balance for this calorimetry experiment is:

$$0 = Q_{cal} + Q_{wire} + Q_{comb}$$

The heat flow for the calorimeter, Q_{cal}, is determined from the heat capacity of the calorimeter and the temperature change for the calorimetry experiment. Typically the amount of water in the calorimeter is always the same; therefore C_{cal} includes the heat capacities of the calorimeter, the water, and the bomb itself.

The burning of the ignition wire releases heat, q_{wire}, and this heat must be included in the calculations. (This heat is treated separately, because the amount of ignition wire used varies from one measurement to the next.)

The heat released by the combustion reaction is Q_{comb}, which is related to the molar internal energy of combustion by:

$$\Delta E_{comb} = Q_{comb} / n_{methane}$$

Combustion experiments are general conducted with a large excess of oxygen, so that the fuel (methane in this case) is the limiting reactant. In this experiment, unlike previous experiments in this sequence, the reaction occurs under conditions of constant volume and no work is performed; thus the heat flow equals the internal energy change for the reaction.

The molar enthalpy of combustion (ΔH_{comb}) is related to the molar internal energy of combustion (ΔE_{comb}) by the equation shown below. (Recall that H = U + PV and the volume is constant in this experiment.)

$$\Delta H_{comb} = \Delta E_{comb} + V \Delta P = \Delta U_{comb} + R \Delta(n\,T)$$

The quantity n is the total moles of gas-phase species. (The assumption implicit in this analysis is that the volume occupied by solids and liquids is negligible compared to the volume of the bomb and thus condensed phases do not contribute significantly to changes in pressure). The term $R \Delta(n\,T)$ is typically small compared with ΔE_{comb}, and thus ΔH_{comb} is usually very close to ΔU_{comb}.

For example, suppose the bomb has a volume of 271 mL and initially contains 10 mmole of methane and excess oxygen at 25.0 ^{o}C. Further suppose that after combustion the system reaches a temperature of 27.0 ^{o}C, at which time 10.0 mmole of methane and 20.0 mmole oxygen have reacted to form 10.0 mmole of carbon dioxide and 20.0 mmole of liquid water. The initial n T for gaseous species is 8.94 K mole and the final value is 3.00 K mole. The term $R \Delta(n\,T)$ is thus -49.4 J per 10.0 mmole methane or - 4.94 kJ mole^{-1}. Compare this quantity with the molar heat of combustion as determined in the experiment described below. Combustion reactions are often used to calculate the molar enthalpies of formation. For example, the standard molar enthalpy of combustion for methane can be expressed in terms of the standard molar enthalpies of formation of the reactants and products:

$$\Delta H^o_{comb} = 2\,\Delta H^o_{f,water} + \Delta H^o_{carbon\ dioxide} - \Delta H^o_{f,methane} - 2\,\Delta H^o_{f,oxygen}$$

ΔH^o_{comb} is measured experimentally. $\Delta H^o_{f,oxygen} = 0$, because oxygen is a pure element. The other molar enthalpies of formation are known from independent measurements. For example, one could determine the heat of combustion of hydrogen to obtain the molar enthalpy of formation for water. For liquid water, $\Delta H^o_f = -285.8$ kJ mole^{-1}

For gaseous carbon dioxide, $\Delta H^o_f = -393.5$ kJ mole^{-1}.

Chapter 16

Thermal Analysis& Methods

The basic concepts in calorimetry were extended to new techniques today well known as: DTA- differential thermal analysis, DTG- differential thermal gravimetry, DSC- differential scanning calorimetry, DMTA- dynamic mechanical thermal analysis, etc. Actually, the thermal methods are extensively used in investigations of the thermal properties.

Heat flow into a substance induces many physical and chemical changes which can help to identify and characterize a sample.

Thermal Analysis Techniques are a group of techniques in which a physical property is measured as a function of temperature, while the sample is subjected to a predefined heating or cooling program:

Differential Thermal Analysis (DTA): The temperature difference between a sample and an inert reference material, $\Delta T = T_S - T_R$, is measured as both are subjected to identical heat treatments.

Differential Scanning Calorimetry (DSC): The sample and reference are maintained at the same temperature, even during a thermal event (in the sample) the energy required to maintain zero temperature differential between the sample and the reference, $d\Delta Q/dt$, is measured.

Thermogravimetric Analysis (TGA): The change in mass of a sample on heating is measured.

Dynamic mechanical thermal analysis (DMTA)- mechanical properties are studied in thermal regim (young modulus, loss modulus)

TGA and DTA have found important roles to play in industrial chemistry, particularly with the analysis and development of polymers. DSC is an important research tool, providing access to accurate thermodynamics data as well as information regarding reactivity and phase transformations.

We will examine three thermal analytical techniques

16.1 Thermogravimetric Analysis (TGA) Thermogravimetry

The change in mass of a sample on heating is measured. Analysis of mass changes in a sample as a function of temperature.

*Usually observes mass **loss***:
• decomposition
• sublimation
• reactivity and desorption of products
*Can observe mass **gain**:*
• oxidation, forming non-volatile oxides

Instrumental Components

There are three principal components in a TGA (figure 16.2)
• analytical balance
• furnace and temperature control system
• control of atmospheric gases exposed to sample
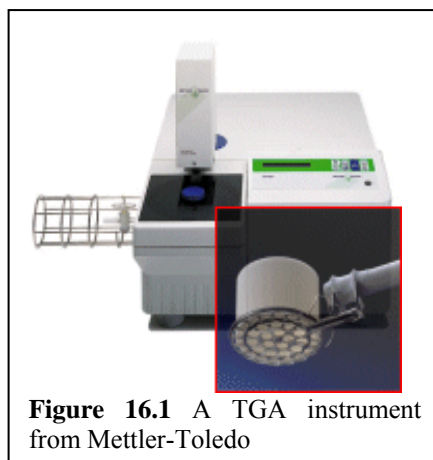
Figure 16.1 A TGA instrument from Mettler-Toledo
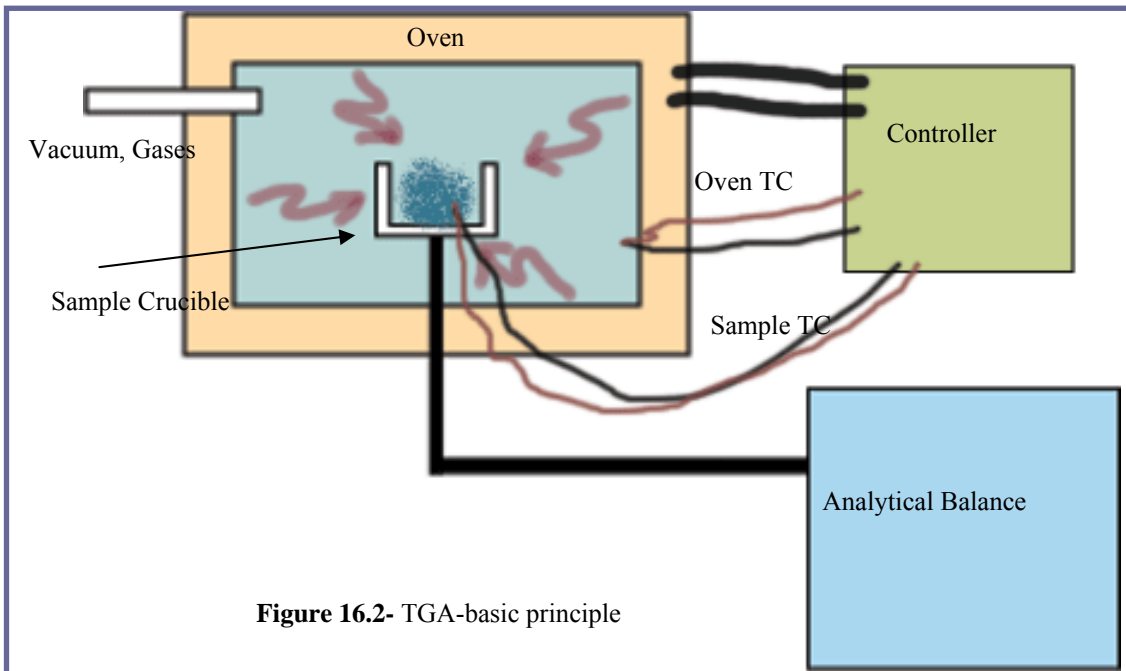
Figure 16.2- TGA-basic principle
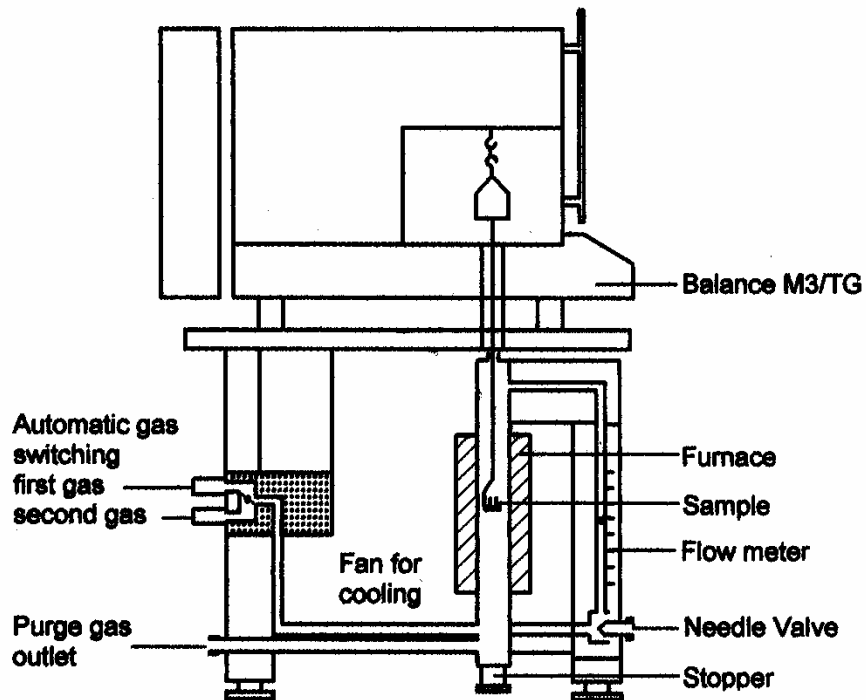
Thermobalance allows for monitoring sample weight as a function of temperature. Two most common instrument types: **reflection and null**

Weight calibration uses calibrated weights. Temperature calibration based on ferromagnetic transition of Curie point standards (e.g., Ni). Larger sample masses lower temperature gradients, and higher purge rates minimize undesirable buoyancy effects.

A typical thermogram is presented in figure 16.3

Figure 16.3 Thermogram is graph of mass *versus* temperature. Sometimes given as % of original mass.
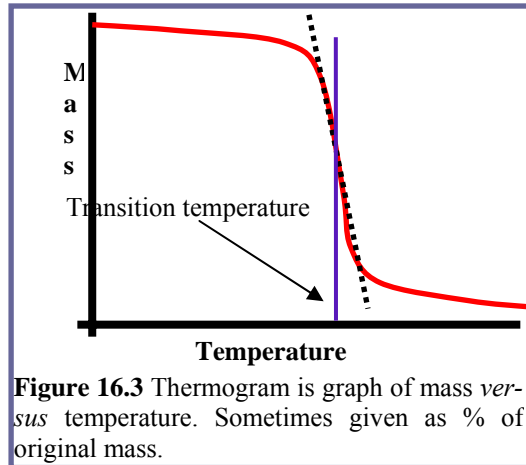
TGA – examples

1. Calcium oxalate decomposition

TG curve of calcium oxalate
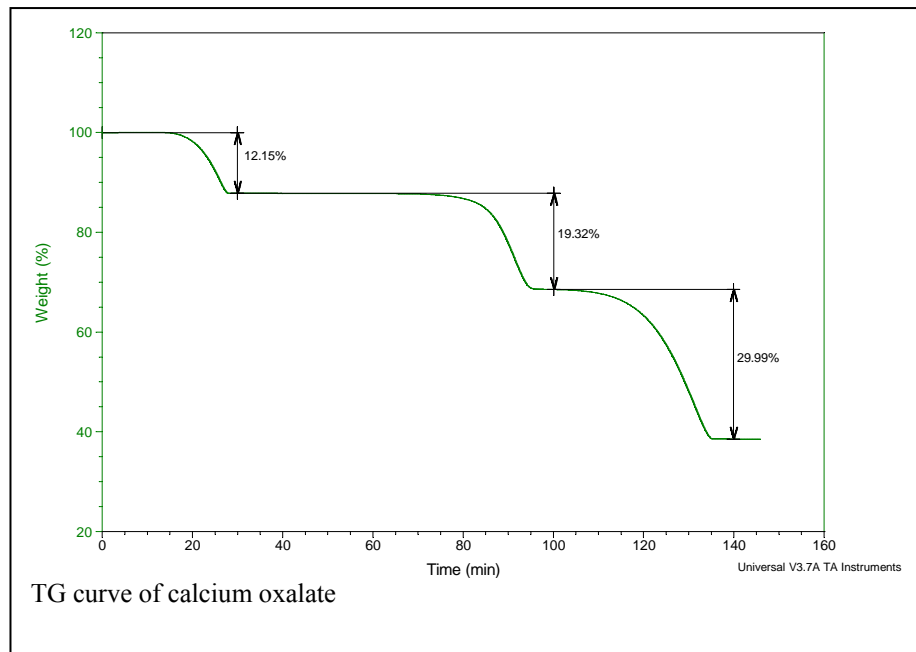
2. Theophylline (180.17 g/mol) is a pharmaceutical used for chronic asthma treatment. Its stable form is that of the monohydrate (198.18 g/mol). The amount of water in an actual sample is important to measure in order to ensure accurate dosage. Dehydration is complete at 110 ˚C. Complete hydrate should lose 9.1% of mass, based on stoichiometry. Sample A loses only 4.13%.

Stoichiometric Content
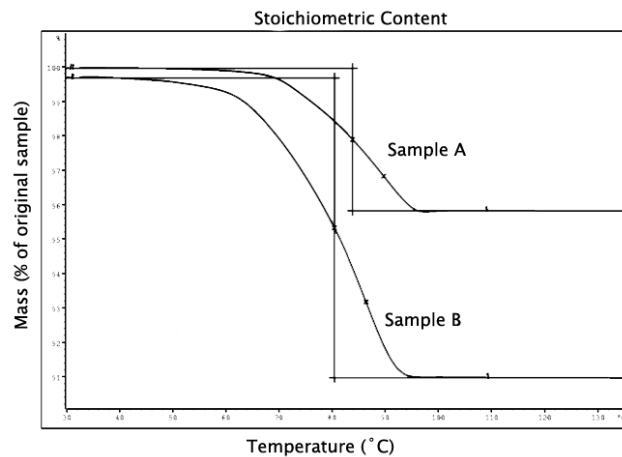
Hence, it is only 45.54% pure hydrate. Sample B loses 8.69% and is therefore 95.79% pure. Note that it loses a small of adsorbed mositure before scan even started.

3. Calcium carbasalate is a salicylate like aspirin with its analgesic effects but seems to do less damage to the stomach lining. The pure, active compound shows a 49.46% weight less starting at 210 ˚C due to decomposition. A particular preparation of it (called Alcacyl), shows a 5% weight loss, due to moisture and followed by a 24.45% weight loss at the decomposition temperature. This indicates that the original sample was 49.46% carbasalate.
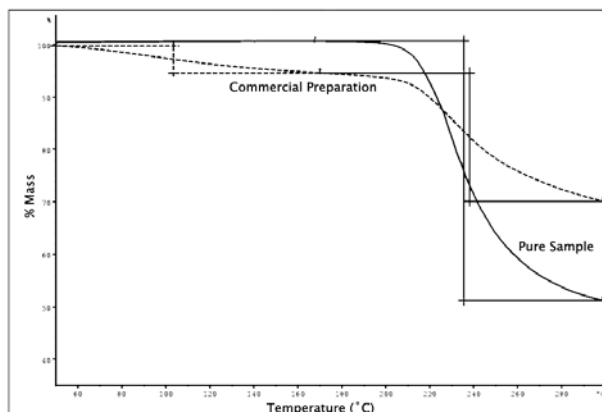
4. The thermal stability of polymeric insulation layers used in coating electrical wires is investigated for quality assurance. Shown here are two different polymers. Note that they both decompose in several steps; the thermogram can be used as a fingerprint for identifcation and confirmation.
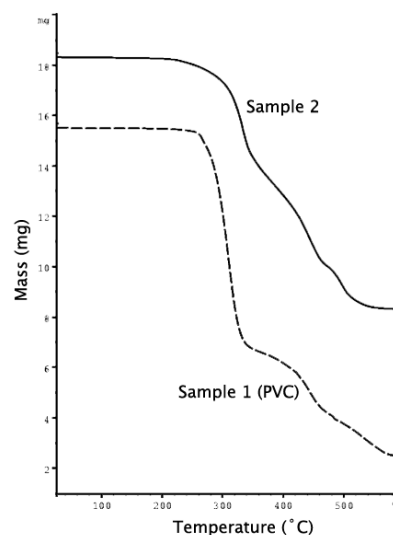
16.2 Differential Thermal Analysis (DTA)

- the temperature difference between a sample and an inert reference material, $\Delta T = T_S - T_R$, is measured as both are subjected to identical heat treatments

Basic Principles of Thermal Analysis

Modern instrumentation used for thermal analysis usually consists of four parts:
1. sample/sample holder
2. sensors to detect/measure a property of the sample and the temperature
3. an enclosure within which the experimental parameters may be controlled
4. a computer to control data collection and processing

Figure 16.4 shows DTA scheme with a single heater consisting of:

Sample holder: sample and reference cells (Al)

Sensors Pt/Rh or chromel/alumel thermocouples one for the sample and one for the reference joined to differential temperature controller

Furnace: alumina block containing sample and reference cells

Figure 16.4 DTA- principle: a- constructive details b- principle where a single heater. Supplies heat to sample and reference. Thermocouples measure the difference of temperature S and R. The grayish shielding for R and S is alumina block

An analysis sample is heated in a linear temperature ramp. Its temperature is compared to that of a similarly heated inert reference sample. Any physical or chemical process that occurs in the analysis sample will be accompanied by an additional enthalpic change. The enthalpic change can be either endothermic or exothermic. The temperature of the analysis sample will respectively be less than or greater than expected, thereby identifying the physical process.

Instrumental Components

Principal components of the experiment include an oven for the controlled heating of the samples; separate temperature sensing transducers for both the analysis and reference samples;

Modern instrumentation used for thermal analysis usually consists of four parts: sample/sample holder; sensors to detect/measure a property of the sample and the temperature; an enclosure within which the experimental parameters may be controlled; a computer to control data collection and processing

The sample holder and reference cells are made of (Al, or alumina, or Au, Pt) function of working temperature

The sensors: Pt/Rh or chromel/alumel thermocouples, one for the sample and one for the reference joined to differential temperature controller furnace.

