

PHYS1B28 – Thermal Physics

Course Information 2004/2005

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Prerequisites

A-level Physics, Chemistry and Mathematics

Aims of the Course

This course aims to:

- introduce and apply the laws of Classical Thermodynamics;
- obtain predictions from the kinetic theory of ideal gas van der Waals theory of real gas;
- show how the three primary states of matter result from competition between thermal kinetic energy and inter-particle potential energy.

Objectives

After completing this course, students will:

- be familiar with the Bohr model of the hydrogen atom;
- be aware of the origin of covalent, ionic, and van der Waals interactions;
- be able to describe the structures of ideal gases, real gases, liquids and solids;
- understand the meanings of heat and thermal equilibrium, state variables, state functions and equations of state;
- be able to state the Zeroth Law of thermodynamics;
- understand what is meant by an ideal gas and the ideal gas equation of state;
- understand the role of Avogadro's number and the mole;
- be familiar with simple kinetic theory of gases, and be able to obtain the mean energy of each degree of freedom (equipartition of energy) by combining with the ideal gas equation of state;
- understand the concepts of internal energy, heat and work, and be able to state and apply the first law of thermodynamics;
- be able to define specific heats and latent heat, and understand and manipulate C_p and C_v for ideal and real gases;
- be able to define isolated, isothermal and adiabatic processes;

- be able to derive from thermodynamic arguments the form of the Maxwell-Boltzmann distribution, and obtain the normalized velocity and speed distributions in an ideal gas;
- be aware of the ubiquity of the Maxwell-Boltzmann distribution for systems in thermal equilibrium;
- be able to obtain expressions for the mean collision and diffusion lengths from simple kinetic theory;
- be able to distinguish between reversible and irreversible processes;
- understand the concept of entropy and its relationship to disorder;
- be able to state the Second Law of thermodynamics;
- be able to obtain the ideal adiabatic equation of state;
- understand free adiabatic expansion as an example of an irreversible process;
- be able to derive the efficiency of the Carnot cycle, and understand the ideal operation of heat engines, refrigerators and heat pumps;
- be able to combine the First and Second Laws of thermodynamics;
- be able to state the Third Law of thermodynamics;
- explain how certain macroscopic quantities such as latent heat, surface energy and the critical point may be related to parameters of the microscopic inter atomic/molecular potential;
- understand the van der Waals equation of state for a real gas, and the form of the Lennard-Jones model for atomic interactions;
- be able to sketch typical phase diagrams, including the triple and critical points.

Methodology and Assessment

The course consists of 27 lectures covering main course material, and 6 hours of other activities, including discussion of problem sheets and advanced topics. Assessment is based on an unseen written examination (85%) and four sets of homework: (15%)

Textbooks

- *“Physics”*, Serway and Beichner, Saunders College Publishing.
- *“Physics”*, Thornton, Fishbane and Gasiorowitz, Prentice Hall.
- *“Physical Chemistry”*, G. M. Barrow, McGraw-Hill
- *“Physical Chemistry”*, Atkins, Oxford.
- *“The Properties of Matter”*, Flowers and Mendoza, Wiley.
- *“Understanding Matter”*, de Podesta, UCL.
- *“Statistical Physics”*, Mandl, Wiley.

1B28 Course Plan:

Ideal gas

Definition and approximations

Volume

Pressure, Pascal's Law, Boyle's Experiment, measuring pressure (Torricelli's device)

Temperature, thermal equilibrium, Zeroth Law, calibration and different temperature scales

Ideal gas law, Avogadro's Hypothesis, mole unit, Avogadro's number, gas constant, early atomistic theories in chemistry, partial pressure

Kinetic theory of gasses, kinetic energy of molecules and temperature, RMS speed, law of atmospheres

Boltzmann and M-B distributions, random systems, probability distributions, molecular speeds, equipartition of energy

Atoms and molecules; nature of chemical bonds

The Bohr model of atom, orbital momentum, atomic orbitals, electronic shells

Ionic and covalent bond, potential energy curves, methods of studying molecules

Properties of different compounds, van der Waals bonding

Crystal structure, close packing

Potential energy functions

Real gasses, real gas laws, properties of inter-atomic interaction from real gas laws

Thermal expansion of solids and liquids

Internal energy and heat

Mechanical equivalent of heat

Specific heat capacity, calorimetry; Dependence on measurement conditions

Latent heat

Work and heat

Different processes: constP, constV, constT, **internal energy change and work**

First Law

Common **thermodynamic processes**: adiabatic, isobaric etc.

Molar specific heat of ideal gas,

Properties of Cp and Cv, degrees of freedom, monoatomic and polyatomic gases

Adiabatic expansion and cooling of gases

Energy transfer mechanisms, conduction, convection, radiation, Dewar's flask.

Second Law

Reversible and irreversible processes, engines

Carnot theorem, Carnot efficiency

Different types of **engines**

Refrigerators and heat pumps

Entropy

Definitions, thermodynamic functions

Entropy and disorder

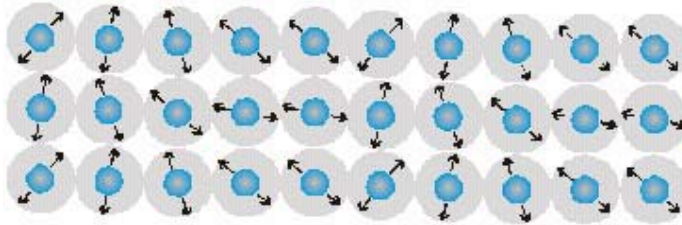
Entropy changes in different processes

Third Law and Absolute zero

Temperature scale; Extremely low temperatures; The Third Law

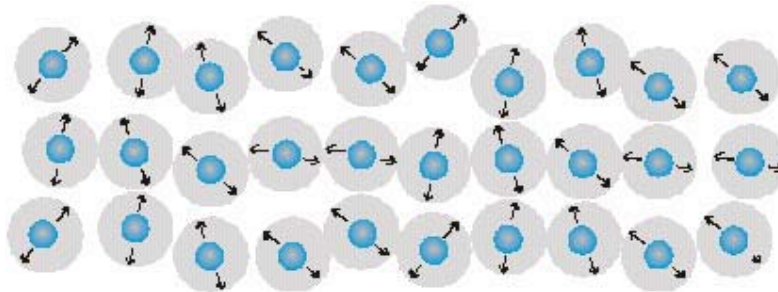
1. INTRODUCTION AND STATE PROPERTIES

Solids



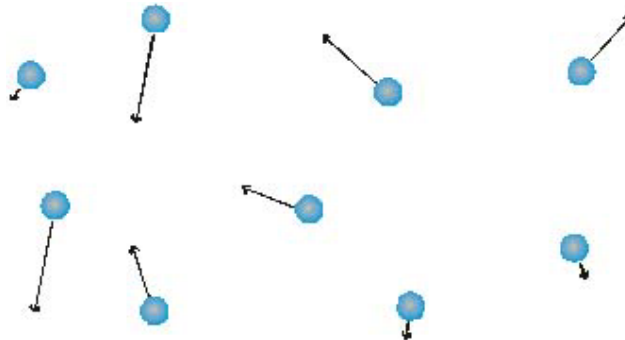
The particles **vibrate around fixed positions**. They are close together and so attract each other strongly. This is why solids maintain their shape.

Liquids



The particles are still relatively close together but now have **enough energy to "change places" with each other**. This is why liquids can **flow**.

Gases



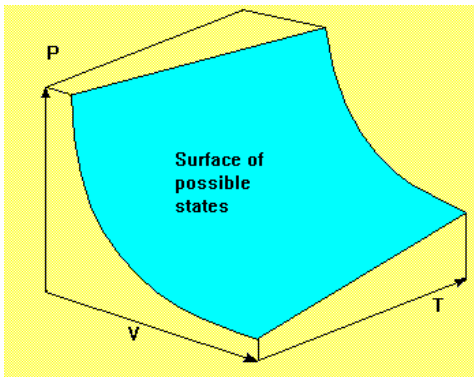
Average distance between particles typically **10 times greater** than in solids and liquids. The particles now move **freely at random**, occupying all the space available to them.

