

STUDYNAMA.COM

India's Mega Online Education Hub for Class 9-12 Students, Engineers, Managers, Lawyers and Doctors.

Free Resources for Class 9-12 Students

- [Lecture Notes](#)
- [Project Reports](#)
- [Solved Papers](#)

[View More »](#)

Free Resources for Engineering Students

- [Lecture Notes](#)
- [Project Reports](#)
- [Solved Papers](#)

[View More »](#)

Free Resources for MBA/BBA Students

- [Lecture Notes](#)
- [Project Reports](#)
- [Solved Papers](#)

[View More »](#)

Free Resources for LLB/LLM Students

- [Lecture Notes](#)
- [Project Reports](#)
- [Solved Papers](#)

[View More »](#)

Free Resources for MBBS/BDS Students

- [Lecture Notes](#)
- [Project Reports](#)
- [Solved Papers](#)

[View More »](#)



▼▼ Scroll Down to View your Downloaded File! ▼▼

Disclaimer

Please note none of the content or study material in this document or content in this file is prepared or owned by Studynama.com. This content is shared by our student partners and we do not hold any copyright on this content.

Please let us know if the content in this file infringes any of your copyright by writing to us at: info@studynama.com and we will take appropriate action.

I. MOLECULAR COLLISIONS

Atomic and molecular collision processes are the physical interactions of atoms and molecules when they are brought into close contact with each other and with electrons, protons, neutrons or ions. This includes energy-conserving elastic scattering and inelastic scattering. Such collisions are an important probe of the structure and properties of matter.

II. MEAN FREE PATH

The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. Serway's approach is a good visualization - if the molecules have diameter d , then the effective cross-section for collision can be modeled by using a circle of diameter $2d$ to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t , the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.

$$\text{Mean free path} = \frac{Vt}{\pi d^2 V t n_V} = \frac{1}{\pi d^2 n_V}$$

The mean free path could then be taken as the length of the path divided by the number of collisions. The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules. The mean free path λ is related to the cross section σ and the number density n of particles by

$$\lambda \sim \frac{1}{n\sigma} \quad (1)$$

To see this, notice that a particle that undergoes a large number N of collisions will exhibit a zig-zag pattern of total length $L = N \lambda$, since the average distance between collisions is λ . We can think of the particle as sweeping out a volume

$$V = L\sigma = N\lambda\sigma \quad (2)$$

The number density of particles in this volume is n :

$$n = \frac{N}{V} = \frac{N}{N\lambda\sigma} = \frac{1}{\lambda\sigma} \quad (3)$$

where we are assuming that the number of collisions in the volume is the same as the number of molecules in the volume, and that the number density in the volume is the same as the number density in the sample as a whole. We can rewrite this equation as same as the number density in the sample as a whole. We can rewrite this equation as

$$\lambda \sim \frac{1}{n\sigma} \quad (4)$$

III. TRANSPORT PHENOMENA

The study of transport phenomena concerns the exchange of mass, energy, and momentum between observed and studied systems. While it draws from fields as diverse as continuum mechanics and thermodynamics, it places a heavy emphasis on the commonalities between the topics covered. Mass, momentum, and heat transport all share a very similar mathematical framework, and the parallels between them are exploited in the study of transport phenomena to draw deep mathematical connections that often provide very useful tools in the analysis of one field that are directly derived from the others. The fundamental analyses in all three subfields of mass, heat, and momentum transfer are often grounded in the simple principle that the sum total of the quantities being studied must be conserved by the system and its environment. Thus, the different phenomena that lead to transport are each considered individually with the knowledge that the sum of their contributions must equal zero. This principle is useful for calculating many relevant quantities. For example, in fluid mechanics, a common use of transport analysis is to determine the velocity profile of a fluid flowing through a rigid volume.

Transport phenomena are ubiquitous throughout the engineering disciplines. Some of the most common examples of transport analysis in engineering are seen in the fields of process, chemical, biological,[1] and mechanical engineering, but the subject is a fundamental component of the curriculum in all disciplines involved in any way with fluid mechanics, heat transfer, and mass transfer. It is now considered to be a part of the engineering discipline as much as thermodynamics, mechanics, and electromagnetism.