Alumina block contains sample and reference cells temperature controller, controls for temperature program and furnace atmosphere

advantages: instruments can be used at very high temperatures, instruments are highly sensitive, flexibility in crucible volume/form, characteristic transition or reaction temperatures can be accurately determined

disadvantages: uncertainty of heats of fusion, transition, or reaction estimations is 20-50%

Thermogram is graph of the temperature difference between the analysis and reference samples as a function of the oven temperature. Sometimes, the temperature difference is plotted directly as the thermocouple potential difference (usually in µV).

Exothermic processes will make the analysis sample hotter than the reference, and *vice versa*.
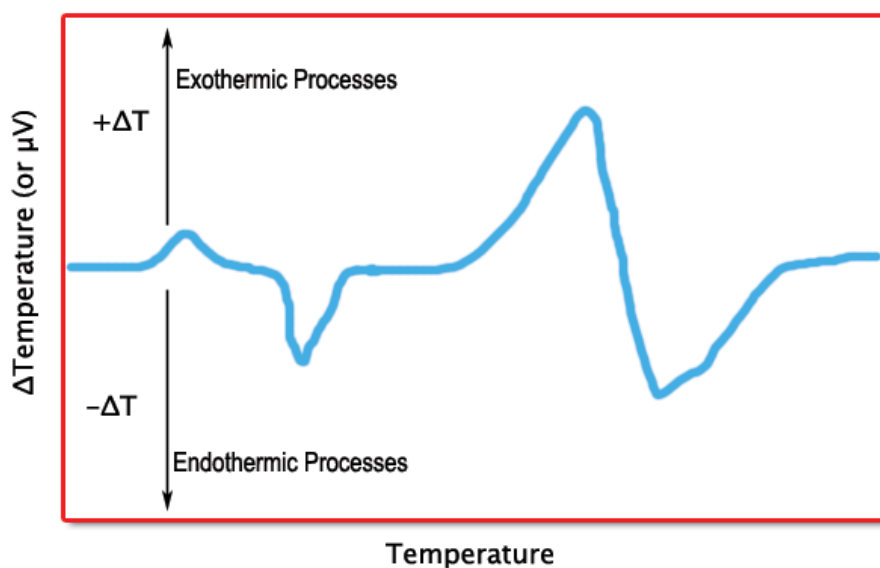
Data can be acquired while either heating or cooling the system. Often both are preferred. Be aware of irreversible processes. Baseline changes can arise due to differences or changes in heat capacity, even if no enthalpic changes occur - often associated with structural phase transitions.

Area under a DTA peak is proportional to enthalpy change and is independent of heat capacity.

$$A = \frac{mq}{g\lambda}$$

where A- peak area, m- sample mass, q-enthalpy change per unit mass, g- peak form factor, λ- thermal conductivity for sample.

16.2.1 DTA examples

1. Here we have a sample of clay. We observe, dehydration, oxidation, phase transitions, and recrystallization process. The enthalpy changes associated with each can be determined by finding the area under the curve for each process.

DTA @ 10°C/minute in Air
Structural Clay Body - High Silica Shale
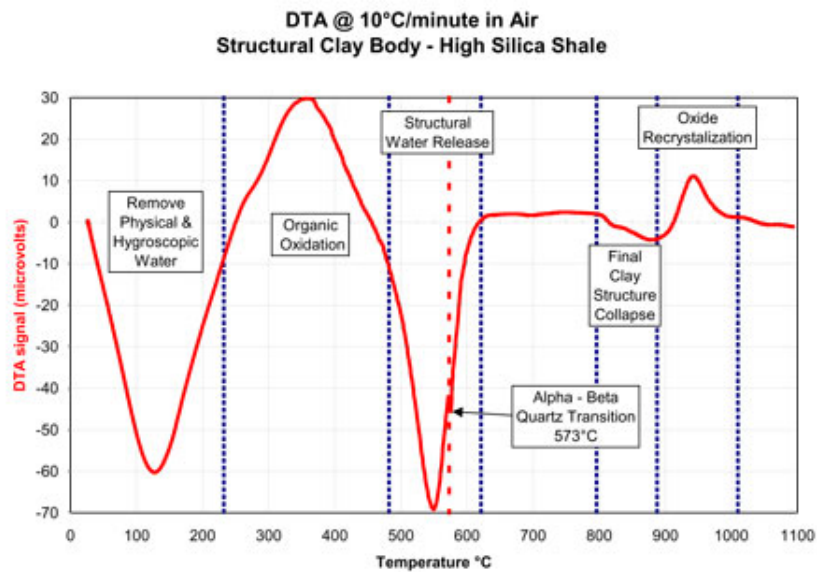
2. This is a metal alloy used for brazing (high temperature soldering). When automating the joining process, knowledge of the temperature when it becomes a liquid (liquidus) and when it returns to its solid form (solidus) are critical

2 Cycle DTA of Braze Alloy
Second Heat Up Cycle
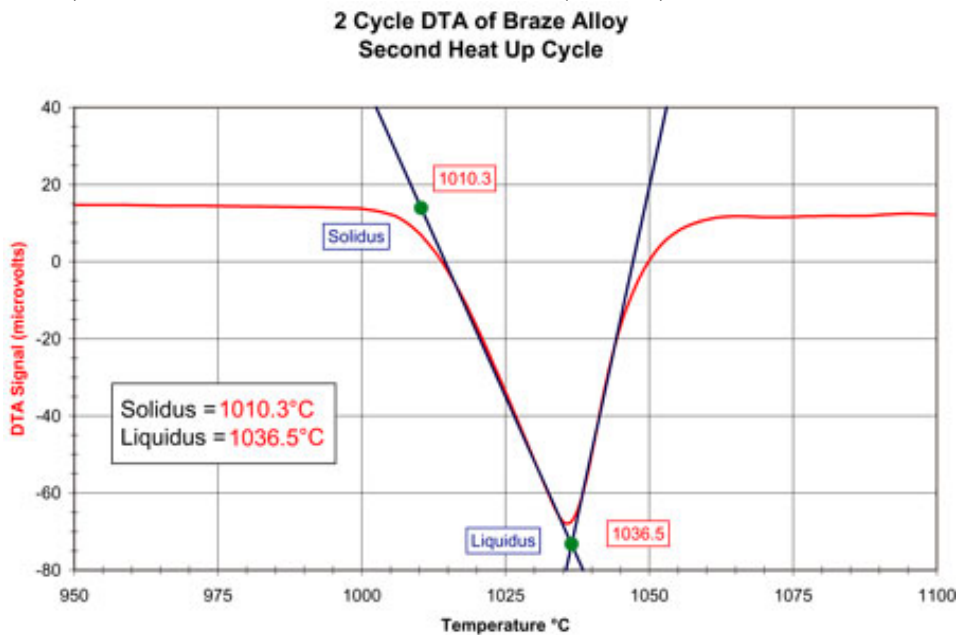
16.3 Differential Scanning Calorimetry

DSC differs fundamentally from DTA in that the sample and reference are both maintained at the temperature predetermined by the program. During a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans

The sample and reference being maintained at the same temperature, even during a thermal event (in the sample) the energy required to maintain zero temperature differential between the sample and the reference, $d\Delta q/dt$, is measured

DSC is the most sophisticated and advanced of the thermal methods. DSC differs fundamentally from DTA in that the sample and reference are both maintained at the temperature predetermined by the program. During a thermal event in the sample, the system will transfer heat to or from the sample pan to maintain the same temperature in reference and sample pans

There are two principal variants:
  • heat-flow DSC
  • power compensated DSC
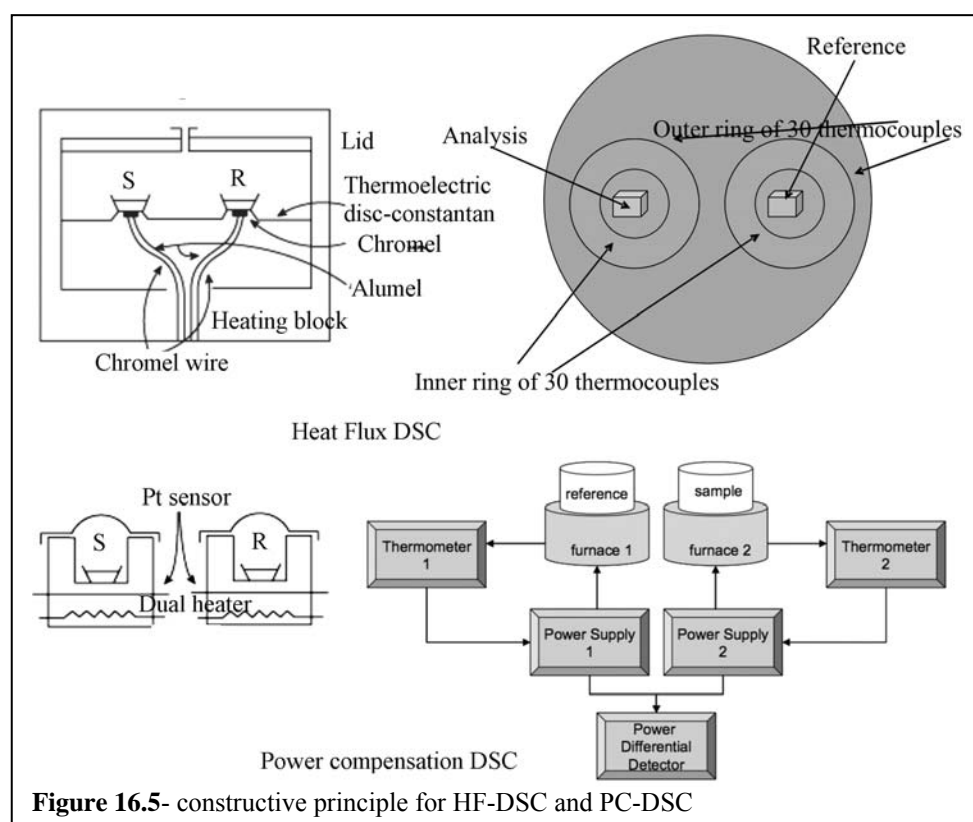
Figure 16.5- constructive principle for HF-DSC and PC-DSC
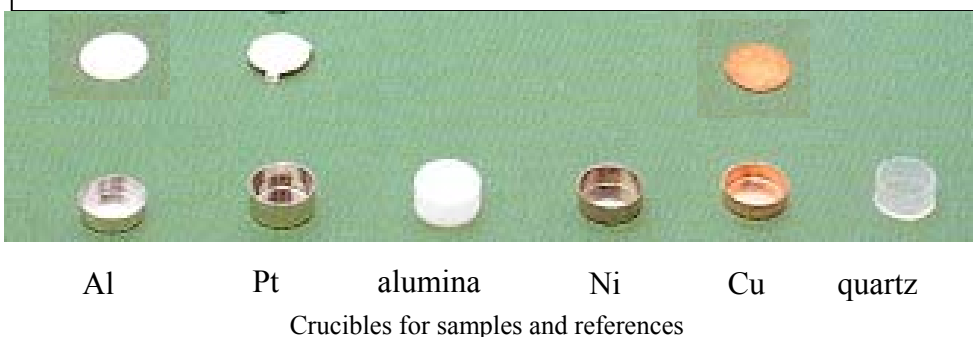
| Al | Pt | alumina | Ni | Cu | quartz |

Crucibles for samples and references

Heat-Flow DSC: Set-up is similar to DTA: analysis sample and reference sample, each sample is surrounded by an inner ring and an outer ring of thermocouples. The average temperature difference between the two measures the heat flow into or out of the sample

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$$\frac{dq}{d\tau} = \frac{1}{R}\left(\overline{\Delta T}_{sample} - \overline{\Delta T}_{reference}\right)$$

where R- thermal resistance and temperatures are averaged on all thermocuples, q- is heat flow measured by the two thermocouples rings

Sample holder : sample and reference are connected by a low-resistance heat flow path Al or Pt pans placed on constantan disc

Sensors: chromel®-constantan area thermocouples (differential heat flow), chromel®-alumel thermocouples (sample temperature)

Furnace: one block for both sample and reference cells

Temperature controller: The temperature difference between the sample and reference is converted to differential thermal power, dq/dτ, which is supplied to the heaters to maintain the temperature of the sample and reference at the program value

<u>**Power Compensated DSC**</u>: Two samples, each heated independently. Temperature difference is monitored. Control heat flow into analysis sample (adjusting heater power) to keep the temperature difference $\Delta T = 0$. This is a null experiment with feedback. The power supplies attempt to heat the two samples at an identical rate. When an exothermic process begins to occur in the analysis sample, the power decreases, in order to keep the temperature correlated with the reference. Similarly with an endothermic process. It uses much smaller sample sizes than with heat flow DSC

sample holder: Al or Pt pans

sensors: Pt resistance thermocouples, separate sensors and heaters for the sample and reference

Furnace: separate blocks for sample and reference cells

Temperature controller: differential thermal power is supplied to the heaters to maintain the temperature of the sample and reference at the program value

Analysis of Heat-Flow in Heat Flux DSC

Temperature difference may be deduced by considering the heat flow paths in the DSC system thermal resistances of a heat-flux system change with temperature. The measured temperature difference is not equal to the difference in temperature between the sample and the reference

$$\Delta T_{exp} \neq T_S - T_R$$

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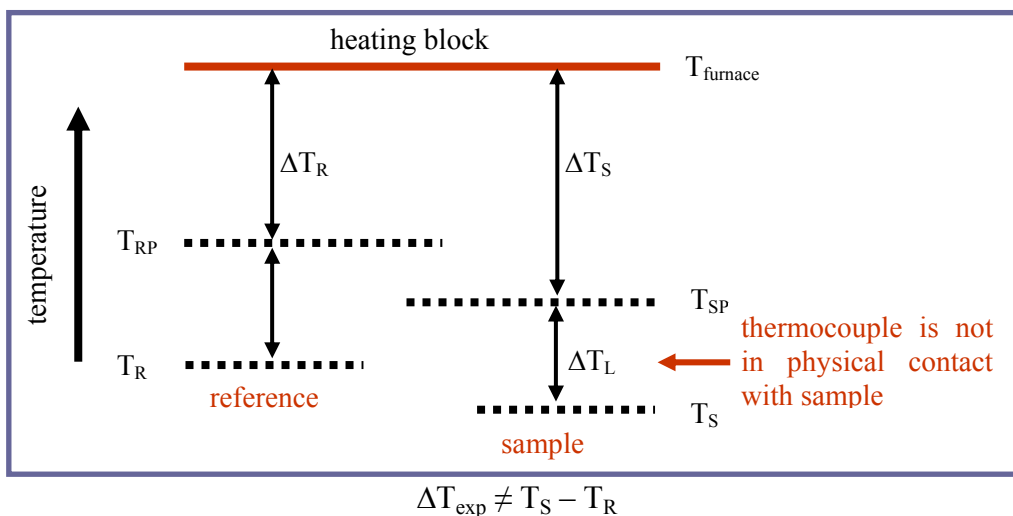
16.3.1 DSC- analysis

The power differences are plotted as a function of the sample temperature. The unit is usually differences in power, given in mW. Here is the DSC curve for a polymeric material such as high density polyethylene (HDPE). We see three phase transitions temperatures identified: the glass transition temperature, the crystallization temperature, and the melting temperature. Integrate area under a peak as a function of time: signal is power (W = J/s). Integral gives total energy associated with the process: ΔH. Can determine average heat capacity and entropy of process
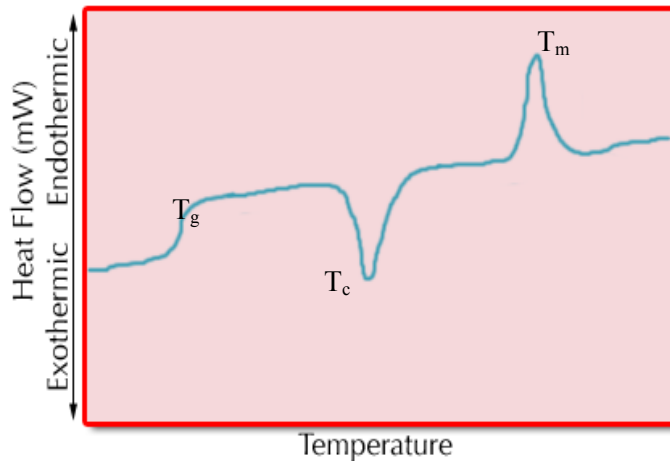
$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

When C_p is constant, the enthalpy increases linearly in time. The DSC curve is a straight line with slope C_p.

16.3.2 DSC Calibration

baseline

Evaluation of the thermal resistance of the sample and reference sensors measurements over the temperature range of interest

    2-step process
- the temperature difference of two empty crucibles is measured
- the thermal response is then acquired for a standard material, usually sapphire, on both the sample and reference platforms
- amplified DSC signal is automatically varied with temperature to maintain a constant calorimetric sensitivity with temperature
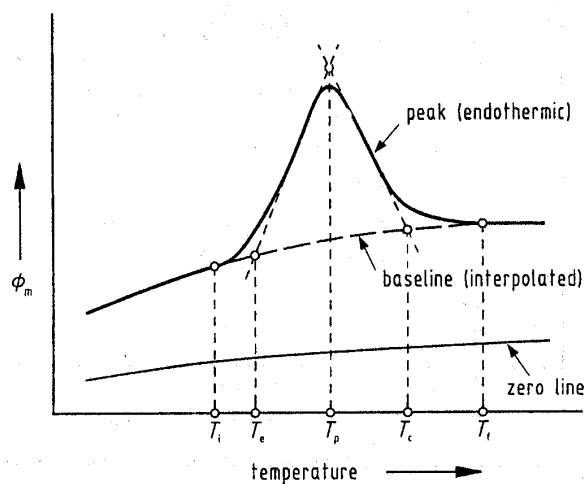
temperature
- goal is to match the melting onset temperatures indicated by the furnace thermocouple readouts to the known melting points of standards analyzed by DSC
- should be calibrated as close to the desired temperature range as possible

heat flow: use of calibration standards of known heat capacity, such as sapphire, slow accurate heating rates (0.5–2.0 °C/min), and similar sample and reference pan weights.

calibrants

- high purity
- accurately known enthalpies
- thermally stable
- light stable (hn)
- nonhygroscopic
- unreactive (pan, atmosphere

metals
- In 156.6 °C; 28.45 J/g
- Sn 231.9 °C
- Al 660.4 °C

inorganics

KNO3 128.7 °C

KClO4 299.4 °C

organics
- polystyrene 105 °C
- benzoic acid 122.3 °C; 147.3 J/g
- anthracene 216 °C; 161.9 J/g

Sample Preparation
- accurately-weigh samples (~3-20 mg)
- small sample pans (0.1 mL) of inert or treated metals (Al, Pt, Ni, etc.)
- several pan configurations, e.g., open , pinhole, or hermetically-sealed pans
- the same material and configuration should be used for the sample and the reference
- material should completely cover the bottom of the pan to ensure good thermal contact
- avoid overfilling the pan to minimize thermal lag from the bulk of the material to the sensor

* small sample masses and low heating rates increase resolution, but at the expense of sensitivity

16.3.3 DSC- examples

1. Ammonium perchlorate is an important component of high explosives. The stability of this material is critical to their safe handling. We see at 242 ˚C, the solid-solid phase transition to the cubic phase. At higher temperatures, one observes decomposition reactions. This work was part of a study to investigate the mechanism of decomposition. Literature values for the activation energy ranged from 37 to 260 kJ/mol with different mechanisms proposed. This work clarified

Decomposition of Ammonium Perchlorate

the mechanism and identified the activation energy as 115 kJ/mol.