<http://www.saburchill.com/physics/chapters/0098.html>

- ◆ Thermodynamics is very successful in explaining the bulk properties of **matter** and the correlation between these properties and the mechanics of atoms and molecules
 - ◆ **Matter** - gases, liquids, solids and plasma
 - ◆ We start with gasses and apply a **model** = “Ideal Gas”
 - ◆ **Other models** of matter: incompressible liquid; ideal crystal
 - ◆ Another general model we will be using is that of **system** and **surroundings**
 - ◆ **Main assumptions** of the **Ideal** gas model
 - ◆ When the ideal gas model **does not work?**
 - ◆ **State properties:**
 - I) **Volume:** definition, units (m^3 , $1 = 10^{-3} \text{ m}^3$)
 - II) **Pressure:** Boyle’s experiment, definition, Boyle’s law, units

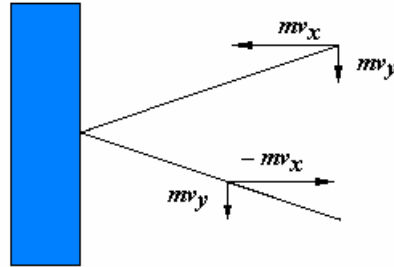
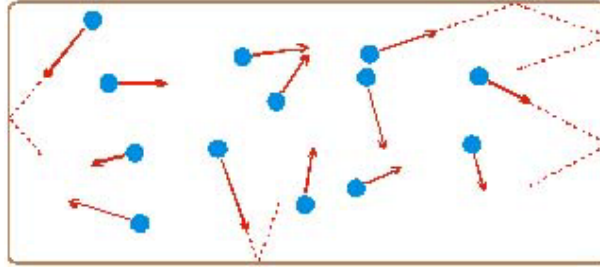
 $1 \text{ Pa (Pascal)} = 1 \text{ N m}^{-2}$ $1 \text{ bar} = 10^5 \text{ Pa}$
 - ⇒ **Boyle’s law:** The volume of a sample of a gas varies inversely as the pressure, if the *temperature* remains constant : **$PV = \text{const.}$**
 - ⇒ How to **measure** pressure: barometers and monometers
 - III) **Temperature:** Heat, thermal equilibrium
 - ⇒ **The Zeroth Law of Thermodynamics** allows us to use a system C (thermometer) to treat the systems A and B separately: **If systems A and B are separately in thermal equilibrium with a third object C, then objects A and B are in thermal equilibrium with each other**
 - ⇒ **Thermometer:** Calibration; temperature scales, units ($^{\circ}\text{C}$, $^{\circ}\text{F}$, K)
 - ⇒ **Absolute Temperature (T)**
- All gas law problems will be done with Kelvin temperatures.** If you were to use degrees Celsius in any of your calculations, YOU WOULD BE WRONG. Kelvin = Celsius + 273.15.

2. IDEAL GAS LAW



- ◆ Boyle's Law: $P_1 V_1 = P_2 V_2$
- ◆ Charles Law: $V_1 / T_1 = V_2 / T_2$
- ◆ Gay-Lussac's Law: $P_1 / T_1 = P_2 / T_2$
- ◆ The combined **Ideal Gas Law**: $P_1 V_1 / T_1 = P_2 V_2 / T_2$
- ◆ **Mole unit**: The mole unit is equal to the number of atoms in a 12 g sample of carbon-12
⇒ One mole of substance **A** **contains the same number of particles as** there are in one mole of any other substance **B**
- ⇒ The **mass in one mole of any element** is the element's atomic mass expressed in grams
- ◆ **Avogadro's Hypothesis** (1812) –samples of different gases which contain the same number of molecules – of any complexity, size, or shape – occupy the same volume at the same temperature and pressure: $V = (\text{constant})n$
- ◆ **Avogadro's number**: $N_A = 6.022\ 137 \times 10^{23}$ particles/mol
- ◆ Ideal gas law: $PV = R \times nT$
- ◆ **Universal Gas Constant**: $R = PV/nT = 0.083\ 143\ \text{L bar K}^{-1}\ \text{mol}^{-1} = 8.315\ \text{J K}^{-1}\ \text{mol}^{-1}$
- ◆ **Boltzmann's constant**: $k_B = R/N_A = 1.38 \times 10^{-23}\ \text{J/K}$
- ◆ Dalton's law of **partial pressures**: $P = P_1 + P_2 + P_3 + \dots$

3. KINETIC THEORY OF GASES



◆ **One particle:** $P = (1/3) m \overline{V^2} / L^3 = (1/3) m \overline{V^2} / V$ or $PV = (1/3) m \overline{V^2}$

◆ **N particles:** $\overline{V^2}$ is the average square of the velocity.

◆ **The root-mean-square velocity**

$$PV = \frac{1}{3} N m \overline{V^2} \quad \text{Boyle's law!}$$

◆ **PV and kinetic energy of molecules:**

◆ **Kinetic energy and temperature:** $KE = \frac{3}{2} RT$

◆ **Speeds of molecules:** $\sqrt{3RT / M} =$ root-mean-square (RMS) speed

◆ **Equipartition of energy:**

◆ **Degree of freedom:** translation, rotation, vibration.

◆ **Theorem of equipartition of energy:** Each degree of freedom contributes $\frac{1}{2} k_B T$ to the energy of the system.

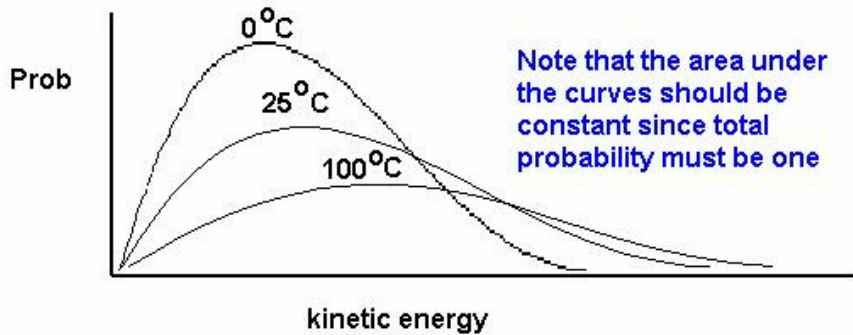
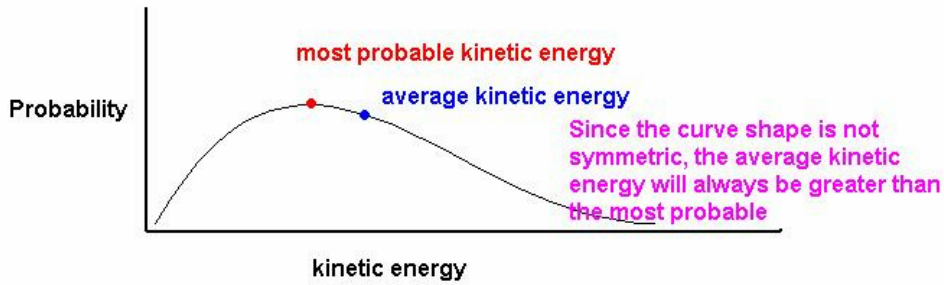
◆ **The Law of Atmospheres**

◆ **Boltzmann distribution law:** $n(E) = n_0 \times \exp(-E/k_B T)$

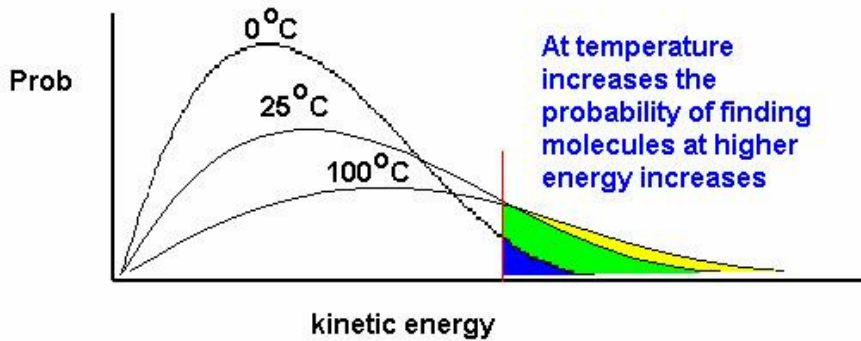
◆ Energy states $N_i/N_j = \exp\{- (E_i - E_j)/k_B T\}$

◆ Maxwell-Boltzmann distribution function

$$dN_v = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \times \exp(-mv^2/2k_B T) dv$$



⇒ the most probable speed $v_{mp} = \sqrt{2k_B T/m} = 1.41 \sqrt{k_B T/m}$



⇒ average and root-mean-square velocities:

$$\bar{v} = \sqrt{8k_B T/\pi m} = 1.60 \sqrt{k_B T/m}$$

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{3k_B T/m} = 1.73 \sqrt{k_B T/m}$$

• Mean free path

4. MOLECULES and SOLIDS: NATURE OF CHEMICAL BOND

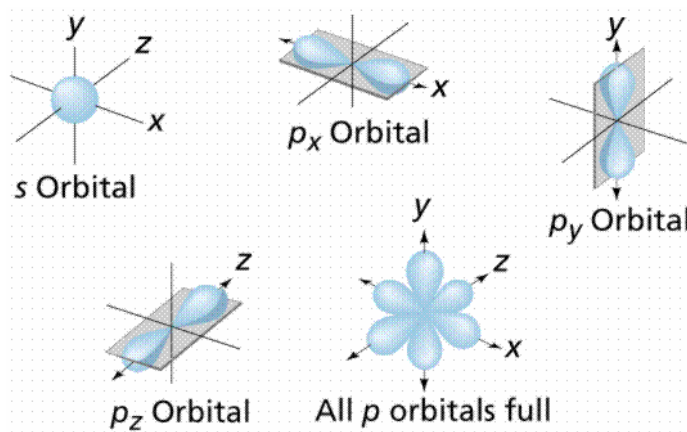
- ◆ Quantization
- ◆ The **Bohr** model of atom
- ◆ The ‘new’ quantum mechanics and **orbital angular momentum:**

$$L = |\mathbf{L}| = \sqrt{l(l+1)} \times h, \quad l = 0, 1, 2, \dots, n - 1.$$

⇒ The **orbital magnetic quantum number** m_l :

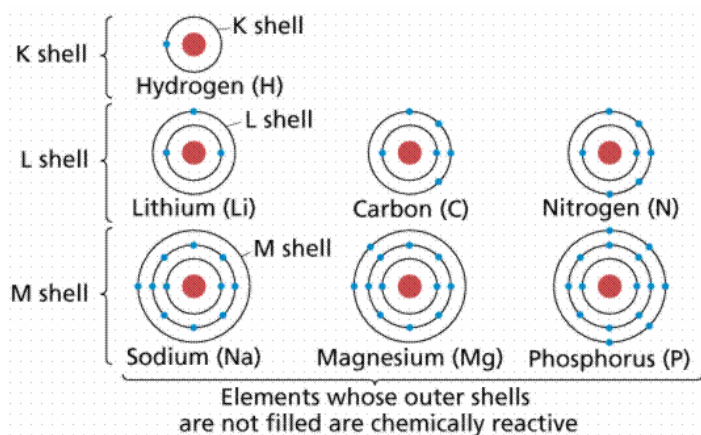
$$L_z = m_l \times h, \quad m_l = -l, -(l-1), \dots, 0, \dots, (l-1), l.$$

- ◆ **The Periodic table**



Geometry of orbitals. S-orbitals are spherical, p-orbitals are shaped like a dumbbell or figure 8. Image from W.H. Freeman and Sinauer Associates, used by permission.