A. Momentum Transfer

In momentum transfer, the fluid is treated as a continuous distribution of matter. The study of momentum transfer, or fluid mechanics can be divided into two branches: fluid statics (fluids at rest), and fluid dynamics (fluids in motion). When a fluid is flowing in the x direction parallel to a solid surface, the fluid has x-directed momentum, and its concentration is x. By random diffusion of molecules there is an exchange of molecules in the z direction. Hence the x-directed momentum has been transferred in the z-direction from the faster- to the slower-moving layer. The equation for momentum transport is Newton's Law of Viscosity written as follows:

$$\tau_{zx} = -\nu \frac{d\rho v_x}{dz} \quad (5)$$

here τ_{zx} is the flux of x-directed momentum in the z direction, ν is $\frac{\mu}{\rho}$, the momentum diffusivity, z is the distance of transport or diffusion, ρ is the density, and μ is the viscosity. Newton's Law is the simplest relationship between the flux of momentum and the velocity gradient.

B. Mass Transfer

When a system contains two or more components whose concentration vary from point to point, there is a natural tendency for mass to be transferred, minimizing any concentration difference within the system. Mass Transfer in a system is governed by Fick's First Law: 'Diffusion flux from higher concentration to lower concentration is proportional to the gradient of the concentration of the substance and the diffusivity of the substance in the medium.' Mass transfer can take place due to different driving forces. Some of them are:

1. Mass can be transferred by the action of a pressure gradient (pressure diffusion)
2. Forced diffusion occurs because of the action of some external force
3. Diffusion can be caused by temperature gradients (thermal diffusion)
4. Diffusion can be caused by differences in chemical potential This can be compared to Fick's Law of Diffusion:

$$J_{Ay} = -D_{AB} \frac{dC_a}{dy} \quad (6)$$

where D is the diffusivity constant.

C. Energy Transfer

All processes in engineering involve the transfer of energy. Some examples are the heating and cooling of process streams, phase changes, distillations, etc. The basic principle is the first law of thermodynamics which is expressed as follows for a static system:

$$q = -K \frac{dT}{dx} \quad (7)$$

The net flux of energy through a system equals the conductivity times the rate of change of temperature with respect to position. For other systems that involve either turbulent flow, complex geometries or difficult boundary conditions another equation would be easier to use:

$$Q = h.A.\Delta T \quad (8)$$

where A is the surface area, ΔT is the temperature driving force, Q is the heat flow per unit time, and h is the heat transfer coefficient. Within heat transfer, two types of convection can occur:

Forced convection can occur in both laminar and turbulent flow. In the situation of laminar flow in circular tubes, several dimensionless numbers are used such as Nusselt number, Reynolds number, and Prandtl. The commonly used equation is:

$$Nu_a = \frac{h_a D}{T} \quad (9)$$

Natural or free convection is a function of Grashof and Prandtl numbers.

IV. JOULE EXPANSION OF IDEAL GAS

A Joule expansion is an irreversible expansion of a gas into an initially evacuated container with adiabatic walls. No work is done on the gas and no heat enters the gas, so $\Delta U = 0$. The temperature change is described by the Joule coefficient,

$$\mu_J = \left(\frac{dT}{dV}\right)_U \quad (10)$$

$$\mu_J = -\frac{1}{C_V} \left[T \frac{dP}{dT} \right]_V - P \quad (11)$$

For an ideal gas, $\mu_J = 0$. For a van der Waals gas, $\mu_J = \frac{a}{C_V V^2}$

In a Joule-Kelvin expansion, the gas is expanded adiabatically from pressure p_1 to p_2 by a steady flow through a porous plug (throttle valve). $\Delta Q = 0$, so enthalpy is conserved:

$$\begin{aligned} \Delta U &= \Delta W \\ U_2 - U_1 &= p_1 V_1 - p_2 V_2 \\ H_1 &= H_2 \end{aligned} \quad (12)$$

The temperature change is described by the Joule-Kelvin coefficient,

$$\begin{aligned} \mu_{JK} &= \left(\frac{dT}{dP}\right)_H \\ \mu_{JK} &= \frac{1}{C_P} \left[T \left(\frac{dV}{dT}\right)_P - V \right] \end{aligned} \quad (13)$$

For a van der Waals gas,

$$\lim_{p \rightarrow 0} \mu_{JK} = \frac{1}{C_P} \left(\frac{2a}{RT} - b \right) \quad (14)$$

This can be positive or negative, so both heating and cooling are possible.