2. An important test in the automotive industry is to determine the stability of lubricating oils at elevated temperatures and pressures. This will impact its utility as a lubricant in motors. In these case, the oil is brought to a high operating temperature and held there
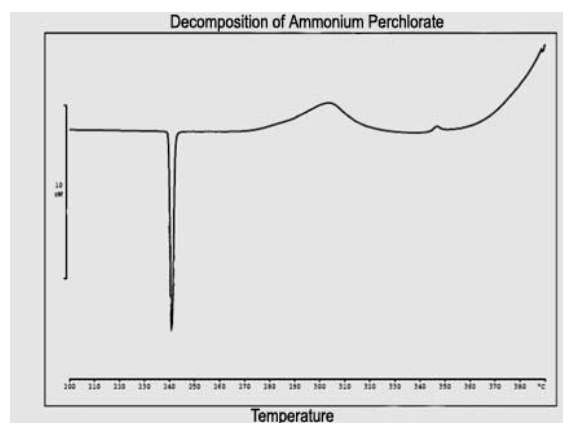
under an oxygen atmosphere. At some point, the oil begins to oxidize and then quickly decomposes exothermically. Note how the synthetic oil has a much longer OIT than does the mineral oil.

Oxidation Induction Time - Oils
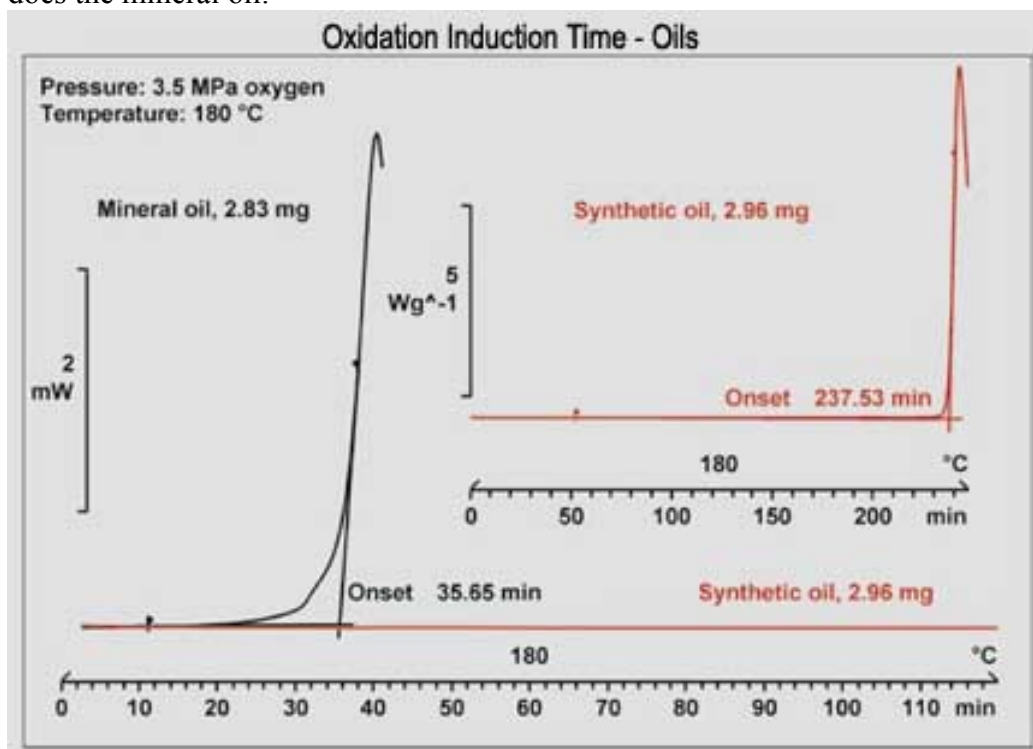
3. *40 μL of H2O is placed in an Al crucible at various elevated pressures*. The boiling point is observed as a sharp, endothermic event. With the Clausius-Clapeyron equation, the enthalpy of vaporization can be measured. Note how there is a small exothermic event that follows the vapourization. It is attributed to a reaction between the water and the aluminum, which is confirmed by carrying out the reaction in a gold crucible.

Vapourization of Water at High Pressures

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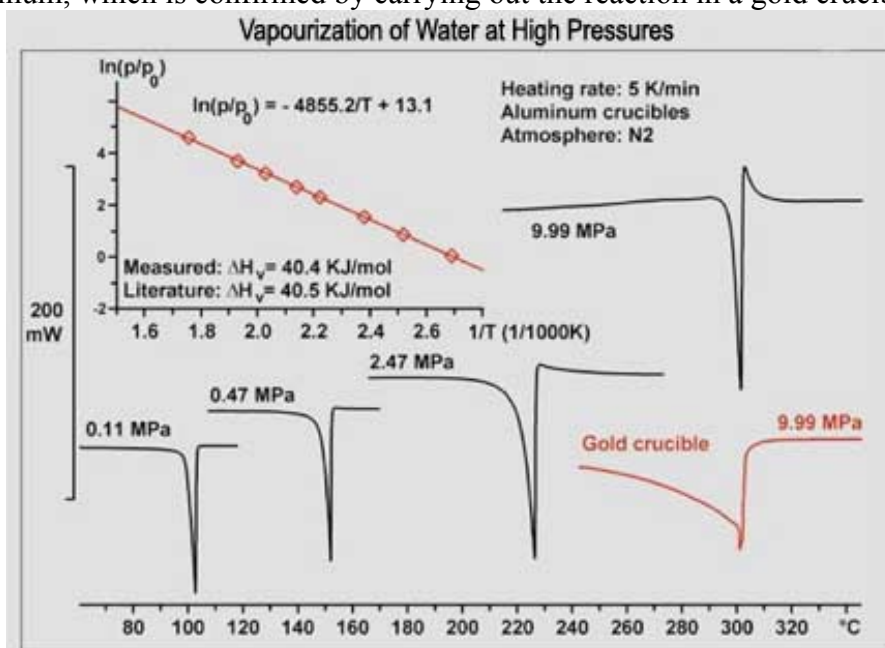
4. Typical Features of a DSC Trace for a Polymorphic System

Endothermic events: melting, sublimation, solid-solid transitions, desolvation chemical reactions

Exothermic events: crystallization, solid-solid transitions, decomposition, chemical reactions

Baseline shifts

Glass transition

exo

B

Crystallization

Phase transition

Crystallization of stable modification peak 177.30 °C

C

E

A

Glass transition
Onset   54.78 °C
Midpoint 56.89 °C

D

Melting of metastable modification peak 175.30 °C

sulphapyridine

Melting of stable modification peak 190.30 °C

F

40   60   80   100   120   140   160   180   °C

0   5   10   15   20   25   min
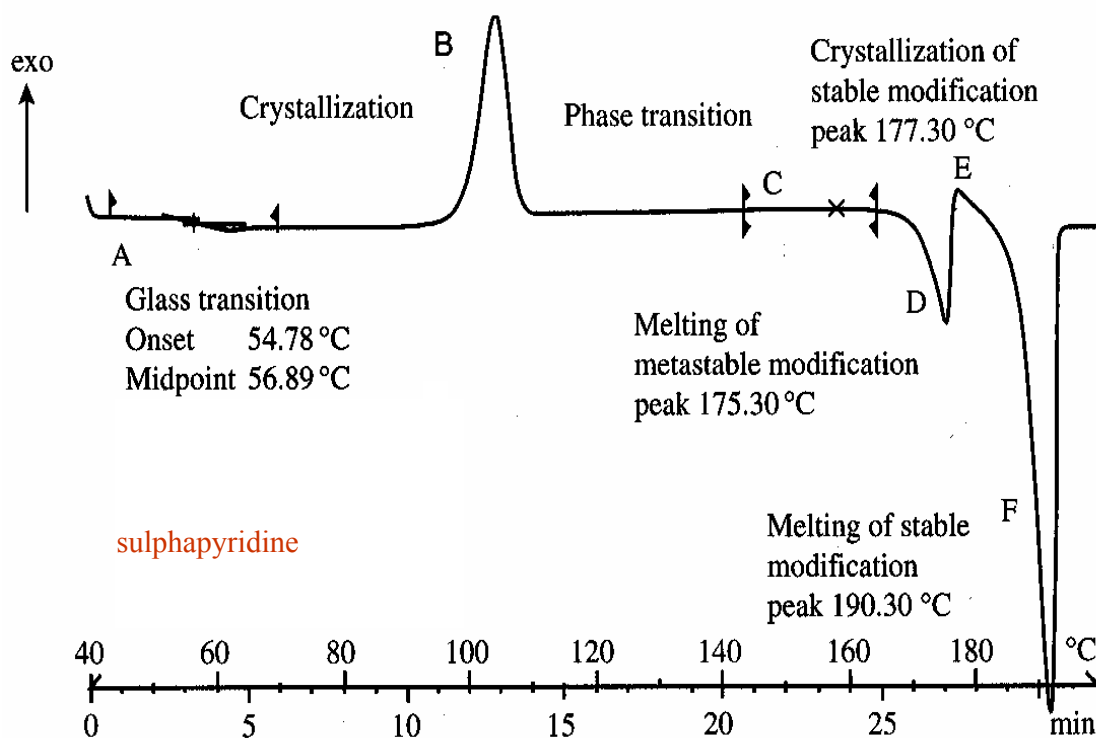
5. Recognizing Artifacts

sample topples over in pan

sample pan distortion

shifting of Al pan

mechanical shock of measuring cell

cool air entry into cell

exo

sensor contamination

endo

electrical effects, power spikes, etc.

RT changes

burst of pan lid

intermittant closing of hole in pan lid
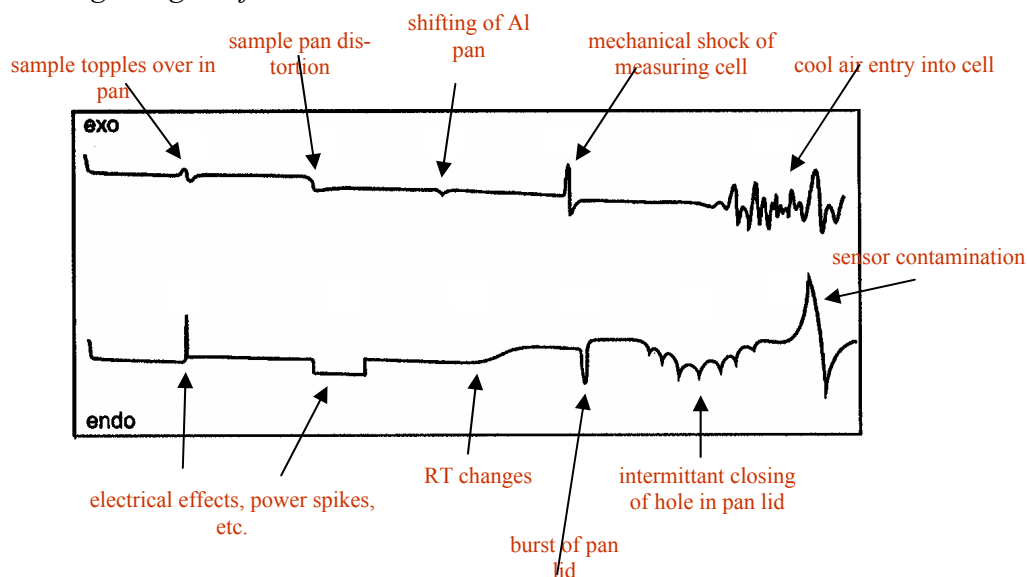
6. Thermal Methods in the Study of Polymorphs and Solvates

Polymorph screening/identification

Thermal stability
- melting
- crystallization
- solid-state transformations
- desolvation
- glass transition
- sublimation
- decomposition

heat flow
- heat of fusion
- heat of transition
- heat capacity

mixture analysis
- chemical purity
- physical purity (crystal forms, crystallinity)

phase diagrams
- eutectic formation (interactions with other molecules)
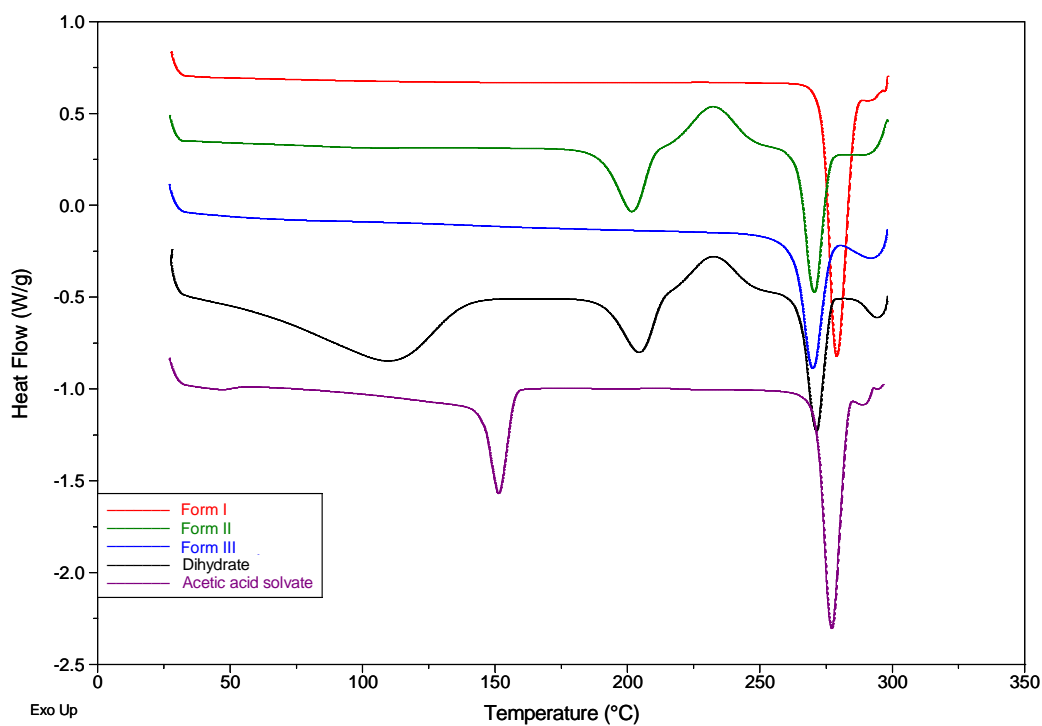
7. Definition of Transition Temperature

156.50°C
28.87J/g

extrapolated
onset tempera-

peak melting
tempera-

157.81°C

Heat Flow (W/g)

Temperature (°C)

Exo Up   Universal V3.3B TA Instruments
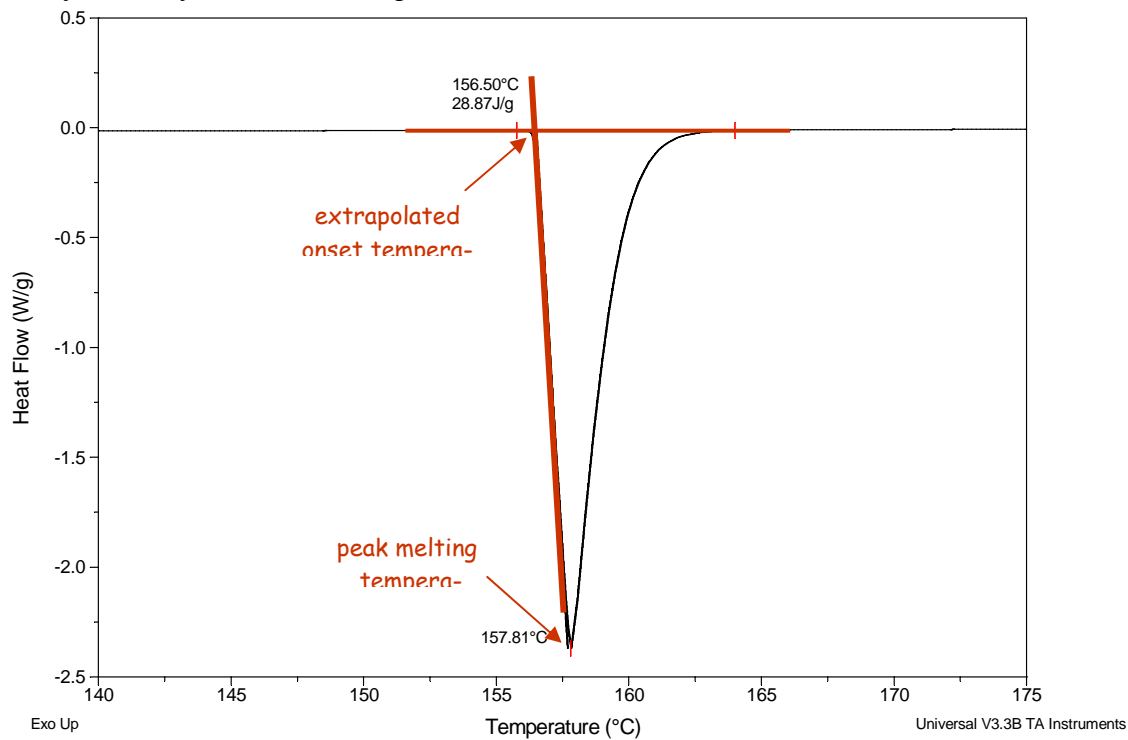
8. Melting processes by DSC

pure substances

- linear melting curve

- melting point defined by onset temperature

eutectic melt

melting with decomposition

- exothermic
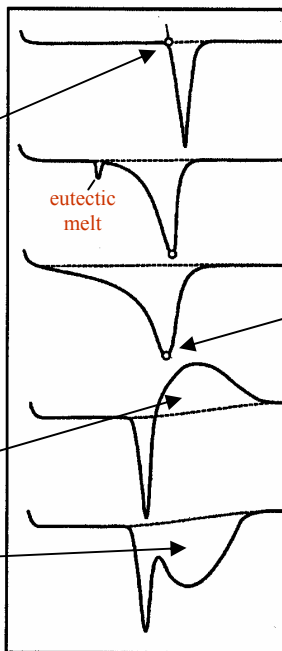
- endothermic

impure substances

- concave melting curve

- melting characterized at peak maxima

- eutectic impurities may produce a second peak

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9. Glass Transition

- second-order transition characterized by change in heat capacity (no heat absorbed or evolved)