<http://gened.emc.maricopa.edu/bio/bio181/BIOBK/BioBookCHEM1.html>



Atomic diagrams illustrating the filling of the outer electron shells. Image from W.H. Freeman and Sinauer Associates, used by permission.

<http://gened.emc.maricopa.edu/bio/bio181/BIOBK/BioBookCHEM1.html>

The fluorine molecule. F—F

Fluorine has an electron configuration $1s^2 2s^2 2p^5$. It is difficult to consider it bonded by one orbital similar to that in the hydrogen molecule. The $2p$ orbitals are split into three suborbitals under the influence of a magnetic field. These volumes are shown in Fig 27 (a) and Fig. 11.

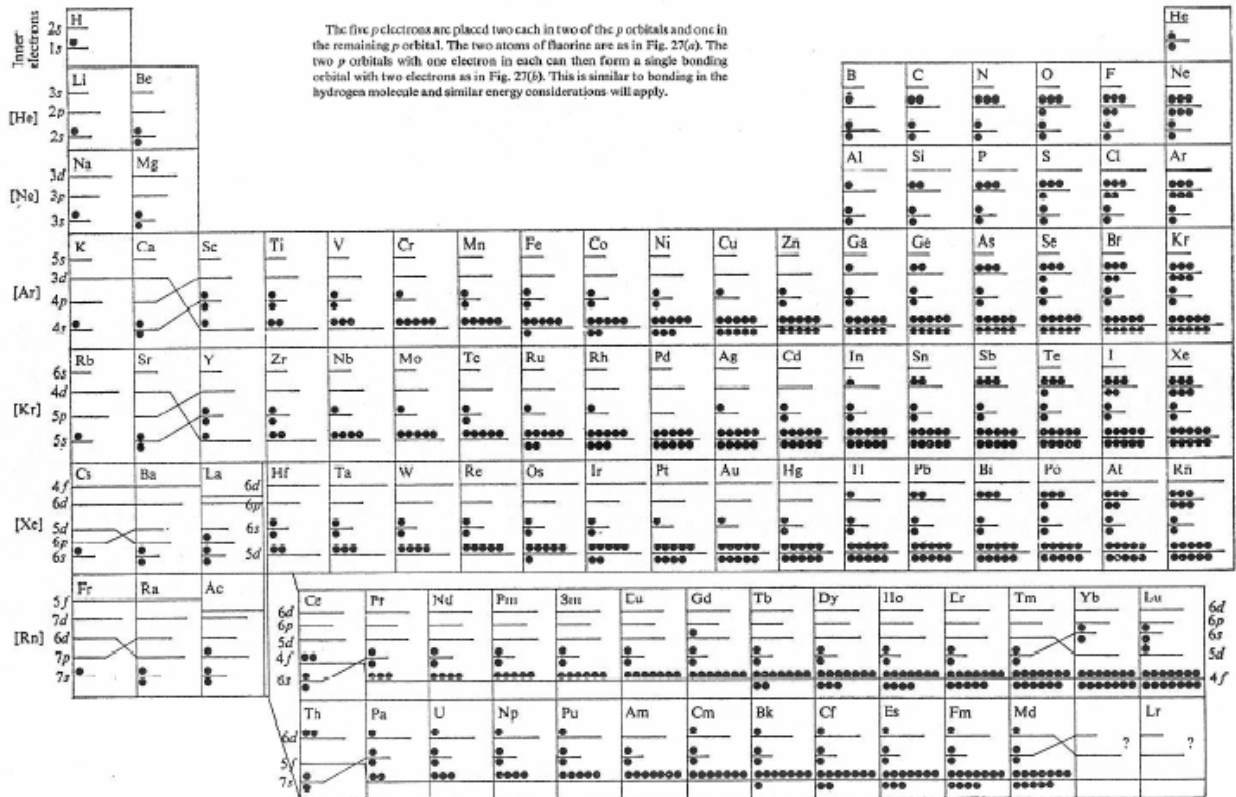
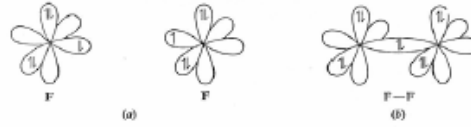
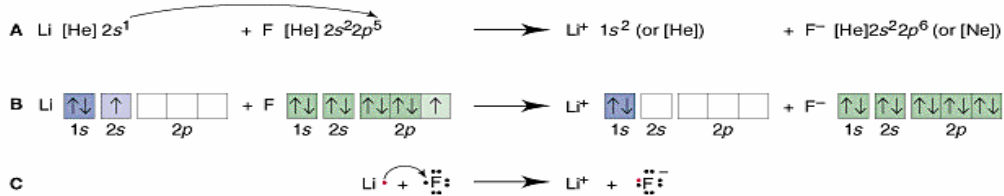


Fig. 16. Electron configuration of elements in ground state

- **Chemical bonds in molecules and solids**

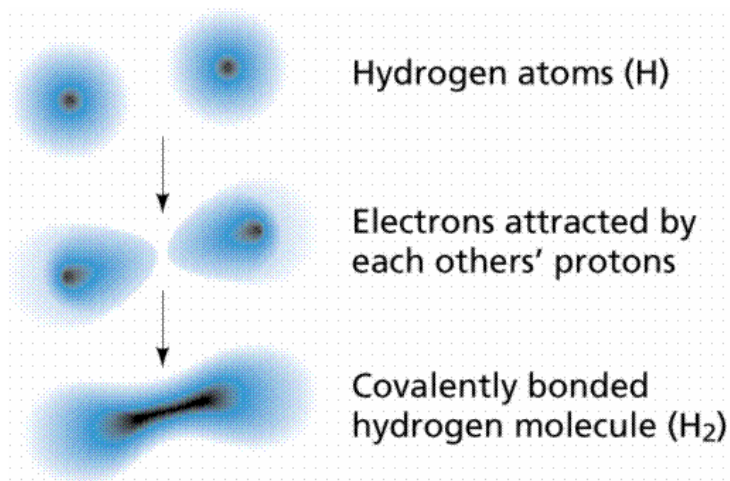
⇒ **Ionic bond**



The formation of ionic bond between Li and F in terms of electron transfer.

http://www.chem.ufl.edu/~chm2040/Notes/chapter_11/types.html

⇒ **Covalent bond**



Formation of a covalent bond between two Hydrogen atoms. Image from W.H. Freeman and Sinauer Associates, used by permission.

<http://gened.emc.maricopa.edu/bio/bio181/BIOBK/BioBookCHEM1.html>

- ◆ **Potential energy functions**

⇒ Lennard-Jones potential: $U(\mathbf{r}) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$.

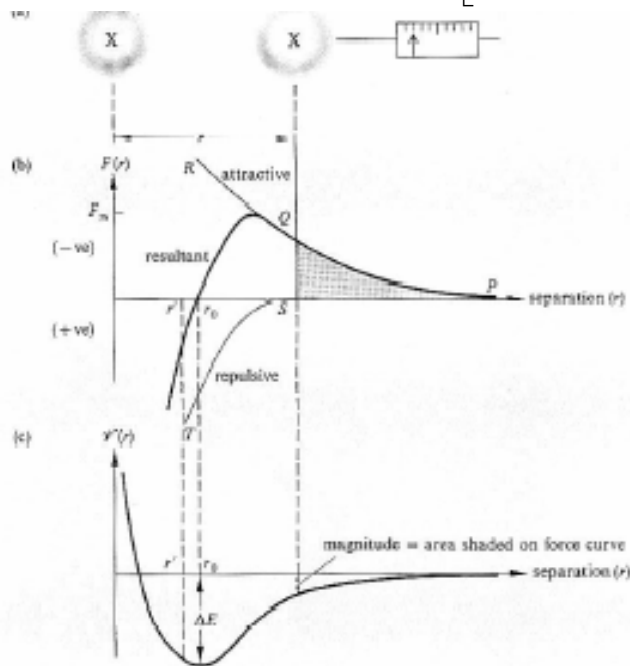
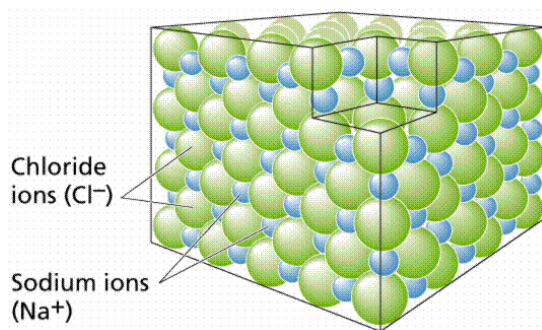


Fig. 2.6. (a) A thought experiment in which the position of the left-hand atom is fixed. The right-hand atom may be set various distances r (measured between centres) from the left-hand atom and the force of attraction (or repulsion) 'read' on a Newton balance. (b) The general form of the interatomic force between the two atoms of (a). Note that negative forces are plotted along the upward ordinate and positive forces along the downward ordinate. (c) The corresponding variation in potential energy.