V. LIQUEFACTION OF GASES

Liquefaction by the Linde cycle. A Joule-Kelvin gas expansion from the region in the p - T diagram where $\mu_{JK} > 0$ to the region where $\mu_{JK} < 0$ can produce strong cooling. Gas at a high initial pressure p_1 and temperature T_1 expands into a chamber at a much lower pressure $p_L \sim 1 \text{ atm}$. The exhaust gas flows back to the compressor at a pressure p_2 , where it is re-pressurized and the cycle repeated. The cold exhaust gas is passed through a heat exchanger in order to cool the incoming gas. This increases the efficiency of the process.

An advantage of the Joule-Kelvin liquefier is that the lower the temperature, the larger the drop in temperature for a given pressure drop. This is because the slope of the isenthalps increases as the temperature decreases.

VI. EQUATION OF STATE: REAL GASES: VAN DER WAALS AND OTHER EQUATIONS

The van der Waals equation is one of the most revered achievements in statistical physics. It is based on a picture which is perceived as an interpolation scheme. Accordingly, the equation of state of an ideal classical gas reads

$$p = nT \quad (15)$$

where p is the pressure, $n = \frac{N}{V}$ is the gas concentration, N is the number of molecules in gas, V is the volume and T is temperature. As it is well-known, it holds for rarefied gases at high temperature. On the other side, at high densities, the volume of the gas is limited by introducing an excluded volume b , according to the scheme $V \rightarrow V - Nb$. Consequently, the equation of state reads

$$p = \frac{NT}{(V - Nb)} = \frac{nt}{(1 - nb)} \quad (16)$$

It is usually thought that the van der Waals equation is an interpolation between equations

FIG. 1.

VII. DEVIATION FROM IDEAL GAS BEHAVIOR

A gas which obeys the gas laws and the gas equation $PV = nRT$ strictly at all temperatures and pressures is said to be an ideal gas. The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another. But no real gas strictly obeys the gas equation at all temperatures and pressures. Deviations from ideal behaviour are observed particularly at high pressures or low temperatures.

The deviation from ideal behaviour is expressed by introducing a factor Z known as compressibility factor in the ideal gas equation. Z may be expressed as $Z = \frac{PV}{nRT}$

In case of ideal gas, $PV = nRT$ $Z = 1$ In case of real gas, $PV \neq nRt$ $Z \neq 1$

Thus in case of real gases Z can be 1 or > 1

A. Causes of deviation from ideal behaviour

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases.

1. The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.
2. The forces of attraction between gas molecules are negligible.

The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas. But at low temperature or at high pressure, the molecules being incompressible the volumes of molecules are no more negligible as compared to the total volume of the gas.

The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored.

B. Critical Constants

The critical temperature, T_c , is characteristic of every gas and may be defined as: The temperature below which the continuous increase of pressure on a gas ultimately brings about liquefaction and above which no liquefaction can take place no matter what so ever pressure be applied

The pressure required to liquefy the gas at critical temperature is called critical pressure and the volume occupied by 1 mole of gas under these conditions is called the critical volume.

Van der Waals equation may be written as:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (17)$$

On solving the above equations, we get

$$V_c = 3bP_c = \frac{a}{27b^2}T_c = \frac{8a}{27bR} \quad (18)$$

C. Van der Waals force

In physical chemistry, the van der Waals forces (or van der Waals interaction), named after Dutch scientist Johannes Diderik van der Waals, are the residual attractive or repulsive forces between molecules or atomic groups that do not arise from a covalent bond, or ionic bonds. It can be shown that van der Waals forces are of the same origin as the Casimir effect, arising from quantum interactions with the zero-point field. The resulting van der Waals forces can be attractive or repulsive.

The term includes:

1. Force between permanent dipoles (Keesom force)
2. Force between a permanent dipole and a corresponding induced dipole (Debye force)
3. Force between instantaneously induced dipoles (London dispersion force).

It is also sometimes used loosely as a synonym for the totality of intermolecular forces.[citation needed] Van der Waals forces are relatively weak compared to covalent bonds, but play a fundamental role in fields as diverse as supramolecular chemistry, structural biology, polymer science, nanotechnology, surface science, and condensed matter physics. Van der Waals forces define many properties of organic compounds, including their solubility in polar and non-polar media.

VIII. VANDER WALLS EQUATION OF STATE

All equations of state, $P(\rho, T)$, should behave as $P = \rho T$ at low density. The second-order virial coefficient is usually negative, as long-range interactions are usually attractive and dominate at low density. For molecules, the long range interaction usually originates from induced dipoles attracting one another and falls off as $\frac{1}{r^6}$ at large r . At high densities, particles tend to run out of space and repel one another, and the contribution to the pressure from interactions tends to rise once again.