- transition from a disordered solid to a liquid

- appears as a step (endothermic direction) in the DSC curve
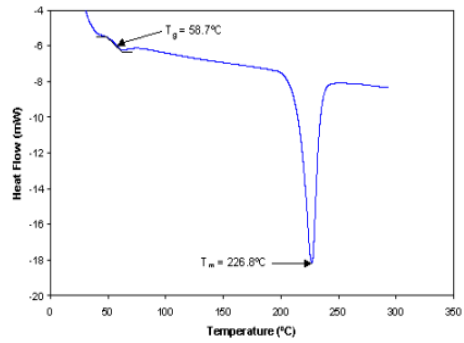
- a gradual volume or enthalpy change may occur, producing an endothermic peak superimposed on the glass transition
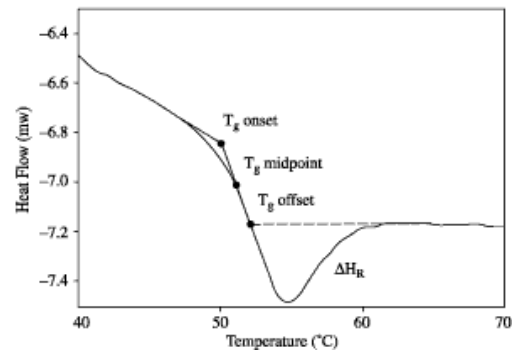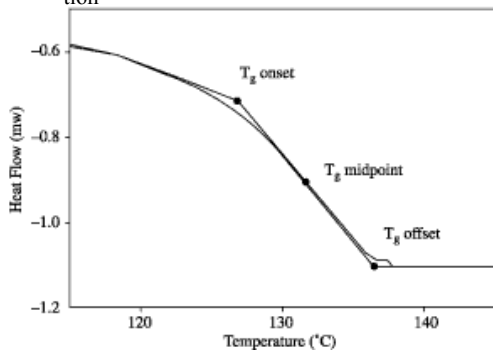
10 Enthalpy of fusion
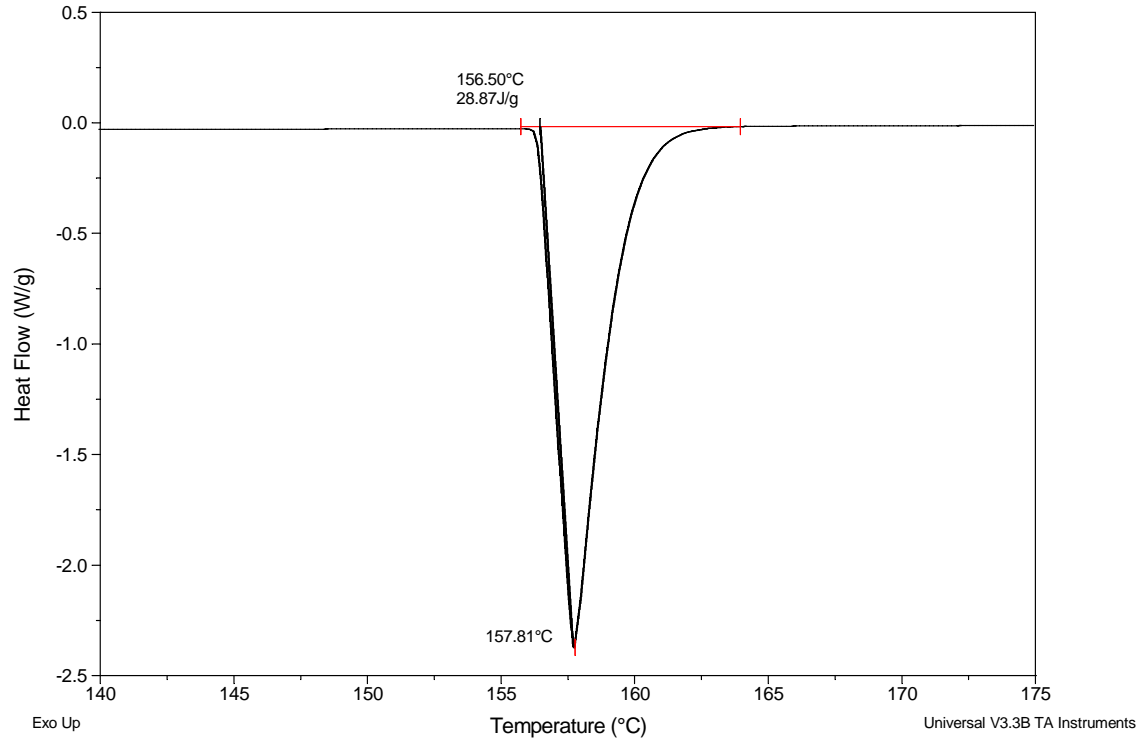
11. Burger's Rules for Polymorphic Transitions
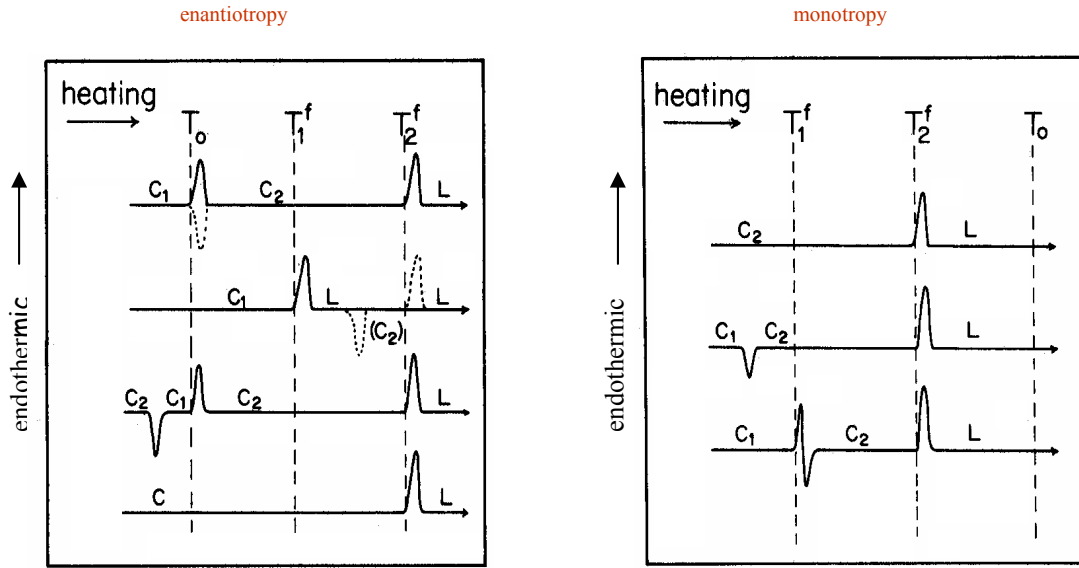
Heat of Transition Rule

- endo-/exothermic solid-solid transition

- exothermic solid-solid transition

Heat of Fusion Rule

- higher melting form; lower DH_f

- higher melting form; higher DH_f

12. Enthalpy of Fusion by DSC

single (well-defined) melting endotherm
- area under peak
- minimal decomposition/sublimation
- readily measured for high melting polymorph
- can be measured for low melting polymorph

multiple thermal events leading to stable melt
- solid-solid transitions (A to B) from which the transition enthalpy (DH$_{TR}$) can be measured (assumes negligible heat capacity difference between polymorphs over temperatures of interest)
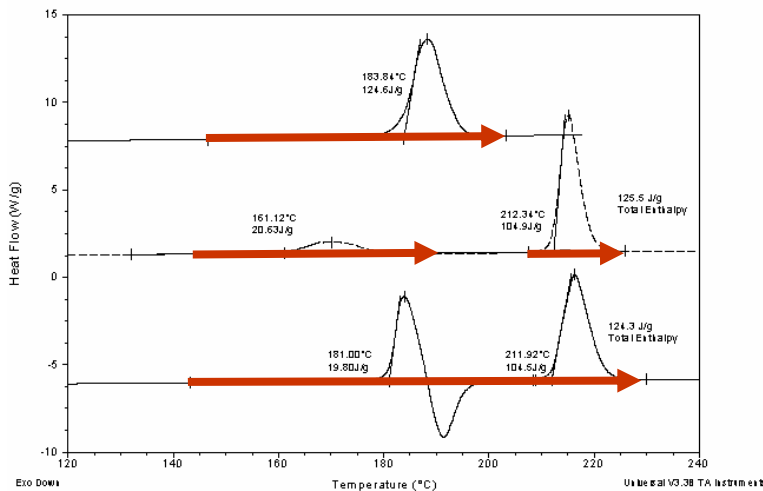
crystallization of stable form (B) from melt of (A)

$DH_f{}^A = DH_f{}^B - DH_{TR}$ $DH_f{}^A$ = area under all peaks from B to the stable melt,

13. Effect of Heating Rate

- many transitions (evaporation, crystallization, decomposition, etc.) are kinetic events

    … they will shift to higher temperature when heated at a higher rate

- the total heat flow increases linearly with heating rate due to the heat capacity of the sample

    … increasing the scanning rate increases sensitivity, while decreasing the scanning rate increases resolution

- to obtain thermal event temperatures close to the true thermodynamic value, slow scanning rates (e.g., 1–5 K/min) should be used
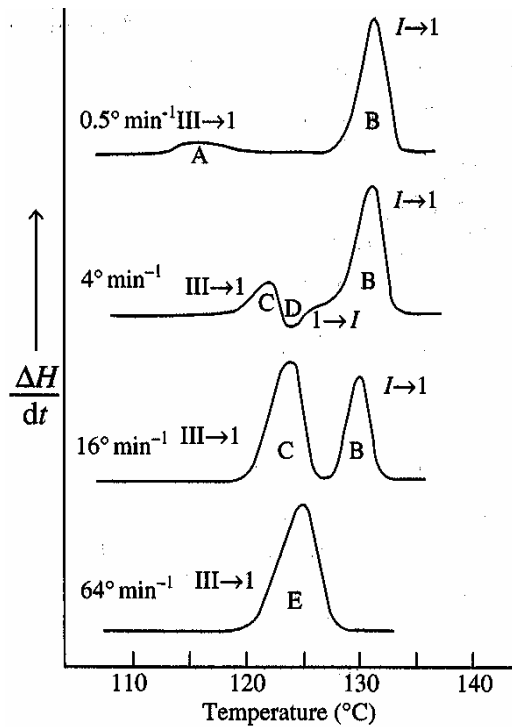
DSC traces of a low melting polymorph collected at four different heating rates. (Burger, 1975)

14. Effect of Phase Impurities

- lots A and B of lower melting polymorph (identical by XRD) are different by DSC
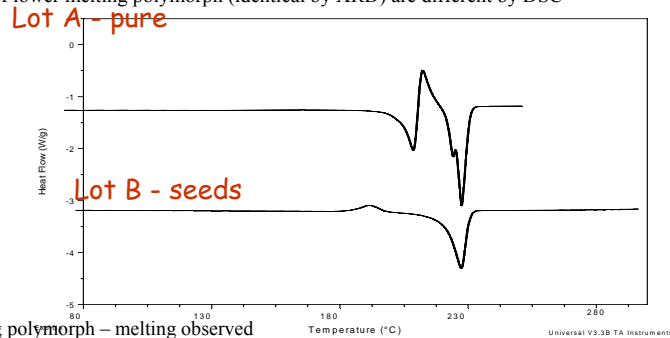
- Lot A: pure low melting polymorph – melting observed

- Lot B: seeds of high melting polymorph induce solid-state transition below the melting temperature of the low melting polymorph

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15. Polymorph Characterization: Variable Melting Point

- lots A and B of lower melting polymorph (identical by XRD) appear to have a "variable" melting point
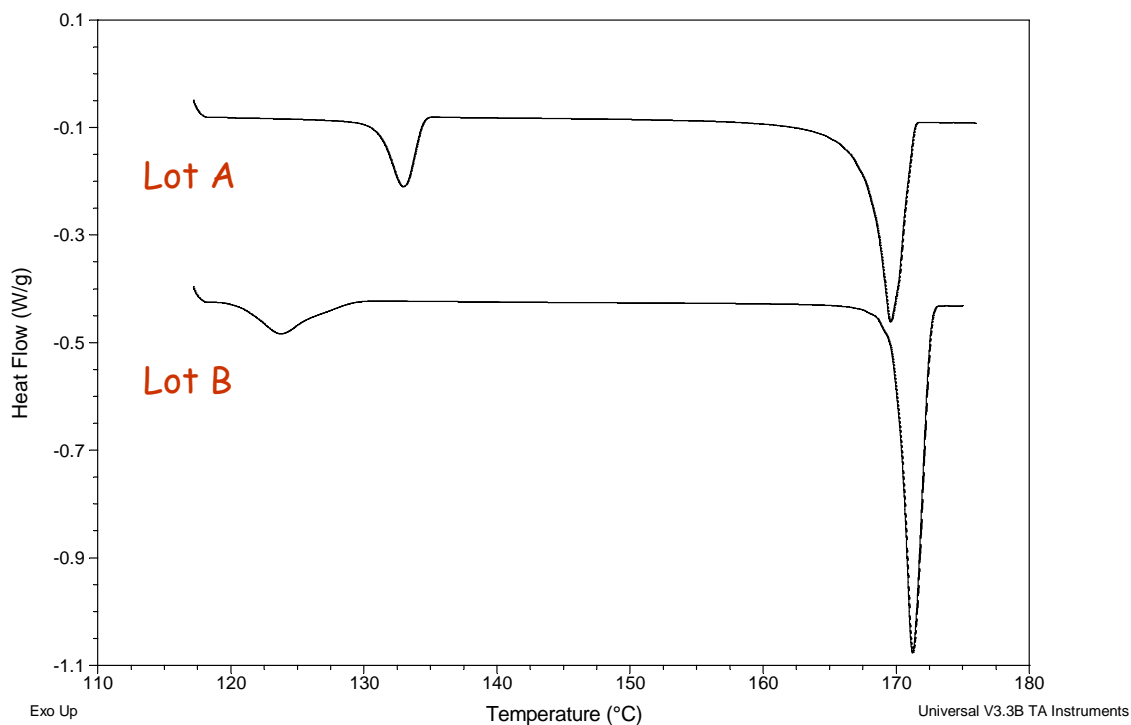
- although melting usually happens at a fixed temperature, solid-solid transition temperatures can vary greatly owing to the sluggishness of solid-state processes

16. Reversing and Non-Reversing Contributions to Total DSC Heat Flow

total heat flow resulting
from average heating rate

$$\mathrm{d}Q/\mathrm{d}t = C_{\mathrm{p}} \cdot \mathrm{d}T/\mathrm{d}t + f(t,T)$$

reversing signal
heat flow resulting from
sinusoidal temperature modulation
(heat capacity component)

non-reversing signal
(kinetic component)
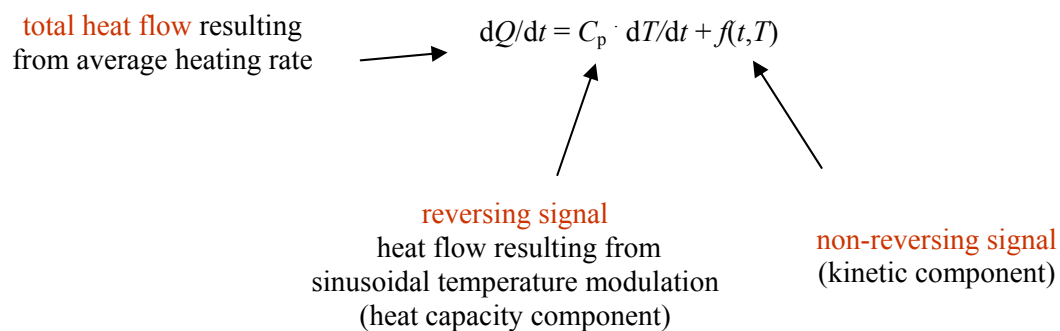
* whereas solid-solid transitions are generally too sluggish to be reversing at the time scale of the measurement, melting has a moderately strong reversing component

17. Polymorph Characterization: Variable Melting Point

- the low temperature endotherm was predominantly non-reversing, suggestive of a solid-solid transition

- small reversing component discernable on close inspection of endothermic conversions occurring at the higher temperatures, i.e., near the melting point
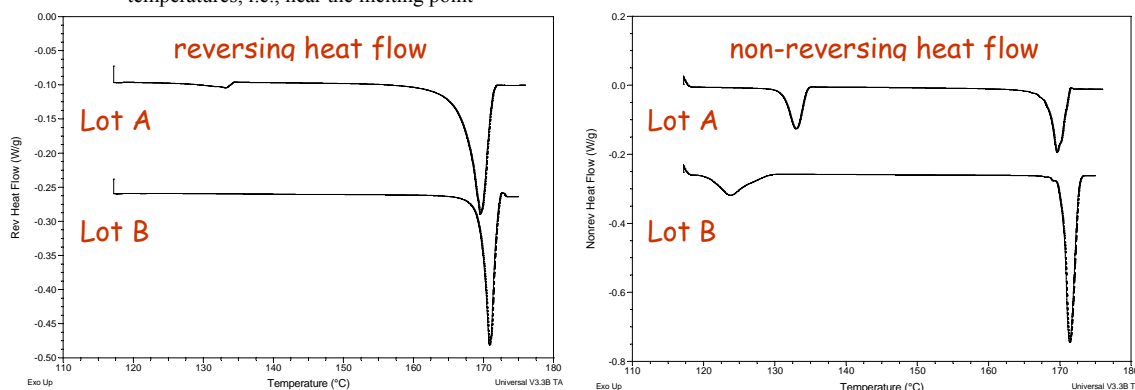
- the "variable" melting point was related to the large stability difference between the two polymorphs; the system was driven to undergo both melting and solid-state conversion to the higher melting form

18. Polymorph Stability from Melting and Eutectic Melting Data (see details volII)

- polymorph stability predicted from pure melting data near the melting temperatures

$$(G_1 - G_2)(T_{m1}) = DH_{m2}(T_{m2} - T_{m1})/T_{m2}$$

$$(G_1 - G_2)(T_{m2}) = DH_{m1}(T_{m2} - T_{m1})/T_{m1}$$

- eutectic melting method developed to establish thermodynamic stability of polymorph pairs over larger temperature range
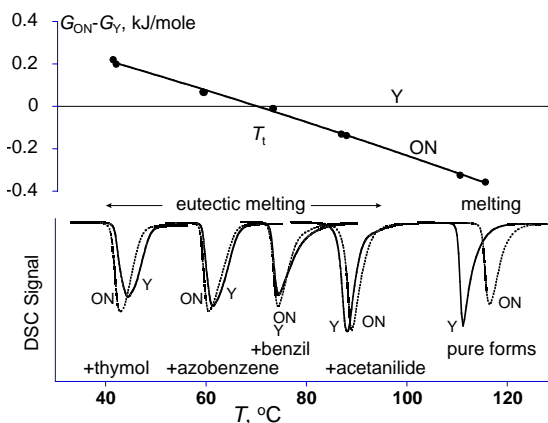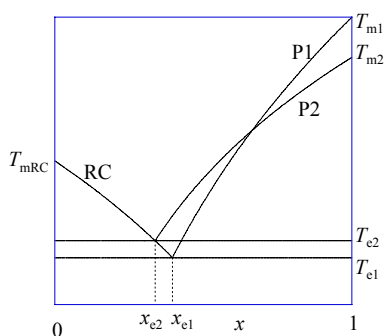
$$(G_1 - G_2)(T_{e1}) = DH_{me2}(T_{e2} - T_{e1})/(x_{e2}T_{e2})$$

$$(G_1 - G_2)(T_{e2}) = DH_{me1}(T_{e2} - T_{e1})/(x_{e1}T_{e1})$$

Yu, L. *J. Pharm*. Sci., **1995**, *84(8)*, 966-974.