⇒ Properties of ionic compounds

⇒ Properties of covalent compounds

◆ Crystal structure



◆ Close-Packed Structures are the most efficient way to fill space with spheres

◆ ⇒ Features of Close-Packing: Coordination Number = 12; • 74% of space is occupied

5. REAL GASES and VAN DER WAALS EQUATION

◆ Any **real gas** exhibits, to some extent, **deviations from ideal-gas laws**.

⇒ Compressibility factor $Z = PV/RT$, where $V = V/n$

⇒ For ideal gas $Z = 1$ at all pressures and temperatures, for real gas $Z \neq 1$.

◆ Van der Waals equation: $(P + an^2/V^2)(V - nb) = nRT$

⇒ The constant "**a**" is a correction term for **intermolecular force** and "**b**" is a correction for the **real volume** of the gas molecules.

⇒ The **observed pressure** is less than the pressure would be without the intermolecular forces, i.e. in ideal gas:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

⇒ **a and b are empirical constants** obtained for each gas so that vdW equation gives a good fit to the experimental PVT data.

◆ **Parameter "b"** in vdW equation can be viewed as **"excluded" volume** in a gas sample due to the presence of molecules.

⇒ Excluded volume per molecule = $\frac{1}{2} \left(\frac{4}{3} \pi d^3 \right) = \frac{1}{2} \left[\frac{4}{3} (2r)^3 \right] = 4 \left(\frac{4}{3} \pi r^3 \right)$.

⇒ $b = 4 \times N_A \times \left(\frac{4}{3} \pi r^3 \right)$, and, knowing the value of b, one can estimate the radius of atom or molecule.

• Phase diagram, critical point and triple point

• A transition from one phase to another ordinarily takes place under conditions of **phase equilibrium** between the two phases.

• The **triple point** is the only condition under which the all three phases – gas, liquid and solid – can coexist.

• Liquid-vapour phase transition, critical pressure and temperature

⇒ A gas at a pressure **above the critical pressure** does not separate into two phases when it is cooled at constant pressure. Instead its properties change gradually and continuously from gas to liquid without a phase transition.

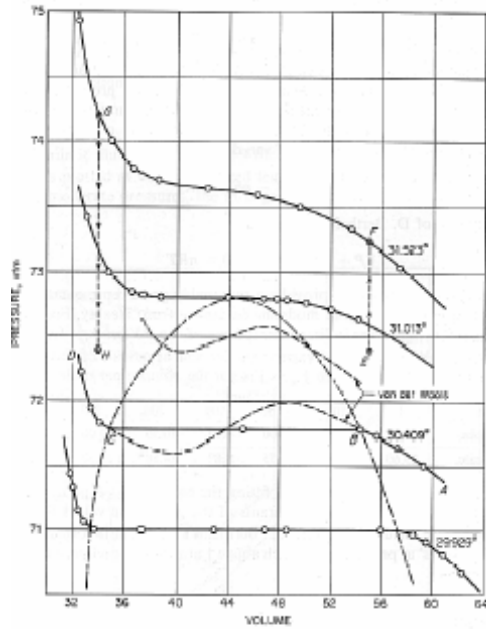


FIG. 1.10 Isotherms of carbon dioxide near the critical point. [Michels, Blaise, and Michels, *Proc. Roy. Soc. A*, 150, 267 (1937).]

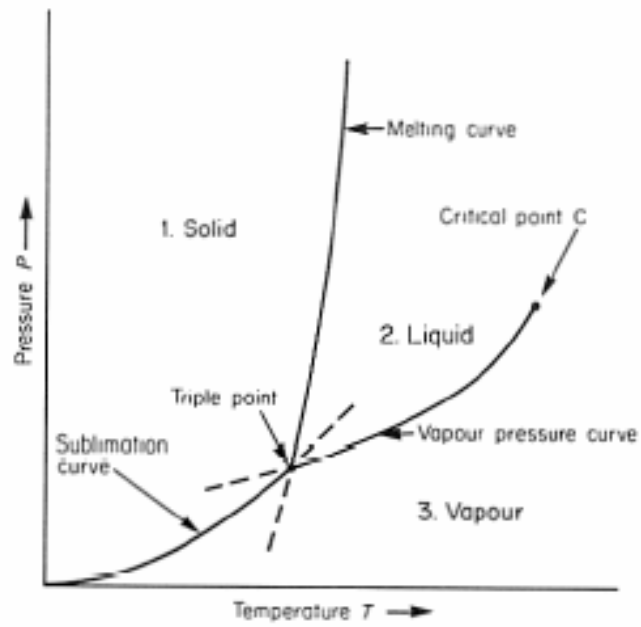
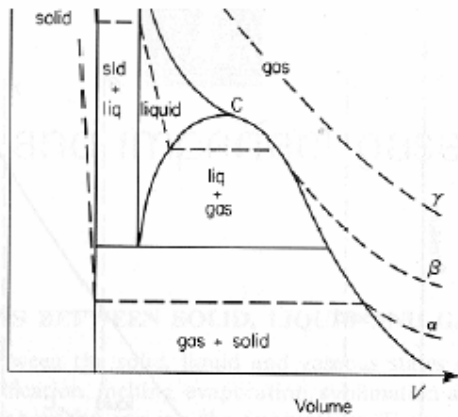
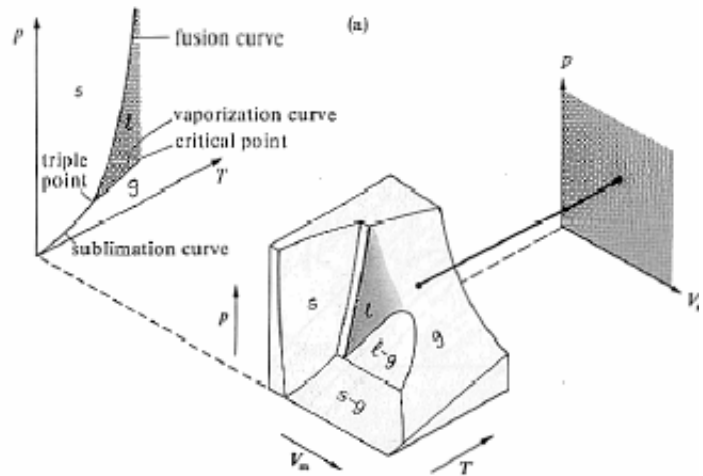


Fig. 8.4. Phase diagram of a one-component system possessing one triple point only.



Pressure-volume diagram for same substance as in Fig. 7.1. Full lines are phase boundary lines, broken lines are isotherms. C is the critical point, the triple point is the horizontal full line.



6. THERMAL EXPANSION of SOLIDS and LIQUIDS

- ◆ If **thermal expansion** is small relative to an object's initial dimensions, the change in any dimension is **linear with the temperature change**.

⇒ Average coefficient of **linear** expansion, α

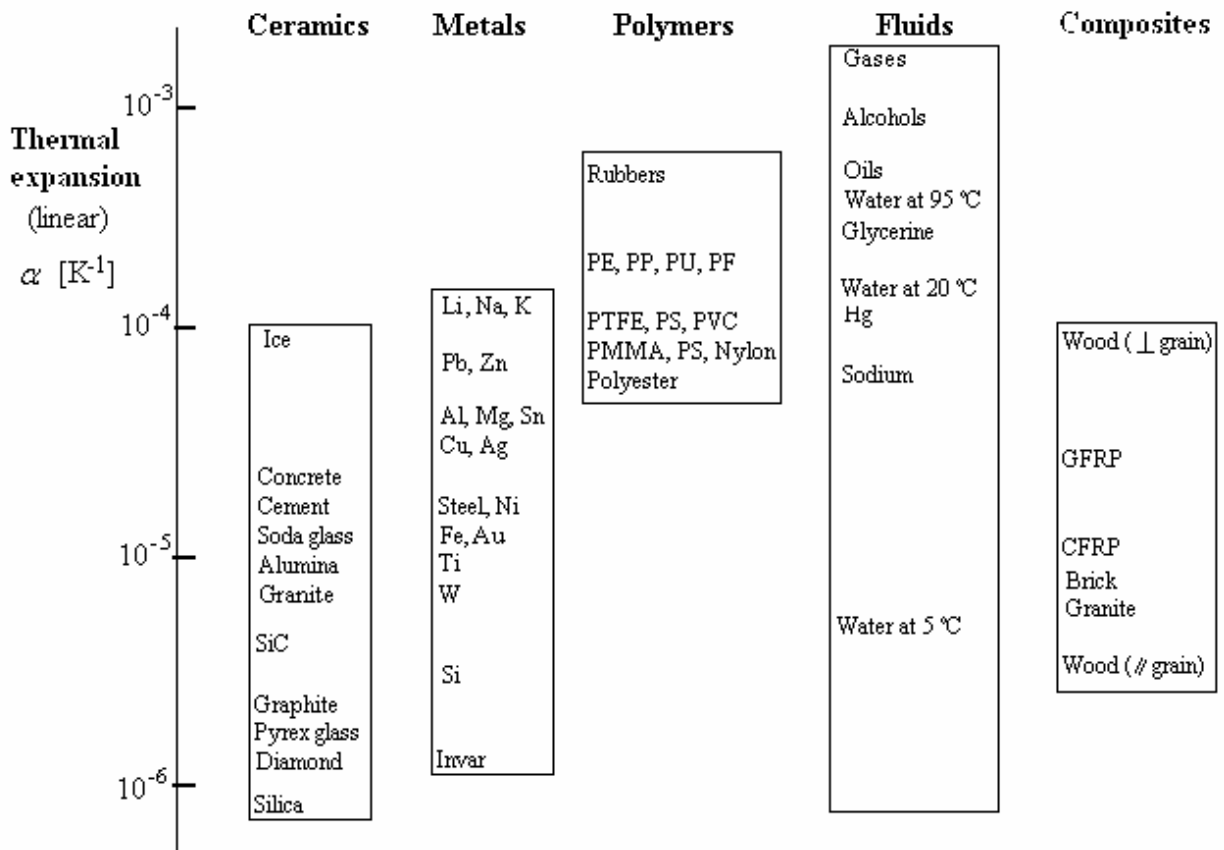
- ◆ If the initial length of the object was L_i and the temperature **change** ΔT , then the length will increase by the amount $\Delta L = \alpha L_i \Delta T$