The Van der Waals parameterization of the equation of state incorporates both an attractive component for low density and repulsion at high density,

$$P = \frac{\rho}{1 - \frac{\rho}{\rho_s}} - a\rho^2 \quad (19)$$

Here, the second order virial coefficient is

$$A_2 = \frac{\rho_0}{\rho_s} - \frac{a\rho_0}{T} \quad (20)$$

and as long as a is large enough, the correction to the pressure to order 2 is negative. However, at high density, the first term in above Equation will dominate, and in fact P as $\rho \rightarrow \rho_s$. The quantity ρ_s is the saturation density, as it is the highest density one can obtain before the pressure jumps to infinity. As the temperature goes to zero, a system will approach the saturation density if there is no pressure. The inverse of ρ_s is often referred to as the excluded volume. The Van der Waals equation of state thus implies a hard-core interaction.

If one plots P vs. V , the behavior is no longer monotonic for low T . For these temperatures below the critical temperature,

$$T_c = \frac{8a\rho_s}{27} \quad (21)$$

multiple densities can provide the same pressure. We refer to the inflection point as the critical point, at which $V_c = \frac{3}{\rho_s}$, and $P_c = \frac{a\rho_s^2}{27}$. We will derive this expression shortly. A region of densities for $T \leq T_c$ is unstable to phase separation. To find the region we consider the conditions for phase co-existence.

$$T_{gas} = T_{Liq}, \quad P_{gas} = P_{Liq}, \quad \mu_{gas} = \mu_{Liq}, \quad (22)$$

The first two conditions can be satisfied by taking any two points on the same isotherm that are at the same pressure. The third condition, that the chemical potentials are equal, can also be illustrated with the isotherm. Beginning with

$$Tds = dE + PdV - \mu dN, \quad TS = PV + E\mu N, \quad (23)$$

one can solve for $N d\mu$,

$$d(E - TS + \mu N) = -PdV - SdT - Nd\mu = -d(PV)Nd\mu = -SdT + VdP \quad (24)$$

$$\mu_{gas} - \mu_{Liq} = \int v dP = \int d(Pv) - \int Pd(v) = P_{gas}V_{gas} - P_{Liq}V_{Liq} - \int PdV = 0 \quad (25)$$

Here, $v = V/N$ is the volume per particle. The condition that $\mu_{liq} = \mu_{gas}$ can then be stated graphically by stating that the integrated area between the P vs. V isotherm in the upper panel and the line between the two points is zero, i.e., there are equal amounts of area above and below the line.

Here, we make only a quick remark that the actual form of the coexistence curve, and the behavior of the matter, in the region near the critical point defies the simple Van der Waals picture. In that region, there are no longer two distinct phases and the density fluctuates wildly. Critical phenomena represents a field in itself, and will be discussed later in the course.

IX. JOULE-THOMSON EXPERIMENT

The apparatus itself is quite simple. Imagine a tube with a porous plate separating it into two parts. The porous plate will allow a gas to go through it, but only slowly. It acts as a throttle. On each side of the plate there is a piston that fits the tube tightly. Each piston can (in principle) be pushed up against the porous plate. The tube itself is insulated so that no heat can enter or leave the tube.

The experiment is also quite simple. Imagine that some gas is placed between the porous plate and the piston on the left side of the tube. This is side 1. On the other side the piston is flush against the porous plate. This is side 2.

The initial volume of gas on side 1 is V_1 . The pressure is p_1 and the temperature T . Now during the experiment gas is pushed through the porous plate by pushing on the piston on the left side. At the same time the piston on the right side is pulled in such a way that the pressure on the right side is always p_2 . At the end of the experiment all of the gas has been pushed through the porous plate. The volume on side 1 is zero. The final volume on the right side (side 2) is V_2 , the pressure is p_2 and the temperature T_2 .

The curious result of this experiment is that careful measurement shows that T_2 is not equal to T_1 . Under some conditions it is higher, under others it is lower

A. Initial analysis

The process starts with volume $V_1 = V_1$ and volume $V_2 = 0$. It ends with volume $V_1 = 0$ and volume $V_2 = V_2$. The work done on the left side is: $w_1 = -p_1(0 - V_1)$. The work done on the right side is: $w_2 = -p_2(V_2 - 0)$

The total work done is then:

$$w = p_1V_1 - p_2V_2 \quad (26)$$

Since the process is adiabatic, the total change in U is just the work, or

$$\Delta U = U_2 - U_1 = P_1V_1 = P_2V_2 \quad (27)$$

so that

$$H_2 - H_1 \quad (28)$$

and the process is isoenthalpic.