Yu, L. *J. Am. Chem*. Soc, **2000**, *122*, 585-591.

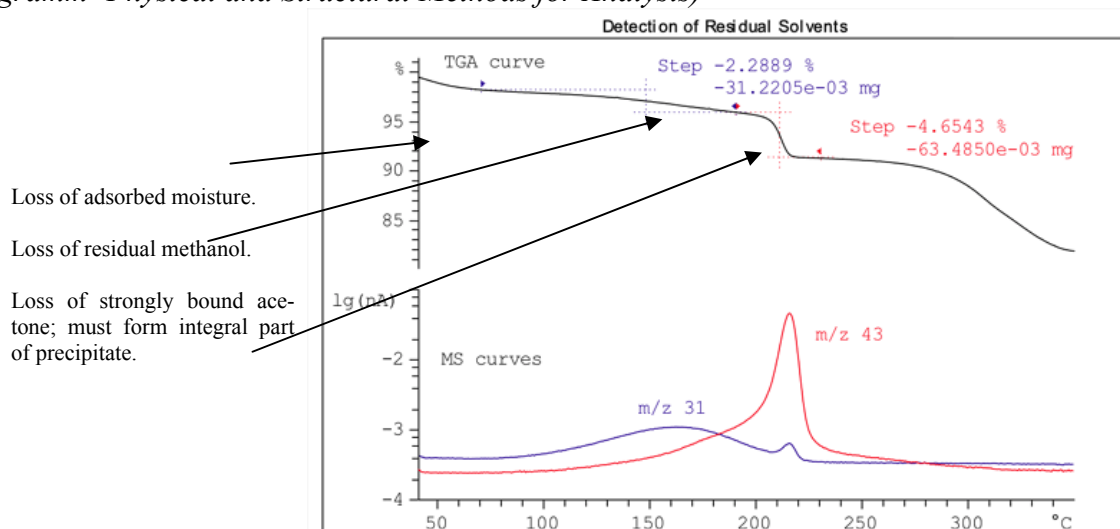## 20. Best Practices of Thermal Analysis
- small sample size
- good thermal contact between the sample and the temperature-sensing device
- proper sample encapsulation
- starting temperature well below expected transition temperature
- slow scanning speeds

- proper instrument calibration
- use purge gas (N_2 or He) to remove corrosive off-gases
- avoid decomposition in the DSC

One can improve the utility of these techniques by combining them with other analytical procedures. Two successful instruments are obtained by combining as follows:

- TGA + Mass Spectrometry: TGA-MS
- TGA + Infrared Spectroscopy: TGA-FTIR

21. A pharmaceutical compound is studied to determine the presence of solvents used in its precipitation. Both methanol and acetone are found.(see details in master programm- Physical and Structural Methods for Analysis)

Detection of Residual Solvents

Loss of adsorbed moisture.

Loss of residual methanol.

Loss of strongly bound acetone; must form integral part of precipitate.

16.4 Differential Scanning Calorimetry-A case study

(A case study for Polymer industry (Plastics-electronics, paints, electronics, lithography, ink-jet printing, flat-display)

The two basic types of DSC instruments: power compensation and heat-flux (figure 16.5) are employed in polymer studies. Need not high temperatures the sample holder is Al or Pt (for inert case) pans; Sensors- Pt resistance thermometers, separate sensors and heaters for the sample and reference; Furnace- separate blocks for sample and reference cells; Temperature controller-differential thermal power is supplied to the heaters to maintain the temperature of the sample and reference at the program value. The most popular DS- calorimeter with computer control using AD card and data acquisition system is shown in figure 16.6. In the most popular DSC design (figure 16.6), two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path. In one pan, is put the sample. The other one is the reference pan or leave it empty. The computer turns on the furnace to heat the two pans at a specific rate, usually something like 10^oC per minute. The computer makes absolutely sure that the heating rate stays exactly the same throughout the experiment. But more importantly, it makes sure that the two separate pans heat at the same rate as each other. The simple reason is that the two pans are different. One has sample in it, and one doesn't. The sample means there is extra material in the sample pan. Having extra material means

that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. Just how much more heat is what we measure in a DSC experiment. We make a plot as the temperature increases. On the *x*-axis we plot the temperature. On the *y*-axis we plot the difference in heat flow between the sample and reference.


Figure16.6- DSC configuration coupled with DAC for heating and temperature control
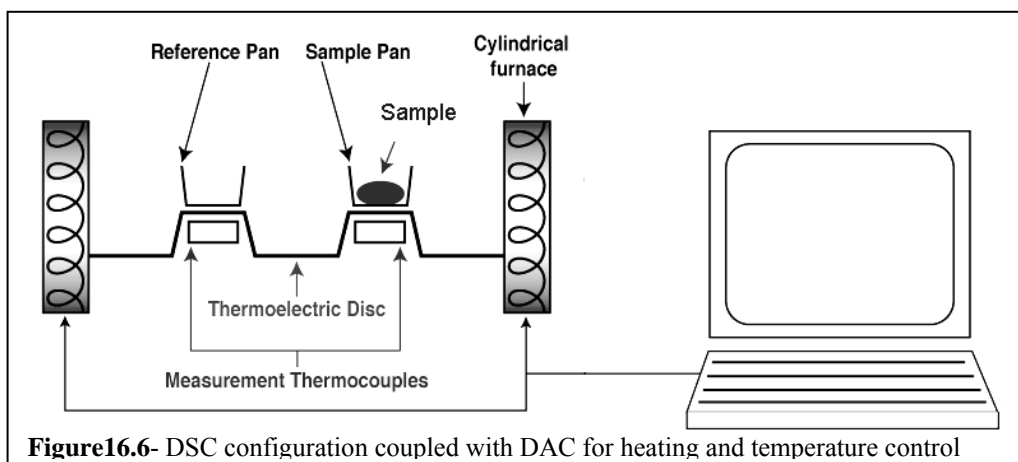
Differential scanning calorimetry studies what we call the *thermal transitions* in all materials spanning from simple to polymer. The melting of a crystalline body or polymer is one example, the glass transition is also a thermal transition, heat capacity, latent heat, etc.

Heat capacity: When we start heating our two pans, the computer will plot the difference in heat flow against temperature. That is to say, we're plotting the heat absorbed by the sample against temperature. In final we calculate heat capacity directly by: $\dot{Q} = mc\dot{T}$. We get the heat capacity by dividing the heat supplied by the resulting temperature increase. We figure the heat capacity from the DSC plot.

Glass transition: when we heat the glass or a polymer, after a certain temperature, our plot will shift downward suddenly, like this:

This means heat is being absorbed by the sample. It also means that we have a change (increase) in its heat capacity. This happens because the glass/polymer has just gone through the glass transition. And as you learned on the glass transition page, glasses and polymers have a higher heat capacity above the glass transition temperature than they do below it. Because of this change in heat capacity that occurs at the glass transition, we can use DSC to measure a glass transition temperature. We may notice that the change doesn't occur suddenly, but takes place over a temperature range. This makes picking one discreet *T*g kind of tricky, but we usually just take the middle of the incline to be the *T*g.
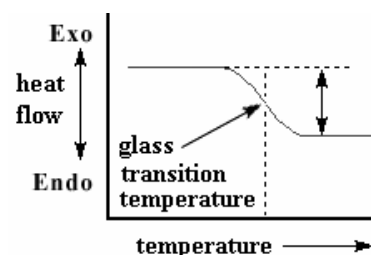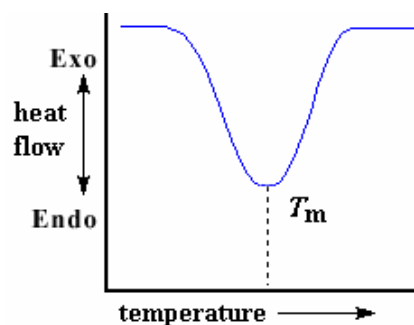
Crystallization

Above the glass transition, the polymers and glasses have a lot of mobility. They wiggle and squirm,

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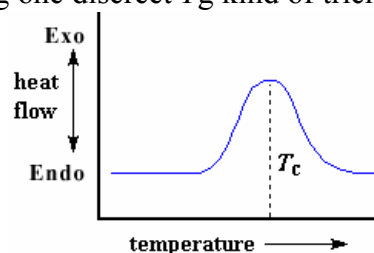
and never stay in one position for very long. When they reach the right temperature, they will have gained enough energy to move into very ordered arrangements, which we call crystals, of course. When liquids fall into these crystalline arrangements, they give off heat. We can see this as a big peak in the plot of heat flow versus temperature. This peak tells us a lot of things. The temperature at the highest point is usually considered to be the crystallization temperature, or T_c. Also, we can measure the area of the peak, and this will tell us the latent energy of crystallization. We call crystallization an *exothermic* transition.

Melting (polymer case)

Heat may allow crystals to form in a polymer, but too much of it can be their undoing. If we keep heating the polymer past its Tc, eventually we'll reach another thermal transition, one called melting. When we reach the polymer's melting temperature, or T_m, those polymer crystals begin to fall apart, that is they melt. The chains come out of their ordered arrangements, and begin to move around freely. Remember the heat that the polymer gave off when it crystallized? Well when we reach the Tm, it's payback time. There is a latent heat of melting as well as a latent heat of crystallization. When the polymer crystals melt, they must absorb heat in order to do so. Remember melting is a first order transition. This means that when it reach the melting temperature, the polymer's temperature won't rise until all the crystals have melted. This also means that the furnace is going to have to put additional heat into the polymer in order to melt both the crystals and keep the temperature rising at the same rate as that of the reference pan. This extra heat flow during melting shows up as a large dip in our DSC plot as heat is absorbed by the polymer. It looks like this on right page. Note this not happen in regualar solids where melting and crystallization temperature are identical.

Review: We saw a step in the plot when the polymer was heated past its glass transition temperature. Then we saw a big peak when the polymer reached its crystallization temperature. Then finally we saw a big dip when the polymer reached its melting temperature. To put them all together, a whole plot will often look something like this:

The entire DSC plot.
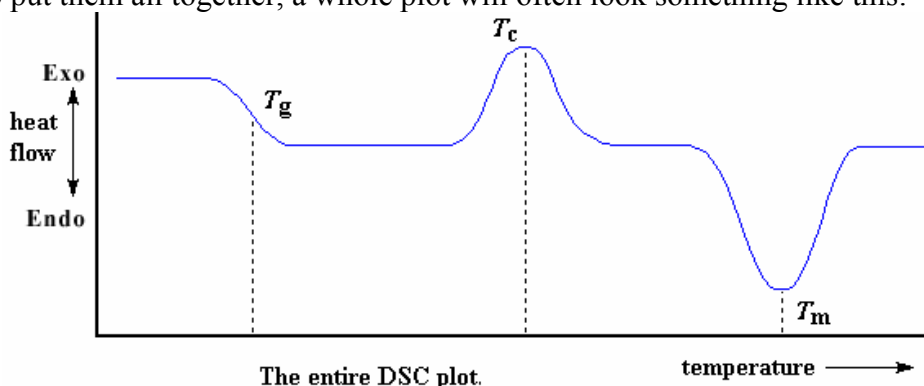
The crystallization peak and the melting dip will only show up for polymers that can form crystals. Completely amorphous polymers won't show any crystallization, or any melting either. But polymers with both crystalline and amorphous domains, will

show all the features you see above. Simple solids have $T_c = T_m$ and no show up glass transition.

Because there is a change in heat capacity, but there is no latent heat involved with the glass transition, we call the glass transition a *second order transition*. Transitions like melting and crystallization, which do have latent heats, are called *first order transitions*.

Counting the crystallinity (for polymers, quasiamorphous solids, etc)

DSC can also tell us how much of a polymer is crystalline and how much is amorphous. If you read the page dealing with polymer crystallinity(see Chapter 7), you know that many polymers contain both amorphous and crystalline material. If we know the latent heat of melting, ΔH_m, we can figure out the answer. The first thing we have to do is measure the area of that big dip we have for the melting of the polymer. Now our plot is a plot of heat flow per gram of material, versus temperature:

$$area = \frac{heat \times temperature}{mass \times time}$$

The heating rate is in units of K/s. So the expression becomes simpler:

$$\frac{area}{heating\ rate} = \frac{J}{g}$$

If we do the same calculation for our peak that we got on the DSC plot for the crystallization of the polymer, we can get the total heat evolved during the crystallization. We'll call the heat total heat given off during melting Hm, total, and we'll call the heat of the crystallization Hc, total: Hm,total-Hc,total =H' . H' is the heat given off by that part of the polymer sample which was already in the crystalline state before we heated the polymer above the Tc. We want to know how much of the polymer was crystalline before we induced more of it to become crystalline. That's why we subtract the heat given off at crystallization. Now with number H' we can figure up the percent crystallinity. We're going to divide it by the specific heat of melting, Hc*. The specific heat of melting? That's the amount of heat given off by a certain amount, usually one gram, of a polymer. H' is in joules, and the specific heat of melting is usually given in joules per gram, so we're going to get an answer in grams, which we'll call mc.

$$m_c = \frac{H'}{H_m^*}$$

This is the total amount of grams of polymer that were crystalline below the Tc. Now if we divide this number by the weight of our sample, mtotal, we get the fraction of the sample that was crystalline, and then of course, the percent crystallinity:

$$\frac{m_c}{m_{total}} = crystalline\ fraction$$

16.5 References Chapter 15 & 16

1. J. Sturtevant, Calorimetry, in A. Weissberger, *Technique of Organic Chemistry*, 3 ed., vol. I, Willey, N.Y, (1959)
2. *Comprehensive Handbook of Calorimetry and Thermal Analysis*. Edited by The Japan Society of Calorimetry and Thermal Analysis English Language Edition 2004 John Wiley & Sons, Ltd ISBN: 0-470-85152-X

Chapter 17

Heat transport

17.1 What is Heat (Energy) Transport?

The transport of the thermal energy, general accepted as heat transport, is everywhere in our daily life from the cofee cup cooling, microave and stove cooking, heat preserving in buiding, solar heating, to cloud formation and rain, global warming, etc. Also we find this subject in welding, iron casting, polymer forming, chemical reaction, etc. In particular in electronic industry where chip-industry is involved with evaporation-deposition of thin layer and chemical vapour deposition(CVD) the heat and mass transport must be considered. There are few examples:

➡ Most CVD processes operate at some temperature other than that of the ambient. Sometimes only the sample is heated ("cold-wall reactors"); in other cases the whole process chamber (often a quartz or glass furnace tube) is heated to the process chamber ("hot-wall reactors"). Some processes operate at reduced temperatures (e.g. deposition of parylene from dimer precursors). All solar cells have in their fabrication process steps where CVD is deeply employee.

➡ Processor heating and its complicated aspects to remove heat to keep the operating temperature in optimum conditions engage a series of thermal engineering. Why our brain does not heat even though make billionth operations more than any ultraperformant computer?

➡ Photosynthesis process is another example: conversion of solar energy into heat and energy to build organics from CO_2, water and minerals

➡ Why our body need 37^0C to have an optimum metabolism and snacks need to get heat by warming under sunlight?

➡ Changes in temperature require transport of heat (thermal energy) from a heating element to the sample. To control and monitor the temperature of the sample, we need to understand the mechanisms by which heat is transported to the sample and the methods by which temperature may be measured.

➡ The temperature of the gas stream will be affected by its surroundings (including heated walls or substrates), and this temperature is in turn likely to affect the rates of chemical reactions in the gas phase, as well as possibly changing the nature of the fluid flow (natural convection). We need to understand how heat is transported in the gas in order to analyze the effects of local temperature on process behavior.

➡ It is important global warming?. If yes, how does change the temperature distribution on earth ?

➡ How we can find one of the best solution for spacecraft shuttle do not overheat when come into atmosphere?. Here we need materials with the best thermal properties

We can continue with series of examples where we are encountering problems with heat transport. Therefore a basics understanding of the phenomena should be considered.

17.2 Mechanisms of Heat Transfer: conduction

There are three modes of heat transfer: conduction (solid, fluids); convection (fluids); thermal radiation (gases, liquids, vacuum)

17.2.1 Conduction heat transfer

Means the transfer of energy in a solid or fluid via molecular contact without bulk motion. The mechanisms to transfer energy is different:

Solids—by lattice vibrations; physical models at atomic level for prediction need.

Fluids—by molecular collisions; atomic level models are involved.

Empirical basis for relating heat flux, q, to temperature difference is given by Fourier's law and its description is in figure 17.1

Figure 17.1- Fourier's law, definition. Flux density is proportional with the temperature gradient
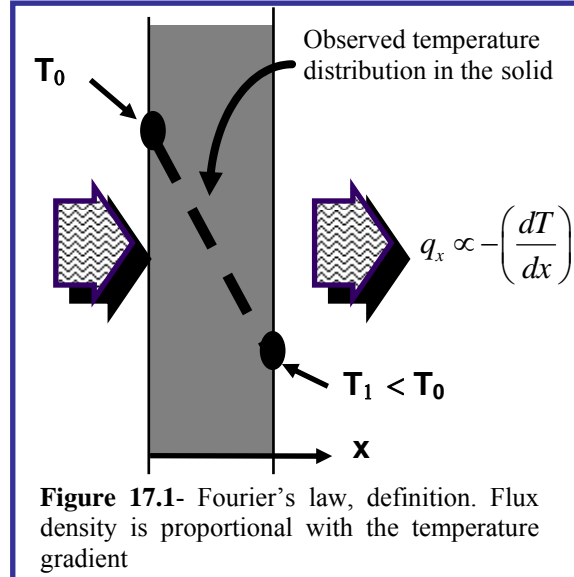
17.2.2 The Fourier's law

The relation between the heat flux, q, and the gradient of temperature is called the constitutive relation. The proportionality constant, k, is defined as the thermal conductivity, a thermophysical property. That is the Fourer's law established in the first quarter of 19th century. Fourier (1768-1830) shown for the energy transport by conduction (figure 17.1)

$$\frac{Q}{\Delta t A} = -k\frac{\Delta T}{l} \xrightarrow{q_x = \frac{Q}{\Delta t A} \text{ and } l = \Delta x} q_x = -k\frac{\Delta T}{\Delta x}$$

$$\text{or} \quad q_x = -k\lim_{\Delta x \to 0}\frac{\Delta T}{\Delta x} = -k\frac{dT}{dx}$$

17.1

where q_x is local heat flow per unit area (heat flux density). This equation is the one-dimensional Fourier's law (the first Fourier'law) of heat conduction valid when T=T(x).