⇒ The average value of α for different solids is about $10 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (note the units)

⇒ Because the linear dimensions of an object change with temperature, it follows that **surface area** and **volume change** as well.

- ◆ The change in volume at constant pressure is proportional to initial volume V_i and to the change in temperature according to similar relation: $\Delta V = \beta V_i \Delta T$

⇒ β is the average coefficient of **volume** expansion, $\beta = 3 \alpha$



7. INTERNAL ENERGY and HEAT

- ◆ **Internal energy** includes kinetic energy of **translation, rotation, vibration** of molecules, **potential energy within** molecules, and **potential energy between** molecules.

⇒ **Heat** and **work** are ways of change the **energy** of the system.

⇒ “**Equilibrium**” is recognised operationally as the circumstance under which bodies have ceased changing their physical state or condition.

- ◆ **Heat** is transferred between two systems when they come to **thermal equilibrium without** doing **work** on each other. Thus one can refer to heat only when **energy has been transferred** as a result of temperature difference.

- ◆ Caloric theory, sensible heat and latent heat.

⇒ **1 cal** is the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C.

- ◆ The mechanical equivalent of heat

⇒ Recognising that **heat** is another **form of energy** means that Joule’s number, which is usually called “**mechanical equivalent of heat**”, is simply a **conversion factor** between different units of measurement: **1 cal = 4.186 Joule**

⇒ **Principle of conservation of energy**, which embraces other forms of energy, such as electromagnetic and nuclear.

How to measure “heat”?

- ◆ **Specific Heat Capacity**

⇒ When different masses of the **same** substance are mixed, the temperature varies inversely as the masses: $\Delta T_h / \Delta T_c = -(m_c) / (m_h)$,

⇒ Different substances: the quantity of energy required to rise the temperature of 1 kg of water by 1 °C is **4186 J**, but for Cu this will be only 387 J.

- ◆ If the temperature of an object changes, the heat (Q) added or removed can be found using the equation: **Q = mcΔT**
- ◆ For a system insulated from surroundings:

$$m_A c_A \Delta T_A + m_B c_B \Delta T_B + m_C c_C \Delta T_A + \dots = 0$$

⇒ **Heat is conserved** when heat exchange takes place **within a thermally isolated system**.

⇒ Each of the quantities in this equation may be **positive or negative** depending on the algebraic sign of ΔT . ΔT is always measured as the difference **between final and initial** temperatures.

◆ **Specific heat capacity** is the quantity of heat required to raise the temperature of a unit of mass of a substance by a unit change in temperature:

$$c = \frac{Q}{m\Delta T}$$

⇒ Units of c J/(kg °C), and ΔT is the **change** in temperature in °C or K.

⇒ The specific heat capacity of a gas depends on whether the pressure or the volume of the gas is kept constant; there is a **specific heat capacity for constant pressure**, and a specific heat capacity for **constant volume**.

⇒ The method of mixtures is usually used under conditions of **constant atmospheric pressure**.

⇒ Recognising c_p to be a function of temperature, we can refine the concept so as to interpret $c_p(T)$ as an instantaneous rate at which heat must be supplied per gram per Celsius degree:

$$Q = \int_{T_1}^{T_2} m_A c_{pA}(T) dT$$

◆ **Changing phase - latent heat**

⇒ When a substance changes phase, **heat can be transferred in or out without any change in temperature**, because of the energy required to change phase.

⇒ The change in internal energy associated with a change in phase is known as the **latent heat**.

⇒ The **specific latent heat** of a substance, L , is the quantity of heat energy required to change the state of a **unit mass** of a substance: $E_L = m \times L$, where L is the latent heat in **J/kg**.

⇒ If heat is going **into** a substance changing phase, such as when it is **melting or boiling**, the Q is **positive**; if heat is being **removed**, such as when it is **freezing or condensing**, the Q is **negative**.

8. WORK and HEAT in THERMODYNAMIC PROCESSES

⇒ Mechanical work is equal to a scalar product of force and displacement of a body caused by that force $\mathbf{W} = \underline{\mathbf{F}} \cdot \underline{\mathbf{d}}$.

⇒ Gas, which was initially in equilibrium in volume V under pressure P , **expands quasi-statically**. Then $dW = Fdy = Pady = PdV$.

⇒ Because the **gas expands**, dV is **positive** and the **work** done by the gas is **positive**. If the **gas** were **compressed**, dV would be **negative** and the **work** done on the gas was **negative**.

◆ The total work done by the gas is $\mathbf{W} = \int_{V_i}^{V_f} PdV$

⇒ The area under the $P - V$ curve is the work done by the gas.

◆ Although both the work, W , done by the system and heat, Q , necessary for changing thermodynamic parameters of the system depend on the path, the difference $Q - W$ is **independent on the path**. This difference is the **change** in the internal energy ΔE_{int} .

◆ This **energy conservation** equation is called the **First Law** of Thermodynamics: $\Delta E_{int} = Q - W$.

◆ Differential form of the First Law: $dE_{int} = dQ - dW$.

⇒ Q is **positive** when energy enters the system; Q is **negative** when energy leaves the system

⇒ W is **positive** when the system does work on the surroundings; W is **negative** when work is done on the system

⇒ **Special cases:**

1) **Isolated system** – does not interact with its surroundings. **Hence no heat transfer, no work done: $Q = W = 0$; $E_{int} = \text{const}$.**

2) **Cyclic process** – the system is not isolated but the process starts and ends at the same state : **$\Delta E_{int} = 0$ and hence $Q = W$.**

3) $W = 0 \Rightarrow \Delta E_{int} = Q$ or $Q = 0 \Rightarrow \Delta E_{int} = -W$.

⇒ **Common thermodynamic processes:**

1) **Adiabatic process** – no energy enters or leaves the system by heat: $Q = 0$, $W = -\Delta E_{int}$

2) **Isobaric process – no pressure change:** $W = P(V_f - V_i)$

3) **Isovolumetric process – volume stays constant:** $W = 0$

4) **Isothermal process – temperature is kept constant:**

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln V \Big|_{V_i}^{V_f} = nRT \ln \left(\frac{V_f}{V_i} \right)$$

◆ **Molar specific heat of an ideal gas**

⇒ The heat capacity depends on conditions, such as temperature or path by which the state of the system was changed. Real thermodynamic processes can often be divided into parts which take place at **constant volume** and at **constant pressure**.

$Q_{const.V} = nC_V \Delta T$, C_V is the molar specific heat at **constant volume**.

$Q_{const.P} = nC_P \Delta T$, C_P is the molar specific heat at **constant pressure**.

⇒ $C_P - C_V = R$ for any ideal gas, i.e. it does not depend on whether gas is comprised by monatomic or polyatomic molecules.

⇒ Properties of C_V and C_P are determined by the complexity of gas molecules.

⇒ The ratio $\gamma = C_P/C_V$ is related to the capacity of the system to do work upon expansion and the number of degrees of freedom.

- The **number of degrees of freedom** (DOF) for a molecule is the number of independent co-ordinates needed to specify its position and configuration. A molecule of n atoms has $3n$ DOF.

1. **Translational degrees of freedom:** 3 independent co-ordinates specify the centre of mass of the molecule.

2. **Rotational degrees of freedom:** diatomic molecule - 2 rotational DOF; non-linear molecules - 3 rotational DOF.

3. **Vibrational degrees of freedom:** $3n-5$ DOF for **linear** molecules and $3n-6$ DOF for **non-linear** molecules.

- ◆ In classical statistical mechanics the **‘equipartition of energy’ theorem** associates an energy of $RT/2$ per mole with each degree of translational or rotational freedom. An energy of RT per mole is associated with each **vibrational** DOF.

⇒ A monatomic gas: $C_V = 1/n \times \Delta E_{int}/\Delta T = \frac{3}{2}R = 12.5 \text{ J/mol}\cdot\text{K}$ for all monatomic gases at constant volume; $\gamma = C_P/C_V = 5/3 = 1.67$.