B. The Joule-Thomson Coefficient

What is measured experimentally is

$$\mu_{JT} = \lim_{\Delta p \rightarrow 0} \frac{T_2 - T_1}{P_2 - P_1} \quad (29)$$

which becomes, taking into account that the process is isoenthalpic:

$$\mu_{JT} = \left(\frac{dT}{dP} \right)_H \quad (30)$$

All that we've done so far is reduced the experiment to mathematics. The experimental result is that μ_{JT} is sometimes positive and sometimes negative. In fact it is found that there is a certain temperature called the inversion temperature such that if the initial temperature T_1 is above the inversion temperature, the final temperature is higher than the initial temperature. If the initial temperature is below the inversion temperature, the final temperature is lower than the initial temperature. The inversion temperature is found, experimentally, to depend on the pressure.

To understand this we need to relate μ_{JT} to quantities that are experimentally measurable. To do this we can start with the total differential of H assuming that T and p are the independent variables:

$$dH = \left(\frac{dH}{dT} \right)_P + \left(\frac{dH}{dP} \right)_T dp \quad (31)$$

Now our process is isoenthalpic, so $dH = 0$. This gives:

$$0 = \left(\frac{dH}{dT} \right)_P + \left(\frac{dH}{dP} \right)_T dp \quad (32)$$

Now I divide through by dp at constant H to get

$$\left(\frac{dH}{dT} \right)_P \left(\frac{dT}{dP} \right)_H + \left(\frac{dH}{dP} \right)_T = 0 \quad (33)$$

Note the subscript H at the appropriate point in above equation. Lastly, let us solve for $\left(\frac{dT}{dP} \right)_H$ to get

$$\left(\frac{dT}{dP} \right)_H = - \frac{\left(\frac{dH}{dP} \right)_T}{\left(\frac{dH}{dT} \right)_P} \quad (34)$$

This result simplifies a bit right away. We know that $\left(\frac{dH}{dT} \right)_P$ is the heat capacity C_P , so:

$$\left(\frac{dT}{dP} \right)_H = - \frac{\left(\frac{dH}{dP} \right)_T}{C_P} \quad (35)$$

but we can't make it any simpler. We need to express $\left(\frac{dH}{dP} \right)_T$ in terms that can be measured. Indeed, this can be done, but it requires one slight bit of magic. A result that will be proven later

$$\left(\frac{dH}{dP} \right)_T = V - T \left(\frac{dV}{dT} \right)_P \quad (36)$$

which finally gives

$$\mu_{JT} = \frac{T \left(\frac{dV}{dT} \right)_P - V}{C_P} \quad (37)$$

a neat equation in which all of the quantities are measurable. So we come to the end of the theory with a formula but no explanation. It all seems to depend on how the volume of the gas changes with temperature and on the heat capacity. How can we learn anything more? Well, we can look at model gases, that is, gases for which we know the equation of state. Looking at some of these may tell us something

C. The Joule-Thomson Coefficient for ideal gas

If we knew the equation of state for a gas, we could calculate the Joule-Thomson coefficient. For instance, for an ideal gas $(\frac{dV}{dT})_P = \frac{V}{T}$, so

$$\mu_{JT} = 0 \quad (38)$$

Ideal gases are boring, but they have told us something. There is no Joule-Thomson effect for an ideal gas at all. And how do ideal gases differ from real gases? They have no interactions at all. No attractions and no repulsions. But that's the only way in which they differ. So we conclude that the Joule-Thomson effect depends on the interactions between gas molecules.

A gas obeying van der Waals equation will prove more interesting. Since we can't solve van der Waals equation for V explicitly, we have to use an approximation. A convenient one is eq 1.10a in Atkins. This can be written

$$Z = 1 + \frac{1}{RT}(b - \frac{a}{RT})p + \dots \quad (39)$$

which is the first two terms of the virial equation approximation for a van der Waals gas.

We want to take this expression, solve it for V , and then differentiate it to get $(\frac{dV}{dT})_P$. With this available we can plug into above equation and calculate μ_{JT} .