It states that the heat flux by conduction is proportional with the temperature gradient. In time scale when two bodies with $T_0 > T$ are in contact the temperature profile shows like in figure 17.2.

Figure 17.2- Two bodies in thermal contact, temperature profile in time scale.
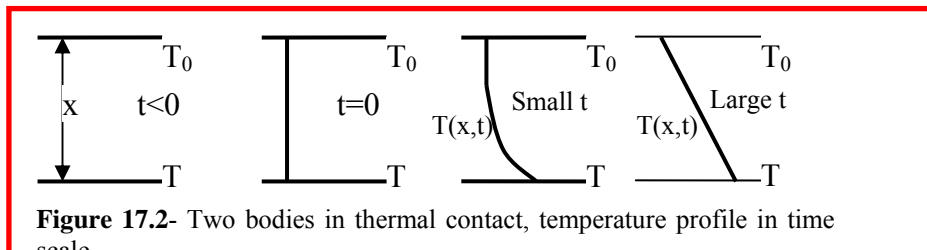
Few examples are in figure 17.3. As we will see the thermal energy can be transported by different mechanisms. In this section we consider energy transport by the mechanism of conduction only. In next sections we consider transport energy by con-

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vection, diffusion and radiation. Figure 17.3 gives a general idea about energy transport by conduction: thermal energy should be poportional with the temperature difference.
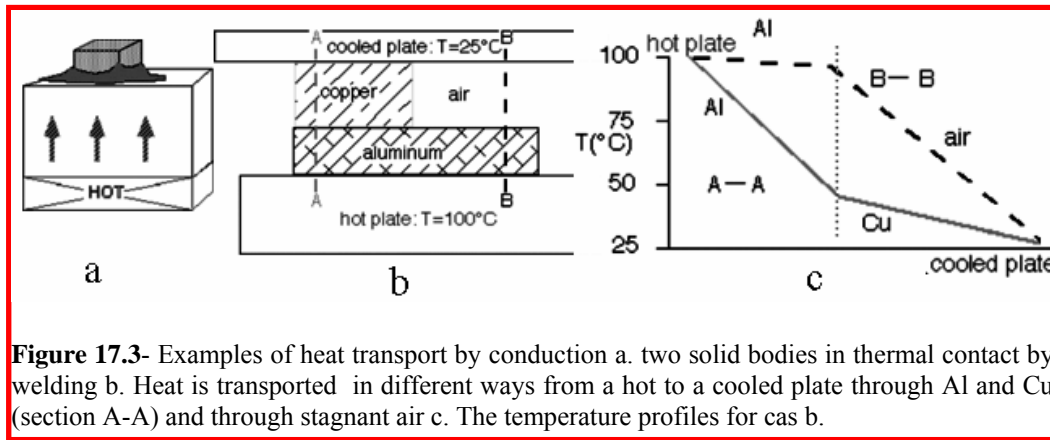

Figure 17.3- Examples of heat transport by conduction a. two solid bodies in thermal contact by welding b. Heat is transported in different ways from a hot to a cooled plate through Al and Cu (section A-A) and through stagnant air c. The temperature profiles for cas b.

We notice k- is the thermal conductivity coefficient of the body and for isotropic conditions we have:

$$q_x = -k\frac{\partial T}{\partial x}, q_y = -k\frac{\partial T}{\partial y}, q_z = -k\frac{\partial T}{\partial z}$$

These three relations are the component of the single equation:

$$\mathbf{q} = -k\nabla\mathbf{T} = -k\left(\frac{\partial T}{\partial x}\vec{i} + \frac{\partial T}{\partial y}\vec{j} + \frac{\partial T}{\partial x}\vec{k}\right) = -k\text{grad}\mathrm{T}$$

which is the three-dimensional form of Fourier's law. It states the heat flux vector **q** is proportional with the temperature gradient $\nabla\mathbf{T}$ and is oppositely directed.

Without loosing in generality we consider in body a small element with mass density, specific heat and w- a heat source defined as power density (energy/time*volume) in x direction with heat flux, q_x, entering in section A and in section B the heat flux out of element (q_{x+dx}). If the element has area A in section A and B then it is easy to calculate from energy balance:
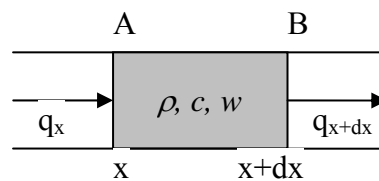
Thermal energy accumulated in element= heat generated+ (heat energy in- heat energy out)

The thermal energy accumulated is: $\delta Q = dM \times cdT = \rho Adx \times cdT$, then results the second Fourier's law:

$$\left.\begin{array}{l} \rho Adxc\,dT = wAdxdt + \left[q_x - q_{x+dx}\right]Adt \\[2mm] q_x - q_{x+dx} = -\dfrac{\partial q_x}{\partial x}dx \end{array}\right\} \rightarrow \rho Adxc\,dT = wAdxdt - \dfrac{\partial q_x}{\partial x}dxAdt$$

and after simplification   17.2

$$\rho c\frac{\partial T}{\partial t} = -\frac{\partial q_x}{\partial x} + w$$

Now we can extend our analysis to three-dimension obtaining:

$$\rho c\frac{\partial T}{\partial t} = -\nabla \mathbf{q} + \mathbf{w} \qquad\qquad 17.3$$

Combining the two Fourier's laws it obtains a general equation for thermal energy transport:

$$\rho c\frac{\partial T}{\partial t} = \nabla(k\nabla T) + \mathbf{w},\ \text{for a non isotropic body}$$

$$\rho c\frac{\partial T}{\partial t} = k\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + \mathbf{w},\ \text{for isotropic body}$$

$$17.4$$

or

$$\rho c\frac{\partial T}{\partial t} = k\Delta T + w \xleftrightarrow{\ \alpha = \frac{k}{\rho c}\ } \frac{\partial T}{\partial t} = \alpha\Delta T + w'$$

α- being known as thermal diffusivity. Sometimes we denote $\alpha = D_{th}$ to indicate the similarity between diffusion coefficient in mass transport and heat transport.

Units: if $[q] = \dfrac{J}{m^2 s} \Rightarrow [k] = \dfrac{J}{m \times s \times K} = \dfrac{watt}{mK}$; $[\alpha] = \dfrac{m^2}{s}$;

if $[q] = \dfrac{cal}{cm^2 s} \Rightarrow [k] = \dfrac{cal}{cm \times s \times K}$; $[\alpha] = \dfrac{cm^2}{s}$

The thermal conductivity, k, is a material property and dependent of conduction mechanisms. Conduction in a gas takes place by the same mechanisms as mass transport. The kinetic theory gives a reliable model connected with molecular motion. Heat conduction in a solid can be thought of as the diffusion of phonons (lattice vibrations).

Conductive heat transfer can be described by the same formalism (the diffusion equation) that we are using to study mass diffusion. However, in heat transport we'll find that even steady-state solutions are interesting, since fluxes generaly don't go to zero at surfaces as in the case of mass transport.

Figure 17.3 shows the influence of the materials properties on the heat transport. For example, air is such a poor thermal conductor [IF it isn't moving!] that most of a temperature gradient will occur across an air space with very little in surrounding good conductors such as metals. The cross-section B-B at right shows this effect: the aluminum is essentially isothermal with all the temperature drop across the air gap. There is few example for thermal conductivity of the materials:

material	c_p (J/gm)	ρ (gm/cm^3)	c_{vol}(J/cm^3)	K_{th} (W/cm°C)
air	1.0	0.0012	.0012	0.0002
wood	2.7	0.6	1.6	0.001
glass	0.75	2.2	1.6	0.01
st. steel	0.4	8.0	3.2	0.15
iron	0.4	7.8	3.1	0.8
silicon	0.75	2.3	1.7	1.2
aluminum	0.9	2.7	2.4	2.4
copper	0.4	8.9	3.6	4
diamond	0.5	3.2	1.6	14

17.3 Convection heat transfer

Convective heat transport occurs when one of the body is a fluid. Convection occurs in liquids and gases. Energy is carried with fluid motion when convection occurs. A schematic idea with convective heat transport is given in figure 17.4.

Convective processes:
- Forced convection

Free convection
- Mixed convection
- Convective phase change: Boiling and condensation

Types of convective processes

Single phase fluids (gases and liquids):
- Forced convection
- Free convection, or natural convection
- Mixed convection (forced plus free)
- Convection with phase change: Boiling, Condensation

Figure 17.4 – Heat transport by convective process. A fluid in contact with a surface body transfer thermal energy from body to ambient

Convective processes involve the physical transfer of gases or liquids containing heat energy. The simplistic treatment of convection we employed in studying mass transport is also useful; again we will find that we can often approximate transport in complex flows by assuming that diffusion takes place across streamlines and convection dominates along them.

*Convective heat transport also introduces a new element: coupling of the fluid motion to the energy transfe*r.

Example: Hot gases are lighter than cool gases, and tend to rise in the presence of gravity. If temperature gradients are large enough, and externally imposed fluid velocities small enough, the expansion leads to convective transport driven by the heat flow: natural convection.

17.3.1 Free convection

Internal flows: Buoyant forces produce the fluid motion. These forces are proportional to the fluid temperature.
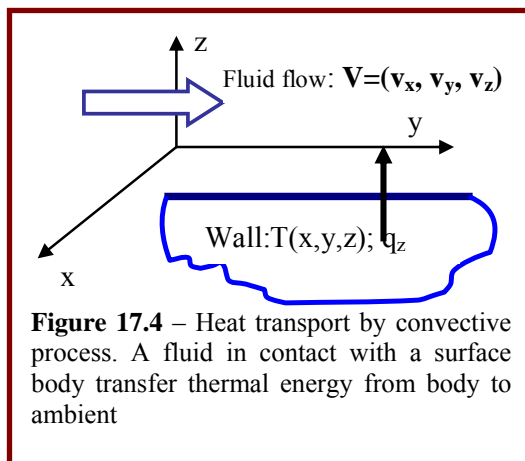
External flows: Buoyant forces produce the fluid motion. These forces are proportional to the fluid temperature

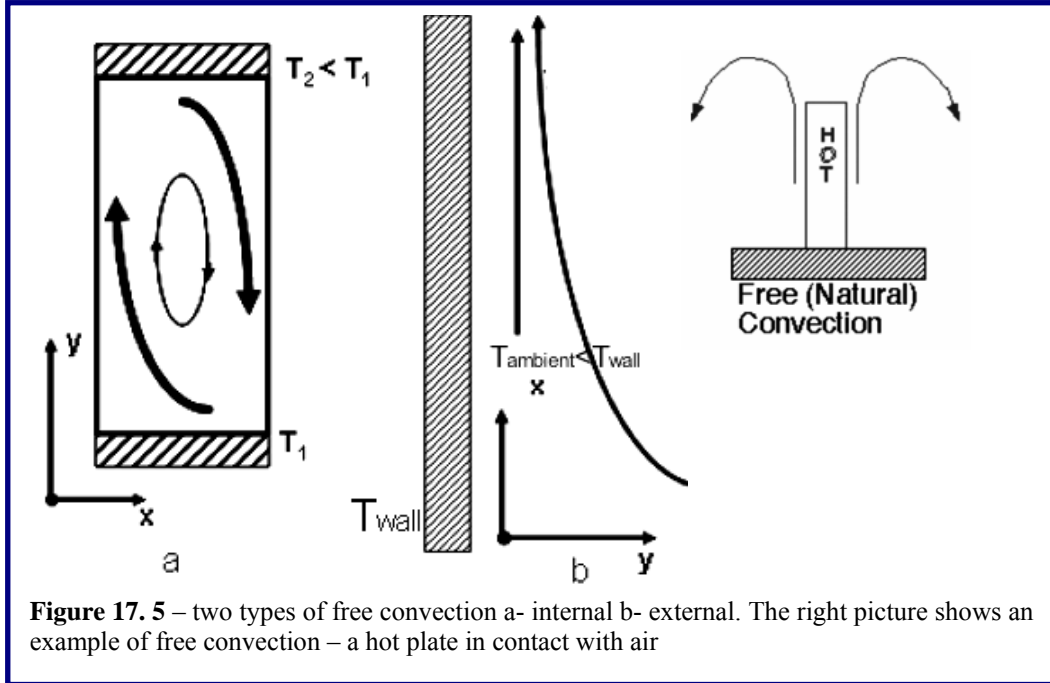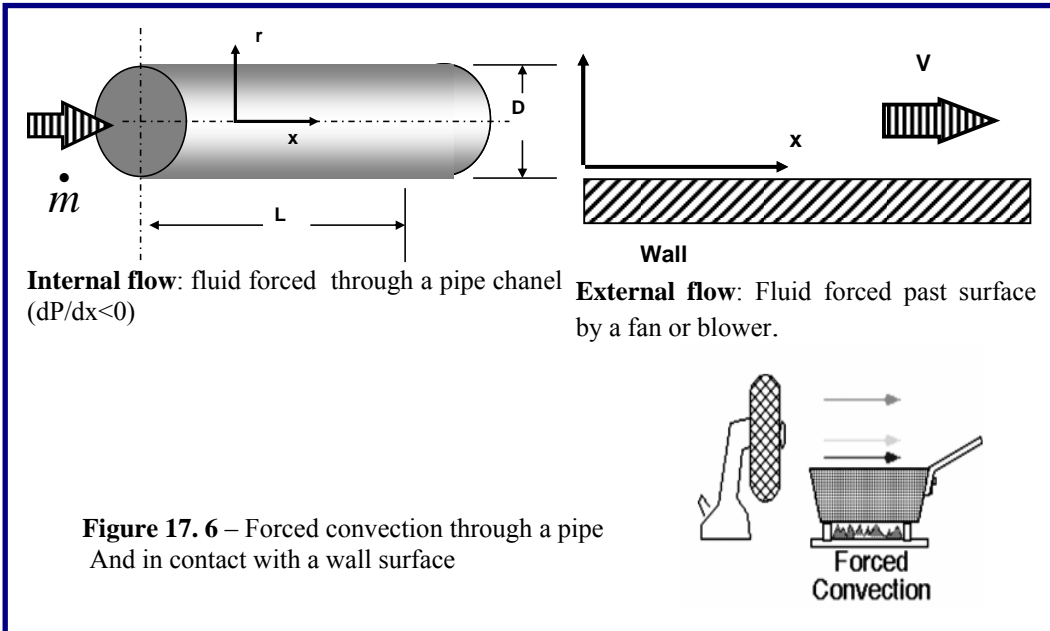Both phenomena are represented in figure 5

Figure 17. 5 – two types of free convection a- internal b- external. The right picture shows an example of free convection – a hot plate in contact with air

17.3.2 Forced convection

Internal flow: fluid forced through a pipe chanel (dP/dx<0)

External flow: Fluid forced past surface by a fan or blower.

Figure 17. 6 – Forced convection through a pipe And in contact with a wall surface

As in the case of mass transport, the combination of simple plug flow with diffusion perpendicular to the streamlines allows simple first approximations for simple situations. Figure 17. 6 gives a general idea where forced convection is involved

17.3.3 Newton's Cooling Law

$$\dot{Q} = hA(T_w - T_a)$$

The quantity **h** is called the <u>convective heat transfer coefficient</u> (*W/m²-K*). It is dependent on the type of fluid flowing past the wall <u>and</u> the velocity distribution. Thus, h is <u>not</u> a thermophysical property.

What is convection doing?
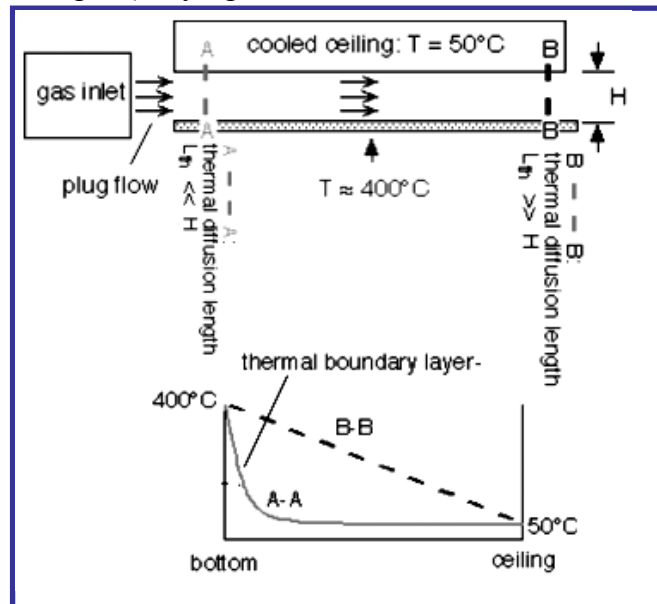
    1. *Clouds –rain circuit--* ➔

- Convection is of crucial importance for the global energy and water balance (Convection transports heat, water vapor, momentum and chemical constituents upwards. Water vapor then condenses and falls out; net convective heating/drying
- Convection generates and/or influences a number of phenomena important to forecasting (thunderstorms, heavy precipitation, hurricanes)
- Convection affects the atmosphere through condensation / evaporation and eddy transports
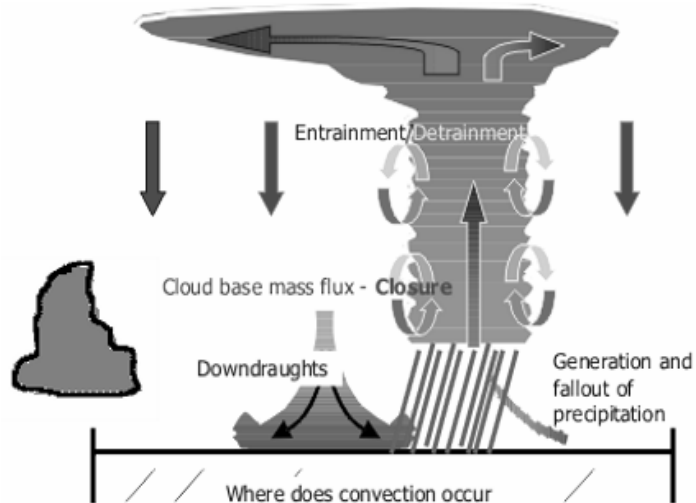
2. *CVD processes.* Let's consider a simple example. We approximate the flow velocity as constant everywhere and assume that heat is carried by convection in the direction of gas flow and by conduction in the gas (obeying a 1-dimensional heat diffusion equation with time being the time in the stream) in the perpendicular direction. Near the entry region (A-A) a narrow boundary layer exists near the hot wall, with the remainder of the gas at the initial temperature.