⇒ The more degrees of freedom available to a molecule, the more “ways” it can store internal energy; this results in a higher molar specific heat.

⇒ The rotational and vibrational motions of molecules **can be activated by collisions** and therefore are “coupled” to the translational motion of the molecules. Hence contribution of different degrees of freedom in heat capacity of gases depends on temperature.

◆ In **adiabatic** expansion and cooling of gases $PV^\gamma = \text{const.}$, where $\gamma = C_P/C_V$, and $P_i V_i^\gamma = P_f V_f^\gamma$, $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$.

◆ Energy transfer mechanisms

(1) **Conduction:** Fourier’s law of heat conduction: $dQ/dt = K \times A \times dT/dx$
The rate of heat flow is proportional to the area and temperature gradient.

⇒ Heat conduction through the interface between two materials

⇒ Mechanisms of heat conduction

(2) **Convection**

⇒ Natural and forced convection

⇒ Newton’s law of cooling states: $T_{obj}(t) = T_{surr} + \Delta T \times \exp(-t/\tau)$, where T_{obj} is the temperature of the object, T_{surr} is the temperature of the surrounding (air), ΔT is the initial temperature difference between the object and surroundings, τ is the cooling constant.

(3) **Radiation**

⇒ Mechanisms of radiation, black body radiation, Stefan-Boltzmann Law

9. SECOND LAW and HEAT ENGINES

- **Second Law of Thermodynamics (1):** Thermal energy always flows spontaneously from an object at a high temperature to one at a cool temperature and never in reverse.
- Heat Engine - device that converts thermal energy to mechanical work:

⇒ Follows a cyclic process: heat is added - work is done by the engine - heat is expelled

- **Second Law of Thermodynamics (2):** It is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of heat from a reservoir and the performance of an equal amount of work.

- Efficiency = $e = \text{Work done} / \text{input heat} = W/Q_h$

Q_h = heat absorbed from hot reservoir; Q_c = heat expelled to cold reservoir;

W = work done by the system.

$$\Rightarrow e = \frac{Q_h - Q_c}{Q_h}$$

How efficient can we make an engine?

- **Reversible Process:**

- the intermediate steps are known
- the system is never far from equilibrium
- the system can be returned to its original state.

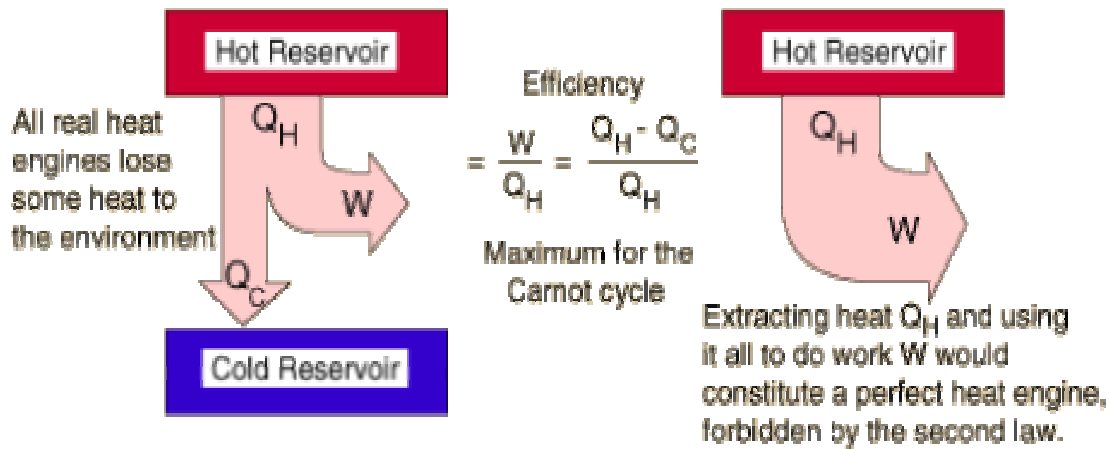
- **Irreversible Process**

- the intermediate steps are not known
- are non-equilibrium states
- the process can't be "retraced"

- **Reservoir:** The source of hot or cool material (steam and river or lake in thermal electric power station; burning gas-air mixture (450 °C) and cooling liquid or air running through the radiator (200 °C))

- **Carnot's Theorem:** "no heat engine operating between two heat reservoirs can be more efficient than a reversible one."

⇒ A corollary to Carnot's Theorem: "all reversible engines operating between the same heat reservoirs have the same efficiency."



- Carnot Cycle

- Carnot Efficiency : $e = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$ but $Q_c/Q_h = T_c/T_h$

$$\Rightarrow e = 1 - T_c/T_h$$

- The efficiency of the Carnot cycle (or any reversible cycle) depends only on the **temperatures** of the hot and cold reservoirs!

- Refrigerators or Heat Pumps

\Rightarrow Coefficient of performance (COP)

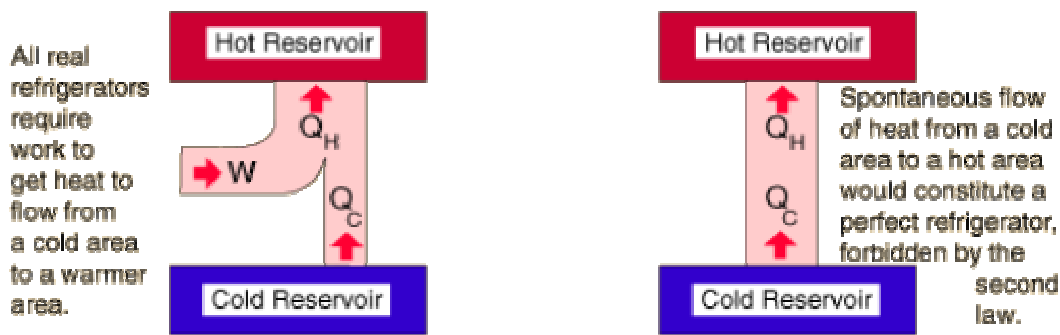
\Rightarrow COP (**heat pump**): heat **transferred** divided by work done by pump = Q_h/W

$$\text{COP}_{\max}(\text{heating mode}) = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c} = \frac{1}{1 - \frac{T_c}{T_h}} = \frac{T_h}{T_h - T_c}$$

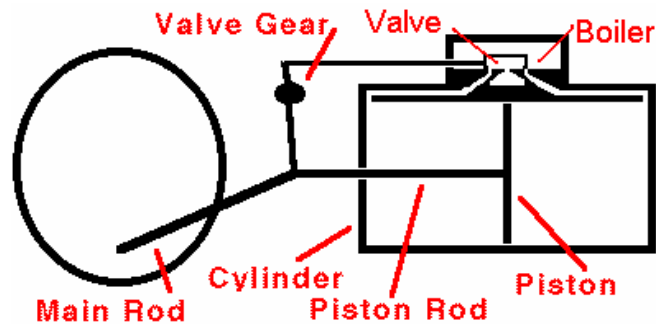
The trick is to keep the working liquid outside cooler than the outside temperature that it can absorb heat

\Rightarrow COP (**refrigerator**): heat **removed** divided by work = Q_c/W .

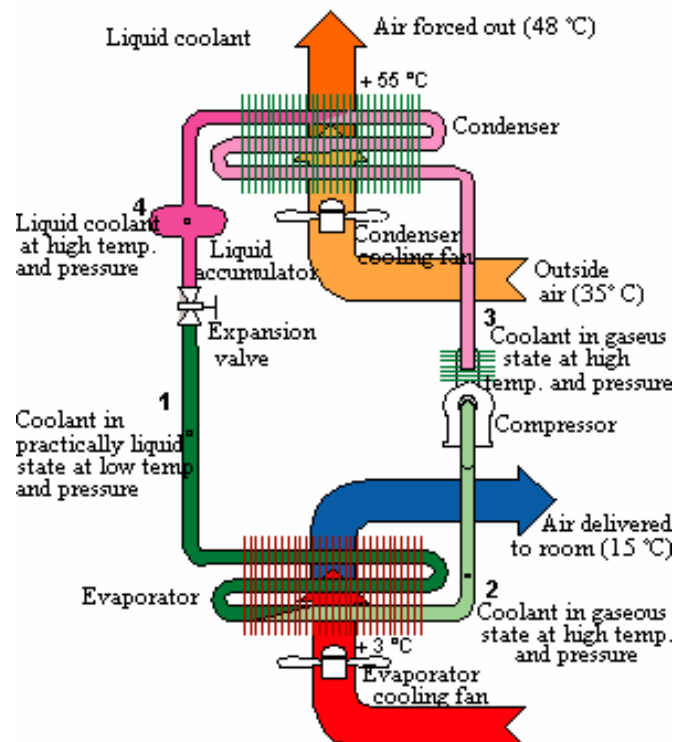
$$\text{COP}_{\max}(\text{cooling mode}) = \frac{Q_c}{W} = \frac{T_c}{T_h - T_c}$$



- Steam engine: $e_{\max} = (T_{\text{steam}} - T_{\text{air}}) / T_{\text{steam}}$.



- An air conditioner uses a material called a “working fluid” to transfer heat from inside of a room to the great outdoors: $e_{\max} = T_{\text{room}} / (T_{\text{outside}} - T_{\text{room}})$.



10. ENTROPY

- **Definition:** Consider any **infinitesimal process** in which a system changes from one **equilibrium state** to another. If dQ_r is the amount of energy transferred by heat when the system follows the **reversible path** between the states, then the **change in entropy dS** is equal to this amount of energy for the reversible process divided by the absolute temperature of the system, T :

$$dS = dQ_r/T.$$

⇒ Temperature was assumed constant because the process is infinitesimal. **Entropy has units of Joules per Kelvin.**

- The **entropy** of any substance is a **function of the condition** of the substance: for an **ideal gas** it is a function of its **temperature and volume**, and for a **solid and liquid** it is a function of its **temperature and internal structure**.
- **Sign:** When the **energy is absorbed** by the system, change in the heat is positive and the **entropy** of the system **increases**. When **energy is expelled** by the system, dQ_r is negative, and the **entropy** of the system **decreases**.
- To **calculate the change in entropy** for a finite process we need to **integrate** the energy transferred by heat divided by the temperature (which is not constant) **along a reversible path**:

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}.$$

How to calculate the entropy change in real life?

- Quasi-static reversible process for an **ideal gas**: $\Delta S = nCV \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$.

⇒ The change in the entropy depends only on the initial and final states and does not depend on the path between the states – **state function**

⇒ Carno-engine: no net change in entropy, but in real engine the entropy the isolated system always increases.

- **Second law (3): The total entropy of the universe is always increasing.**

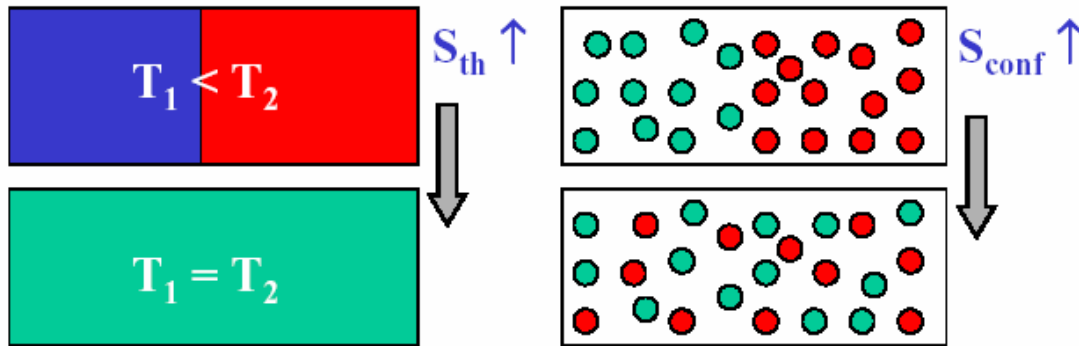
⇒ TdS the energy not available for doing work.

⇒ Entropy change in **calorimetric process**:

$$\Delta S = \int_1 dQ_{cold}/T + \int_2 dQ_{hot}/T = m_1 c_1 \int_{T_1}^{T_f} \frac{dT}{T} + m_2 c_2 \int_{T_2}^{T_f} \frac{dT}{T}.$$

⇒ **Entropy of mixing**: Consider isothermal mixing by diffusion of two different ideal gasses: $\Delta S = nR \sum \ln(V/V_i) = k_B \sum N_i \ln(N/N_i)$, $i = 1, 2$

- **Entropy and disorder**



11. THIRD LAW and ABSOLUTE ZERO TEMPERATURE

- Only entropy differences are determined from $\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$.
- Thermodynamic entropy is defined only up to an integration constant:

$$S(T) = \int dQ_r/T + \text{const.}$$

⇒ **How to choose the integration constant? What happens with thermodynamics properties of matter if T goes to absolute zero?**

- **There is as much physics at low temperatures as it is at high temperatures.**

⇒ **The lowest temperatures, which occur naturally, are:**

On the Earth: **-89 °C** have been recorded in **Antarctica**

In the Solar System: **-235 °C** or **38 K** on **Triton**, a moon of **Neptune**

In deep space: **2.73 K**.

⇒ **Extremely Low temperatures** have been obtained only using special techniques and **cryogenic fluids**, such as Nitrogen and Helium. Some common techniques are: (http://www.physics.carleton.ca/~hardy/75342/Lect_22/Lect_22.html)

⇒ Using elaborate methods, such as ‘magnetic traps’, one can cool groups of atoms to much lower temperatures. In particular, Silver nuclei have been **cooled to 280 pK** (280×10^{-12} K) at the Helsinki University of Technology, Finland (world record).

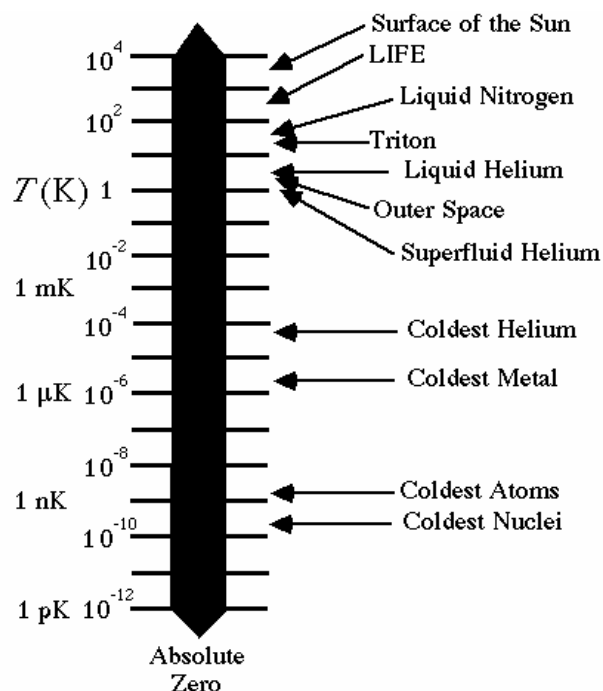
- It seems that we are unable to reach the absolute zero itself. It is forbidden by the **third law of thermodynamics**.

⇒ In the low temperature limit, all heat capacities C go to zero so that for a heat energy input Q the temperature rise $dT = Q/C$ becomes increasingly large. Even absorbed cosmic rays can produce a significant heat leak.

The properties of physical systems as their temperatures approach absolute zero have been first understood by Walther Nernst, and then made precise by Francis Simon during the decade 1927-37.

The two most common of the alternate statements of the **Third Law** are the following:

- Nernst-Simon Statement: **If ΔS is the entropy change during any reversible isothermal process in a condensed system, then ΔS tends to zero as the temperature goes to absolute zero.**
- Unattainability Statement: **It is impossible to reduce the temperature of any part of a system to zero in a finite number of operations.**



⇒ The Third Law encourages us to choose the integration constant so that $S(0) = 0$, and then:

$$S(T) = \int_0^T \frac{dQ_r(t)}{t}, \text{ where } t \text{ is the variable temperature.}$$

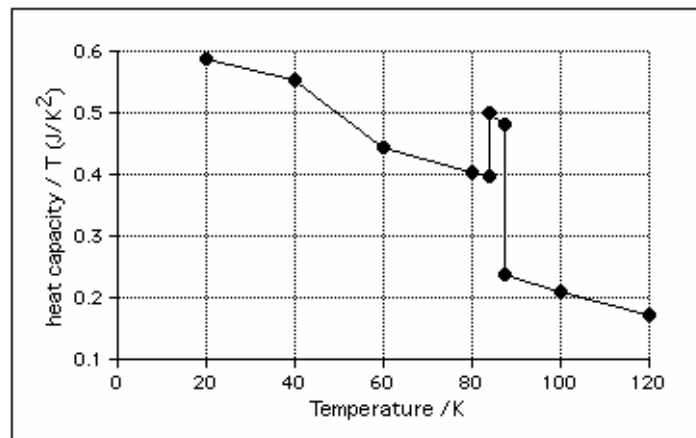
- The implication of S vanishing when T does is that a system so described would lose all randomness, or thermal agitation, at absolute zero. Therefore another common statement of the Third Law is:
- **The entropy of a perfect crystal of an element at the absolute zero of temperature is zero.**