In the downstream region the temperature profile is essentially linear, as for a stationary conductive medium (B-B). Since the heat loss is proportional to the gradient close to the surface, cooling is much larger in regions like A-A, where large gradients exist in the boundary layer. As the gas heats up, thermal expansion must occur according to the ideal gas law. Thus, the velocity actually should increase as we go downstream. However, thermal diffusivity also increases, since the thermal conductivity increases as about $T^{1.5}$, and the density de-

creases. The two effects tend to compensate (for small amounts of heating, anyway), so it's often convenient to ignore them to first order.

17.3.4 Boundary layer

A simple analysis in figures 17.4 and 5 shows that the fluid cool or heat a surface by wetting. The fluid is not static and move with a speed dependent of mechanical conditions. In gravitational field and in a temperature gradient the bouyance forces rises to ascencional fluxes. The fluid in contact with the surface has speed zero and in its volume reach the speed of the fluid. Newton's law is not valid. In figure 17.7 shows schematic the boundary layer which forms as intelayer between surface and fluid. The heat transport in this case should be reconsidered taking in account the fluid movement. In figure 17.8 is considered a elementary volume at moment t with $T(t,x,y,z)$ and, for simplicity, a heat flux $q(x,y,z)$ flow along y-axis through $dydz$. At $t+dt$ the elementary volume has $T(t+dt, x+dx, y+dy, z+dz)$. The energy balance:
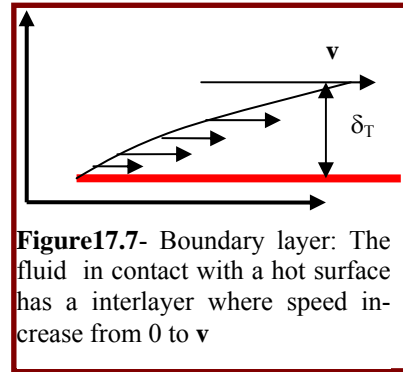

Figure17.7- Boundary layer: The fluid in contact with a hot surface has a interlayer where speed increase from 0 to **v**
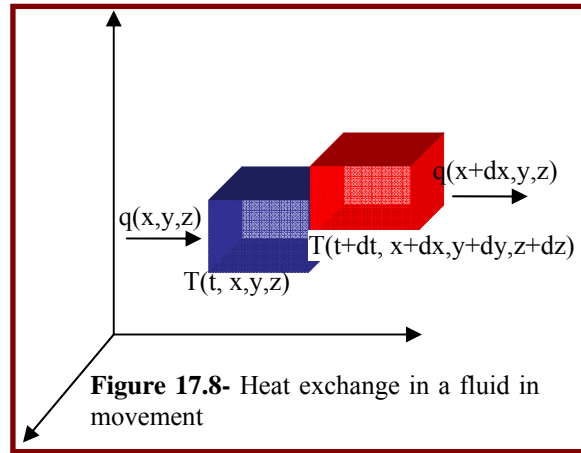

Figure 17.8- Heat exchange in a fluid in movement

$$\delta Q = \rho c_P \left(T(t+dt, x+dx, y+dy, z+dz) - T(t,x,y,z) \right) dxdydz =$$

$$= \rho c_P \left(\frac{\partial T}{\partial t} + \frac{\partial T}{\partial x}\dot{x} + \frac{\partial T}{\partial y}\dot{y} + \frac{\partial T}{\partial z}\dot{z} \right) dxdydzdt; \text{ energy to heat the elementary volume}$$

and

$$\delta Q = -k \left[q(x+dx, y, z) - q(x,y,z) \right] dydzdt = -k\frac{\partial q}{\partial x} dxdydzdt; \text{flux heat through volume}$$

Repeating for all three directions and equilibrating the energy exchange we find:

$$\rho c_P \left(\frac{\partial T}{\partial t} + \frac{\partial T}{\partial x}\dot{x} + \frac{\partial T}{\partial y}\dot{y} + \frac{\partial T}{\partial z}\dot{z} \right) = -k \left(\frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} + \frac{\partial q_z}{\partial z} \right)$$

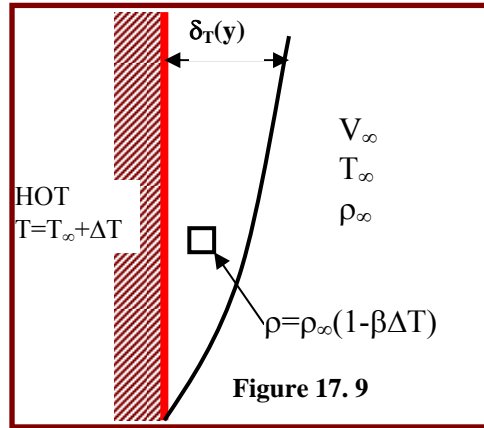or   17.5

$$\rho c_P \left(\frac{\partial T}{\partial t} + \frac{\partial T}{\partial x}\dot{x} + \frac{\partial T}{\partial y}\dot{y} + \frac{\partial T}{\partial z}\dot{z} \right) = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right)$$

The last equation we will use to define the boundary layer for natural convection

17.3.5 Natural Convection

When heat is added to a gas, it expands, and thus changes density. If gravity is present (i.e. pretty much all the cases we're interested in!) this change in density induces a change in the body forces, and the forces may cause the fluid to move "by itself" without any externally imposed flow velocity. This is the phenomenon of **natural convection**, ubiquitous in our daily experience: rising clouds of cigarette or campfire smoke, ripples of heat from a car's hood, thunderheads reaching into the stratosphere. Natural convection is usually very undesirable in a CVD reactor, since it represents an uncontrolled gas flow. We won't try to deal with the full complexity of natural convection flows, but will treat a particularly simple geometry to illustrate the typical sorts of quantities that arise, and how to estimate whether natural convection is

Figure 17. 9

likely to be important in a given configuration. As in our treatment of boundary layer flows, we consider a flow composed of a "free stream" region, in this case with a constant temperature and density as well as velocity, and a relatively narrow thermal boundary layer over which temperature, velocity, and density change (figure17 9). [In the general case one ought to consider two boundary layers one for velocity and one for temperature; however, most gases have similar momentum and energy diffusion rates so we simplify things a bit.] We introduce the modulus of thermal expansion to relate the density to the change in temperature (β).To estimate the velocity, we balance the heat carried through the boundary layer of height H by convection (i.e. transport up) with diffusion of heat into the boundary layer (i.e. transport to the right): in steady state these must be equal. We thus obtain an expression for the velocity in terms of the boundary layer thickness:

$$\rho c_P \left(\frac{\partial T}{\partial t} + \frac{\partial T}{\partial x}\dot{x} + \frac{\partial T}{\partial y}\dot{y} + \frac{\partial T}{\partial z}\dot{z} \right) = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \rightarrow \rho c_P \frac{\partial T}{\partial y}\dot{y} = k \frac{\partial^2 T}{\partial y^2}$$

$$\Leftrightarrow \rho c_P \frac{\Delta T}{H} v_\infty = k \frac{\Delta T}{\delta_T^2} \rightarrow v_\infty = D_{th} \frac{H}{\delta_T^2}$$

We then balance the force due to buoyancy (in a region of unit depth and height in the boundary layer) with the frictional force, to obtain an expression for the boundary layer thickness:

$$\left. \begin{array}{l} \text{buoyancy force=} \rho_\infty g \beta \Delta T \delta_T \\ \\ \text{friction=} \eta \dfrac{dv}{dy} = \eta \dfrac{v_\infty}{\delta_T} \end{array} \right\} \text{set equal: } \rho_\infty g \beta \Delta T \delta_T = \eta \frac{v_\infty}{\delta_T} \rightarrow$$

$$\xrightarrow{\text{use: } v=\frac{\eta}{\rho}} \delta_T^2 = v \frac{v_\infty}{g \beta \Delta T}$$

By combining these expressions we obtain the boundary layer thickness and velocity. These can both be expressed in terms of another dimensionless number: the Rayleigh number Ra, in this case based on the height of the region of interest.

$$v_\infty = D_{th}\frac{H}{\delta_T^2} = \frac{g\beta\Delta T\delta_T^2}{\nu} \rightarrow \delta_T^4 = D_{th}\frac{H\nu}{g\beta\Delta T} \Leftrightarrow \left(\frac{\delta_T}{H}\right)^4 = \nu\frac{D_{th}}{g\beta H^3\Delta T} = \frac{1}{\text{Ra}_H}$$

$$\text{Ra}_H = \frac{g\beta H^3\Delta T}{\nu D_{th}}, \text{ Rayleigh number}$$

$$v_\infty = \frac{D_{th}}{H}\sqrt{\text{Ra}_H}$$

Thus, to figure out if natural convection is significant in a chamber, calculate Ra for the system. If the natural convection velocity is much smaller than the "forced convection" fluid velocity calculated from known inlet flows, then natural convection can be safely ignored. In the other extreme, fluid flow in the reactor is dominated by natural convection, likely leading to recirculations, powder formation due to long residence times in the gas phase, and other undesirable results. We can see that the velocity is strongly influenced by the height: to avoid natural convection in practical situations, make reactors short!. Let's consider an example consider a single-wafer geometry, turned sideways (to resemble the case we studied), figure 17.10. We note that it is easy to find the modulus of thermal expansion for an ideal gas: $\beta=1/T$.

Figure17.10- free vs forced convection
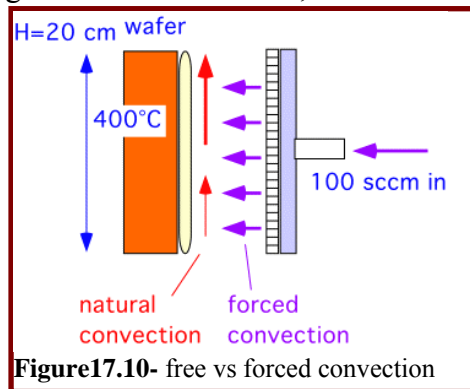
We can therefore find the values for the natural convection velocity and compare them to the inlet velocity (assuming simple volume expansion and plug flow). If the natural convection velocity is much larger than the inlet velocity, natural convection will dominate (and the reactor won't work very well); if the inlet velocity is larger, the forced convection will "blow away" natural convection. Here are the results:

P (torr)	β	Ra$_H$	v	v$_{inlet}$	ratio
760	0.002	2.4x10^7	124	0.009	7x10^5
1	0.002	43	0.16	7.2	44
Use D= 0.5 cm^2/sec at; T(average)=485 k, scale with 1/P					

At high pressures natural convection is completely dominant in this geometry; at low pressures forced convection wins. Naturally the result is quite sensitive to the actual size of the chamber (and also, though not included here, to the separation of the gas injection and the wafer: when that is comparable in thickness to the thermal boundary layer, natural convection has too little room to occur and is suppressed).

Note that the situation is somewhat different in the "boiling water" geometry: a large flat cylinder with a hot bottom and cool top. In this case there is no convection at all until Ra reaches a value of about 2000, after which convection cells, of diameter roughly equal to the system height, begin to form.

17.4 Radiative Heat Transfer

Absorption of incident radiation, emission of radiation

Thermal radiation is electromagnetic energy due solely to the temperature of the emitting surface or body.

Electromagnetic energy is $E=h\nu$, h- Planck's constant, ν-frequency; or $E=hc/\lambda$ when consider c-speed of light and wavelength

Any hot body emits electromagnetic radiation from its surface- thermal radiation

Well known: electromagnetic waves to have both wave and particle properties.

Electromagnetic radiation: Comprises both the visible and invisible wave lengths

- Visible light: $\lambda < 0.7$ microns
- Thermal radiation: $10^{-7} < \lambda < 10^{-4}$ microns

Short wave lengths correspond to ultra-violet light, long wavelength to infrared.

Electromagnetic spectrum

Contains everything from cosmic rays (small λ) to radio waves (large λ)

Thermal radiation has λ that include the visible and infrared spectrum.
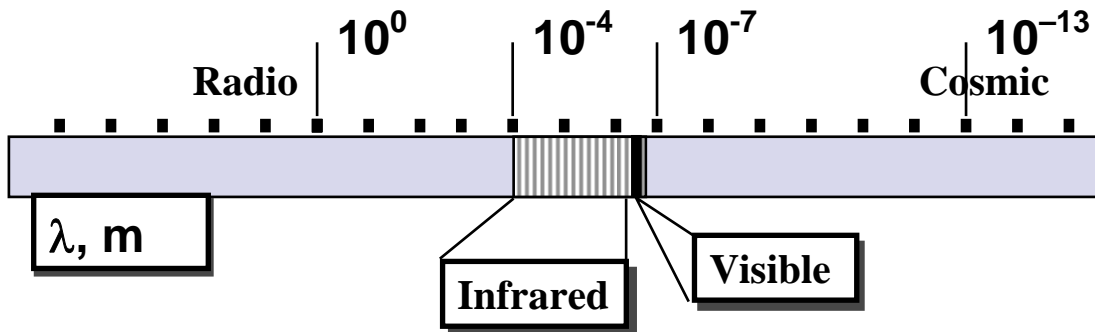
The conduction, diffusion, and convective transfer of heat are generally similar to the comparable mechanisms involved in mass transport. However, energy can also be carried by **photons**. This is radiative heat transport, which has no analog in mass transport.

Emissive power

Experimentally, it is found that the emissive power over all wave lengths combined for the area dA in all directions combined is given by

$$R \propto T_s^4$$

which is total hemispherical emissive power. That is what Stefan and Boltzmann observed and find their law

17.4.1 The Stephan-Boltzman law

$$R = \sigma T_s^4; \quad \sigma = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4 \qquad 17.6$$

Above Equation applies to <u>black surfaces</u>. The black surface, or <u>black body</u>, is the <u>perfect radiation emitter</u>. For actual surfaces, the <u>total hemispherical emissivity</u>, $\varepsilon < 1$. Such surfaces are called <u>grey surfaces</u>. Thus,

$$R_{greyish} = \varepsilon \sigma T_s^4; \text{ emission power by a greyish surface}$$

Radiated Energy as a Function of Energy Density

If we consider energy radiated perpendicular to a small increment of area, then it must be noted that half of the energy density in the waves is going toward the walls and half is coming out if the system is in thermal equilibrium. Evaluating the power seen at a given observation point requires a consideration of the geometry:

When we have to take in account all direction of emitted radiation from a hot surface then we must average on solid angle. Then,

a

Hot Surface at equilibrium with radiation around

The energy E in radiation will go through the area ΔA in +x direction;

$$\frac{dE}{d\lambda} = \text{energy per unit wavelength}$$

$\Delta x = c\Delta t$

R=radiated power per unit area; $\frac{dR}{d\lambda} = $ radiated power per unit wavelength

ΔA

The energy E can be expressed in terms of radiated power R;

$$\frac{dE}{d\lambda} = 2\left[\frac{dR}{d\lambda}\right]_{\vartheta=0} \Delta t \Delta A = 2\left[\frac{dR}{d\lambda}\right]_{\vartheta=0} \frac{\Delta x \Delta A}{c} \; ; \; 2\text{- comes from } -x$$

direction radiated power; $\Delta x \Delta A$=volume; then rearranging :

$$\left[\frac{dR}{d\lambda}\right]_{\theta=0} = \frac{c}{2}\frac{du}{d\lambda}; \text{ where } u = \frac{E}{\Delta x \Delta A} \text{ is the energy density}$$

The energy in the projected volume being E then in volume at θ angle is

$$\Delta E = 2\frac{\Delta R}{\cos\theta}\frac{\Delta x}{c\cos\theta}\Delta A$$

↘ radiated power in $\perp$ direction

Rearranging all terms:

$$\left[\frac{dR}{d\lambda}\right]_{\theta} = \frac{c}{2}\frac{dE}{d\lambda}\frac{\cos^2\theta}{dV} \Leftrightarrow \left[\frac{dR}{d\lambda}\right]_{\theta} = \frac{c}{2}\frac{du}{d\lambda}\cos^2\theta$$

θ

R

ΔA

$\Delta x = c\Delta t$

Taking the average on all solid angle 4π
We obtain

$$\frac{dR}{d\lambda} = \frac{c}{4}\frac{du}{d\lambda} \; ; \text{ where } u \text{ is density energy given}$$

by the Planck radiation formula.

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Radiation Energy Density

The total energy radiated from an area in a region of space is given by the **Stefan-Boltzmann law** and the energy density associated with the radiation can be related to that law. In the development of the expression for the radiation from a hot surface, it was found that the radiated power is related to the energy density by the factor c/4 .

$$R = \frac{P}{A} = \sigma T^4 = \frac{c}{4} \times \text{energy density}$$

The Stefan-Boltzmann law can then be related to the energy density by this factor, and the cumulative energy density for all wavelengths of radiation can be expressed:

$$\text{energy density}_{\text{in photons}} = \frac{4}{c}\sigma T^4$$

When the electromagnetic radiation in a region of space is at equilibrium with its surroundings, it can be described by the Planck radiation formula and you get more information in next stages of learning.

Here is for your accounting how to look the Planck radiation formula.

In a closed system each object at a finite temperature T is in equilibrium with a gas of photons, distributed in frequency (or energy) according to the **blackbody distribution** discovered by Planck. In a closed system, the amount of energy absorbed from the photon gas is equal to that emitted by each object. The principle of detailed balance allows us to assert that even in an open system, objects still radiate the same amount of energy. (You will get more details to Optics and Atomic Physics courses). The energy density emitted by a surface per unit wavelength is:

$$e(\omega) = u(\lambda) = \frac{\hbar}{\pi^2 c^3}\left(\frac{kT}{\hbar}\right)^4 \frac{x^3 dx}{\exp x - 1};$$

$$x = \frac{\hbar\omega}{kT}; \omega = \frac{2\pi c}{\lambda}; \hbar = \frac{h}{2\pi}, h - Planck's \text{ const}$$
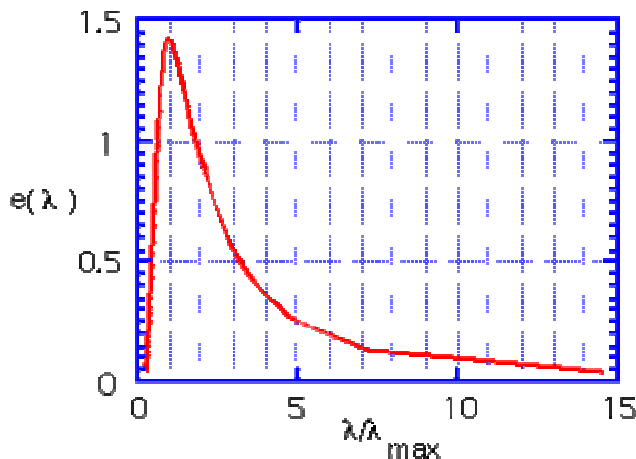
The peak in the distribution is at an energy of about 3 kT. The radiated energy is in the far infrared at room temperature. Even at 1000^0 C, where objects appear to glow brightly, most of the energy is still being emitted in the mid-IR. (3.5 microns is a typical wavelength for e.g. the vibration of O-H bonds in water).