⇒ Since $S(0) = 0$, the entropy of a pure element at any temperature T is given by:

$$S = \int_0^T \frac{C_p}{T} dT$$

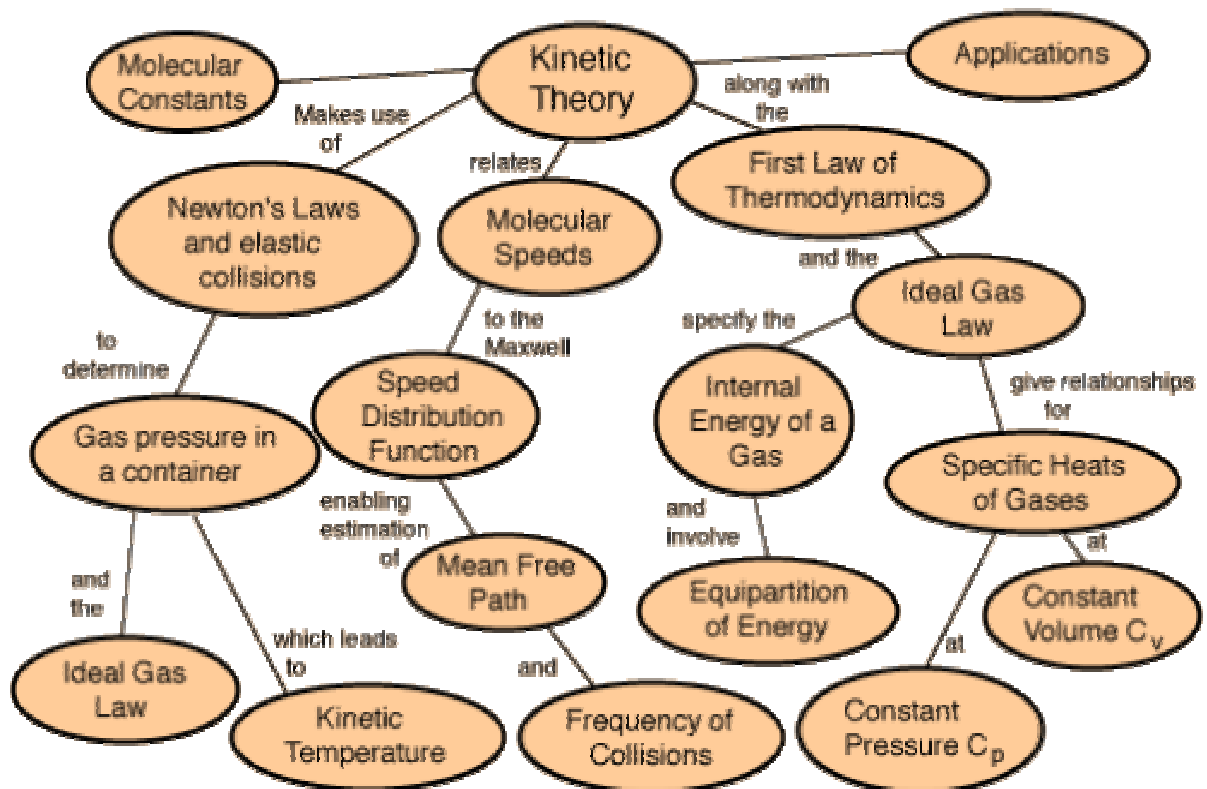
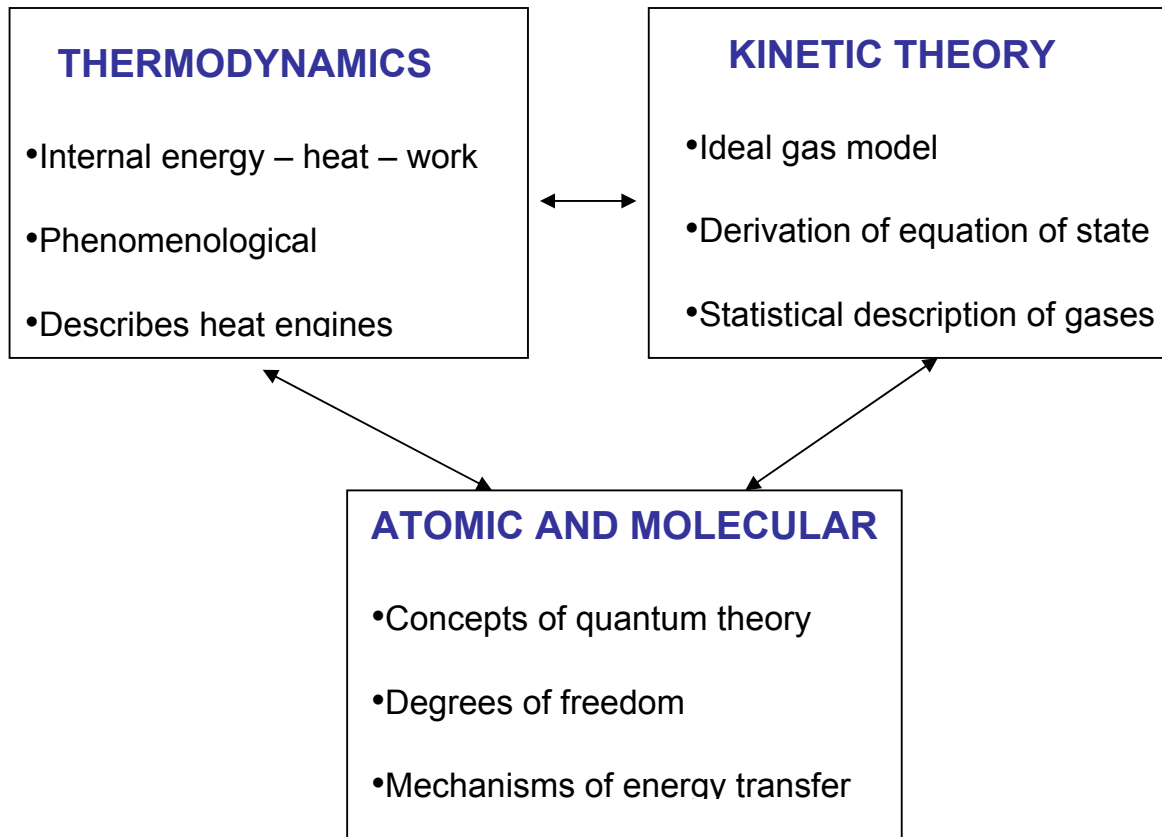
⇒ The values of standard entropies are actually the integral from zero to 298.15 K of $(C_p/T)dT$. The value of the entropy of an element at any temperature, can be obtained from careful measurements of the heat capacity of the element from the desired temperature down to absolute zero. Experimentally, measurements can be and have been made down to within 0.1 K and the heat capacity below measurable range can be accurately estimated.

⇒ (Heat capacities)/T of argon (Ar) are given in the graph below (values are taken from Försterling and Kuhn, "Moleküle und Molekülanhäufungen", Springer, Berlin 1983)



Summary:

1B28 THERMAL PHYSICS



Glossary

- **Adiabatic** processes: occurring without heat transfer.
- **Equation of State** A relationship between the state variables of the system. Simple systems in equilibrium are fully specified by two properties such as temperature and volume; all the other functions of state are functions of these. For an ideal gas, the equation of state is $PV = nRT$;
- **Equilibrium** A system is in equilibrium when its macroscopic properties (temperature, pressure) are uniform and not changing with time.
- **Extensive** Some thermodynamic functions of state are extensive: if the intensive variables (T , P) are kept constant, the extensive variables are proportional to the amount of substance present. Energy, volume, entropy, and heat capacities are all extensive. Extensive properties expressed per unit mass or per mole are then intensive, and are called **specific**: e.g. specific heat capacity. All functions of state are either extensive or intensive.
- **Function of state** A property of a system which only depends of the current state of the system and not on its history. Examples are temperature, pressure, volume, internal energy, entropy. Also called a **state variable** or a **macroscopic variable**.
- **Heat Reservoir** Surroundings at a certain temperature which are large enough to absorb heat from, or donate heat to, the system without appreciable change of temperature. Also **heat bath**.
- **Intensive** An intensive functions of state does not vary with the amount of the substance present. Examples are temperature, pressure, tension and external magnetic field. All functions of state are either extensive or intensive.
- **Isentropic** At constant entropy.
- **Isobaric** At constant pressure.
- **Isochoric** At constant volume.
- **Isothermal** At constant temperature.
- **Macroscopic** Pertaining to aspects of a system which can be measured classically, such as temperature, pressure etc; containing very large numbers of atoms.
- **Macrostate** The current disposition of the system defined in terms of macroscopic variables. Also (in classical thermal physics) **state**.
- **Microscopic** Pertaining to the underlying quantum state of a system
- **Microstate** The state of the system defined in terms of the current behaviour of all the constituent atoms. Also quantum state.
- **Reversible** A reversible process is one which would change direction with an infinitesimal change in external conditions. For a process to be reversible it must be frictionless and quasi-static so that no energy is dissipated and the system is always only infinitesimally removed from equilibrium. Because a reversible process passes through a series of quasi-equilibrium states it can be represented as a solid line on a plot of one state variable against another.
- **Surroundings** That part of an experimental set up, including the ambient air, which exchanges heat with, or does work on, the system.
- **System** That part of an experimental system in which we are primarily interested.

- **Universe** A deliberately grandiose term for the entire experimental set-up, comprising the system and the surroundings. Usually encountered in the phrase "the entropy change of the universe" which of course cannot be negative, though that of the system or surroundings alone may be. It should not be confused with the cosmological universe.

Some useful websites:

General:

<http://www.tass-survey.org/classes/phys312/phys312.html>

<http://hypertextbook.com/physics/thermal/resources.shtml>

<http://scienceworld.wolfram.com/physics/>

<http://dbhs.wvusd.k12.ca.us/webdocs/GasLaw/KMT-Gas-Laws.html>

<http://www.people.virginia.edu/~lz2n/mse305/>

Sketching the History of Statistical Mechanics and Thermodynamics:

http://history.hyperjeff.net/statmech_slim.html

General Chemistry: <http://www.chem.ufl.edu/~chm2040/Notes/>

Avogadro hypothesis: <http://www.carlton.paschools.pa.sk.ca/chemical/molemass/avogadro.htm>

About Temperature:

<http://my.unidata.ucar.edu/content/staff/blynds/tmp.html>

Mechanical work and heat:

<http://honolulu.hawaii.edu/distance/sci122/Programs/p21/p21.html#6.Ê%20Heat%20as%20Energy>

Low Temperature World Record: <http://boojum.hut.fi/Low-Temp-Record.html>