T (°C)	λ(max) [µm]	E(max) [eV]
25	16.5	.075
100	12.9	0.96
300	8.4	1.46
500	6.2	0.20
700	4.9	0.25
900	4.1	0.30
1100	3.5	0.35

Real objects reflect some of the energy impinging on their surfaces. In order to maintain energy balance fin equilibrium, these objects must also emit less: that is, the energy emitted is multiplied by an emissivity <1. Kirchoff's law says that the emissivity must equal the absorbtivity at each wavelength; we can often ignore wavelength dependence and set emissivity = abosrptivity:

$$\alpha(\lambda) = \varepsilon(\lambda)$$

α-absorbtion coeff., ε-emittance

$$R = \varepsilon\sigma T^4$$

Highly reflective objects have emissivities near 0; ; "dull", black objects have emissivities near 1. Some typical emissivities are shown here. Note that white paint has a high emissivity: it is reflective in the visible but not in the IR!
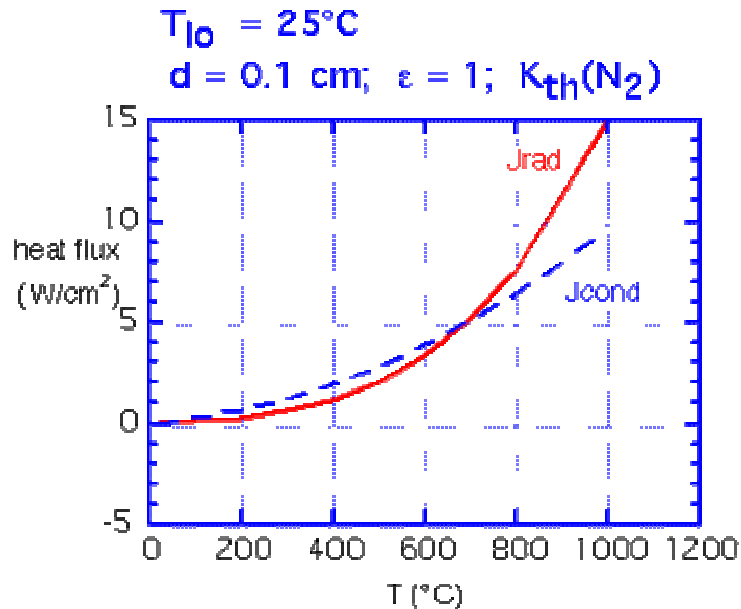
Surface	T(°C)	ε
pure Al	200-600	0.04-0.06
oxidized Al	90-540	0.2-0.33
asbestos	40	0.95
carbon soot	40	0.94
white paint	40	0.9- 0.97

The full treatment of radiation can be extremely complex, since photons can reflect off multiple surfaces and follow complex paths. We'll examine only simple planar geometries to get some sense of what sort of heat fluxes occur in typical situations.

How do conduction and radiation compare in importance? Radiation is essentially independent of spacing, whereas conduction is strongly dependent on spacing.

$$J_{cond} = -K_{th}\frac{\Delta T}{d} \qquad d \qquad R = J_{rad} = \varepsilon\sigma T^4$$
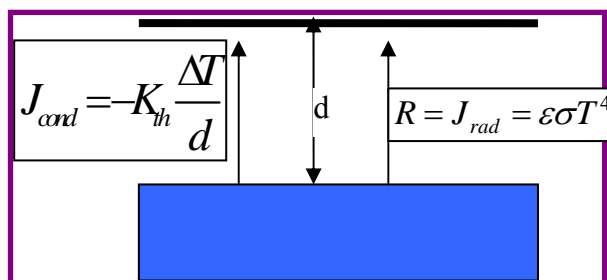
Here we show calculated fluxes in the simple case where the upper (cool) surface is a pefect black abosrber, held at room temperature. For a spacing of about 0.1 mm the two fluxes remain comparable over a wide range of temperatures. Of course, if the plate separation is increased the conducted flux falls rapidly whereas radiated flux is essentially unchanged. Typical heat flux varies from 1-2 W/cm^2 at 200 C, to around 10 W/cm2 at 900 C. (examples from experiments done in CVD processes)

$T_{lo} = 25°C$

$d = 0.1$ cm; $\varepsilon = 1$; $K_{th}(N_2)$

When surfaces are not perfectly absorptive, calculation of the net heat flux from one surface to another is rather subtle. One must account for the energy reflected
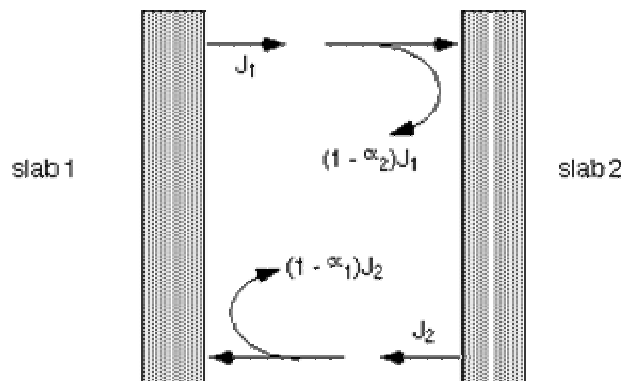
from each slab, and either sum multiple reflections using the geometric series (1 + x + x^2 + ... = 1/[1-x]), or by requiring consistency of energy fluxes.

The final result contains a term of the form $T_1^4 - T_2^4$, as would be the case with simple black objects. The coefficient dependent on emissivities is rather complex: let's look at a few special cases.

$$J_{(rad,net)} = \left(\frac{1}{\left(\dfrac{1}{\varepsilon_1} + \dfrac{1}{\varepsilon_2} \right) - 1} \right) \sigma \left(T_1^4 - T_2^4 \right)$$

When both objects are perfect absorbers, the net heat is just the difference of two blackbody terms. When one emissivity is small and the other close to 1, the smaller emissivity dominates the net flux. When both are comparable but small, they combine in same fashion as two resistors in parallel.

Limits:

$\varepsilon_1 = \varepsilon_2 = 1$
$$J_{(rad,net)} = \sigma \left(T_1^4 - T_2^4 \right)$$

$\varepsilon_1 \ll \varepsilon_2 \approx 1$
$$J_{(rad,net)} = \varepsilon_1 \, \sigma \left(T_1^4 - T_2^4 \right)$$

$\varepsilon_1, \varepsilon_2 \ll 1$
$$J_{(rad,net)} = \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \sigma \left(T_1^4 - T_2^4 \right)$$

The most common instance of this type of heat transfer in CVD is of course the heating of a flat wafer or substrate. Using the simple treatments presented so far, we can estimate heat flux to a wafer sitting on a chuck, and heat loss by radiation and convection through a thermal boundary layer to a flowing gas on top. We should note that complicating such a calculation is the complex emission behavior of silicon: bare silicon is rather transparent in the IR if low-doped (resistivity > a few ohm-cm), but becomes absorptive (emissivity about 0.7) when heated enough to reach intrinsic conductivity, typically about 300 C. Wafers with thick oxide are usually quite absorptive due to strong O-H absorptions are 3 microns and the intrinsic Si-O absorption around 10 microns. Thus wafer optical properties vary depending on temperature, processing history and resistivity.

17.5 References

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Annex

Mathematical Relations

1. Exact and inexact differentials

Since state functions are properties of the *state* of a system, their change in a process depends only on the initial and final states and not upon the path taken between them. The integral of a differential of a state function is simply the difference between the value of the state function in its final and initial states. For example, internal energy is a state function and therefore,

$$\int_a^b dU = U_b - U_a = \Delta U$$

regardless of the path taken between a and b. A differential whose integral is path independent is called an **exact differential**. Quantities, such as Q and L, are not properties of the state of a system, but rather represent different forms of energy *transfer* that occur when a system changes from one state to another. Because the integrals of such non-state functions depend on how the state change is carried out (i.e., they depend on the path between a and b), their differentials are called **inexact differentials**.

2. Partial differentiation

Development of many of the important relationships between the various thermodynamic variables requires a familiarity with some of the fundamental properties of partial derivatives.

1. The total differential

Consider a function of two variables, such as f = f(x,y). Then the total differential of f is defined by:

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

The total differential is the change in the dependent variable resulting from an infinitesimal change in the two independent variables.

2. Second order differentiation

The order of differentiation in a second order partial differential does not matter;

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$

Exercise: Show that the above identity is true for the function $z = 3x^2 y^{-1}$.

$$\frac{\partial z}{\partial x} = 6xy^{-1} \rightarrow \frac{\partial^2 z}{\partial y \partial x} = -6xy^{-2}$$

$$\frac{\partial z}{\partial y} = -3x^2 y^{-2} \rightarrow \frac{\partial^2 z}{\partial x \partial y} = -6xy^{-2}$$

3. Test of exactness

An exact differential satisfies the relationship

$$df = g(x, y)dx + h(x, y)dy$$

$$\frac{\partial g}{\partial y} = \frac{\partial h}{\partial y}$$

It is easy to show that the above is a necessary condition for an exact differential. Since an exact differential can be expressed in terms of the total differential

$$\left. \begin{array}{l} df = \left(\dfrac{\partial f}{\partial x}\right)_y dx + \left(\dfrac{\partial f}{\partial y}\right)_x dy \\[3mm] \left(\dfrac{\partial f}{\partial x}\right)_y = g \text{ and } \left(\dfrac{\partial f}{\partial y}\right)_x = h \end{array} \right\} \text{ since } \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) \Leftrightarrow \frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}$$

Maxwell Relations: If df = Mdx + Ndy is an exact differential, then

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \text{ or } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$$

<u>Exercise</u>:

1. Determine whether or not the following differential is an exact differential;

$$df = (6xy^2 + 2y)\,dx + (6x^2\,y + 2x)\,dy$$

$$\left. \begin{array}{l} g(x,y) = 6xy^2 + 2y \rightarrow \dfrac{\partial g}{\partial y} = 12xy + 2 \\[3mm] h(x,y) = 6x^2\,y + 2x \rightarrow \dfrac{\partial h}{\partial x} = 12xy + 2 \end{array} \right\} \rightarrow \frac{\partial g}{\partial y} = \frac{\partial h}{\partial x}, yes$$

2. Show that $df = -y\,dx + (x - 2x^2\,\ln\,y)dy$ is *not* an exact differential, but is converted to one upon multiplication by the factor $1/x^2$. (This is an example of what is called an **integrating factor**).

$$g = -y \rightarrow \frac{\partial g}{\partial y} = -1$$

$$h = x - 2x^2 \ln y \rightarrow \frac{\partial h}{\partial x} = 1 - 4x \ln y$$

Now multiply with $1/x^2$

$$\left. \begin{array}{l} g = -\dfrac{y}{x^2} \\[3mm] h = \dfrac{1}{x} - 2 \ln y \end{array} \right\} \rightarrow \frac{\partial g}{\partial y} = -\frac{1}{x^2}; \frac{\partial h}{\partial x} = -\frac{1}{x^2}$$

4. Composite functions the chain rule

Consider a function of two variables, f = f(x,y), in which the variables x and y are themselves functions of a third variable, x = g(t) and y = h(t). Then, according to the chain rule,

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial f}{\partial y}\frac{\partial y}{\partial t}$$

Extension of this rule to variables that are functions of two other variables:
$f = f(x,y)$ where $x = g(u,v)$ and $y = h(u,v)$

$$\left(\frac{\partial f}{\partial u}\right)_v = \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial u}\right)_v + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial u}\right)_v$$

$$\left(\frac{\partial f}{\partial v}\right)_u = \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial v}\right)_u + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial v}\right)_u$$

5. Reciprocal rule

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\left(\dfrac{\partial z}{\partial x}\right)_y}$$

The proof of the reciprocal rule proceeds as follows: Let $F(x,y,z)$ = constant (for example $PV - nRT = 0$) and $x = g(y,z)$, $y = h(x,z)$, and $z = f(x,y)$. Then:

$$dF = 0 = \left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y} dz$$

and so

$$dz = -\frac{\left(\dfrac{\partial F}{\partial x}\right)_{y,z}}{\left(\dfrac{\partial F}{\partial z}\right)_{x,y}} dx - \frac{\left(\dfrac{\partial F}{\partial y}\right)_{x,z}}{\left(\dfrac{\partial F}{\partial z}\right)_{x,y}} dy$$

but

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

therefore

$$\left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\dfrac{\partial F}{\partial x}\right)_{y,z}}{\left(\dfrac{\partial F}{\partial z}\right)_{x,y}}$$

Now repetition of this same procedure for dx gives

$$\left(\frac{\partial x}{\partial z}\right)_y = -\frac{\left(\dfrac{\partial F}{\partial z}\right)_{x,y}}{\left(\dfrac{\partial F}{\partial x}\right)_{y,z}}$$

which proves the reciprocal rule.

At this point, it is worthwhile to introduce a shortcut method that will simplify some of the derivations later on. Let's return to the relationship

$$dF = 0 = \left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y} dz$$

This time we will divide both sides by dx while keeping y constant;

$$0 = \left(\frac{\partial F}{\partial x}\right)_{y,z}\left(\frac{dx}{dx}\right)_y + \left(\frac{\partial F}{\partial y}\right)_{x,z}\left(\frac{dy}{dx}\right)_y + \left(\frac{\partial F}{\partial z}\right)_{x,y}\left(\frac{dz}{dx}\right)_y$$

but since $\left(\dfrac{dx}{dx}\right)_y = 1$ and $\left(\dfrac{dy}{dx}\right)_y = 0$

this expression immediately yields the same one obtained before

$$\left(\frac{dz}{dx}\right)_y = -\frac{\left(\frac{\partial F}{\partial x}\right)_{y,z}}{\left(\frac{\partial F}{\partial z}\right)_{x,y}}$$

Exercise: Use the above relationship to determine $\left(\dfrac{\partial V_m}{\partial T}\right)_P$ for the van der Waals equation.

$$F(P,V,T) = (P + a/V_m^2)(V_m - b) - RT = 0$$
$$= PV_m - bP + aV_m^{-1} - abV_m^{-2} - RT$$

hence

$$\left(\frac{\partial V_m}{\partial T}\right)_P = -\frac{\left(\frac{\partial F}{\partial T}\right)_{P,V_m}}{\left(\frac{\partial F}{\partial V_m}\right)_{P,T}} = \frac{RV_m^3}{PV_m^3 - aV_m + 2ab}$$

Exercise: Repeat the above exercise using the reciprocal rule.

6. Euler's chain relation
For any function of three variables, F = f(x,y,z),

$$\left(\frac{\partial z}{\partial x}\right)_y\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x = -1$$

This relationship may be proved by reexpressing each of the partial derivatives in the form used to obtain the reciprocal relationship.

Exact and Inexact Differentials
A Mathematical Digression

We have mentioned, from time to time, that the quantities, *U*, *H*, and so on, are state functions, but that *q* and *w* are not state functions. This has various consequences. One consequence is that we can write things like ΔU and ΔH, but we never write Q or L with a Δ in front them. A more important consequence is that in a process ΔU and ΔH are independent of path. That is, ΔU and ΔH depend only on the initial and final states. However, Q and L do depend on the path one takes to get from the initial to the final state.

Another consequence is that the differentials, dU and dH are mathematically different, in some sense, from δQ and δL. Some writers write dq and dw with a line through the d to indicate this difference. We have not chosen to use such a specialized notation, but expect that we all will be able to just remember that dU and dH are mathematically different, in some sense, than δQ and δL.

We must now consider in detail the nature of this difference. Let's think, for the moment, in terms of functions of the variables x and y and consider the differential,

$$df = 2xy^3 dx + 3x^2 y^2 dy.$$

We ask the question, does there exist a function, $f = f(x,y)$ such that,

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy.$$

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In other words, does a function $f(x,y)$ exist such that,

$$\left(\frac{\partial f}{\partial x}\right)_y = 2xy^3$$

and

$$\left(\frac{\partial f}{\partial y}\right)_x = 3x^2 y^2 ?$$

(1a, 1b)

Euler's test provides a way to see whether such a function, $f(x,y)$ exists. Euler's test is based on the fact that for "nice" functions (and all of our functions are "nice") the mixed second derivatives must be equal. That is,

$$\left(\frac{\partial^2 f}{\partial x \partial y}\right) = \left(\frac{\partial^2 f}{\partial y \partial x}\right).$$

(2)

(On the left-hand side we take the derivative with respect to y first and then take the derivative of the result with respect to x, and vice versa on the right-hand side.

Let's try Euler's test on our differential, df. If f exists then the Equations (1a) and (1b) are correct. Use Equations (1a, 1b) to obtain the proposed second derivatives,

$$\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y = \frac{\partial}{\partial y} 2xy^3 = 6xy^2$$

and

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x = \frac{\partial}{\partial x} 3x^2 y^2 = 6xy^2.$$

(3,4)

The mixed second derivatives are equal. So we conclude that there exists a function, $f(x,y)$ (actually $x^2 y^3$) such that Equations (1) and (2) are equal.

The differential df, is called an "exact differential" for the very reason that a function, f, exists such that Equation (1 and 2) can be used to calculate it.

Now, let's consider the differential,

$$dg = 2x^2 y^3 dx + 3x^3 y^2 dy.$$ (5)

Is dg an exact differential? Use Euler's test to find out. If dg is exact then the coefficients of dx and dy are the respective partial derivatives of g. Euler's test would then compare

$$\frac{\partial}{\partial y} 2x^2 y^3 = 6x^2 y^2$$

with

$$\frac{\partial}{\partial x} 3x^3 y^2 = 9xy^2. \tag{6}$$

These are not equal so that the putative second partial derivatives are not equal to each other. The differential, dg, is not exact and there does not exist a function, $g(x,y)$, such that dg exists..

Both of the differentials, df and dg can be integrated from, say, x_1, y_1 to x_2, y_2. The integral,

$$\int df = f(x_2, y_2) - f(x_1, y_1). \tag{7}$$

depends only on the initial and final points because df is exact and the function f exists.

The differential dg can be integrated, but there is no equivalent to Equation (1) for the integral of dg because there is no function, $g(x,y)$ which gives Equation (6). The integral of dg would have to be carried out along some path and we would find that the value of the integral depends on the path as well as on the initial and final points.

That is what happen with Q and L.