Now since $Z = \frac{pV}{RT}$, we can solve above eq., to get

$$V = \frac{RT}{P} + (b - \frac{a}{RT})p + \dots \quad (40)$$

What we want is $(\frac{dV}{dT})_P$. From above equation we get:

$$(\frac{dV}{dT})_P = \frac{R}{p} + \frac{a}{RT^2} + \dots \quad (41)$$

Now this has to be multiplied by T . This gives

$$T(\frac{dV}{dT})_P = \frac{RT}{p} + \frac{a}{RT} + \dots \quad (42)$$

And now subtracting V as given in above equation, we get after some cancellations

$$T(\frac{dV}{dT})_P - V = -(b - \frac{2a}{RT}) + \dots \quad (43)$$

and so, finally, the Joule-Thomson coefficient for a gas obeying van der Waals equation is:

$$\mu_{JT} = \frac{\frac{2a}{RT} - b}{C_P} \quad (44)$$

OK, you can't tell much from this equation all by itself except that it certainly looks messy. But there is a way theoreticians handle things like this: they look at the extremes. Let's see what happens to the Joule-Thomson coefficient when the temperature gets very low. That is, what is the limit when T goes to 0? Well, as T goes to 0, all terms with T in the denominator get very large. So the term involving $\frac{2a}{RT}$ gets much larger than b . And the b term can be neglected at very low temperatures

$$\mu_{JT} = \frac{2a}{RT C_P} + \dots \quad (45)$$

which is clearly positive since every term in it is positive. This agrees with experiment. A positive Joule-Thomson coefficient means cooling. But also note that the resulting expression only contains the van der Waals a . All of the terms involving b have gone away at low temperature.

D. Estimates of J-T cooling

Joule-Thomson cooling occurs when a non-ideal gas expands from high to low pressure at constant enthalpy. The effect can be amplified by using the cooled gas to pre-cool the incoming gas in a heat exchanger.

This can be understood by referring to the Temperature vs. Entropy diagram for nitrogen shown in Figure 1. Nitrogen at 100 atmospheres in pressure (atm.) passes down a counter current heat-exchanger from A to B. At B it is allowed to expand through a valve or restricting capillary where it cools by the Joule-Thomson effect. The cold gas then passes back up the exchanger from D to E.

This can be used in refrigeration as shown in Figure. Here a compressor compresses the gas to high pressure, forcing it through the filter-dryer, down the counter-current heat exchanger, then through the JT valve where it expands and cools. Eventually the gas liquefies and collect in the reservoir. The evaporated vapor passes back up the heat exchanger, pre-cooling the incoming gas, then returns to the compressor, and the cycle is repeated.

Miniature Joule Thomson refrigerators have been used for the past several decades, primarily for the cooling of infra-red detectors for night vision. Microminiature refrigerators were developed at MMR Technologies, Inc. These are miniature coolers further reduced in size by two orders of magnitude. This was made possible by the development of photolithographic techniques at MMR for the fabrication of the micron size channels needed for the tiny heat exchangers for these devices. The low gas consumption, low cost of operation, and absence of maintenance of the microminiature refrigerators has made them attractive for incorporation in a wide range of laboratory instruments.

X. THERMAL EQUALLIBRUM

Two physical systems are in thermal equilibrium if no heat flows between them when they are connected by a path permeable to heat. Thermal equilibrium obeys the [zeroth law of thermodynamics]. A system is said to be in thermal equilibrium with itself if the temperature within the system is spatially and temporally uniform.

Systems in [thermodynamic equilibrium] are always in thermal equilibrium, but the converse is not always true. If the connection between the systems allows transfer of energy as heat but does not allow transfer of matter or transfer of energy as work, the two systems may reach thermal equilibrium without reaching thermodynamic equilibrium.

XI. INTERNAL ENERGY

The internal energy of a system is the energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields. It keeps account of the gains and losses of energy of the system that are due to changes in its internal state.

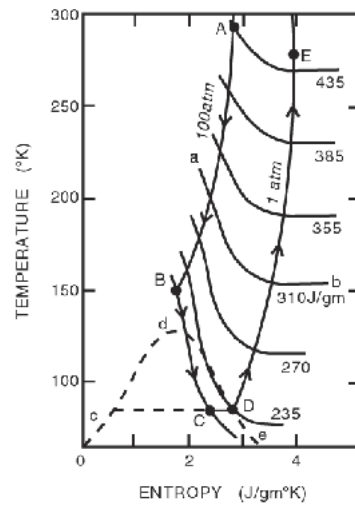
The internal energy of a system can be changed by transfers of matter and by work and heat transfer. When matter transfer is prevented by impermeable containing walls, the system is said to be closed. Then the first law of thermodynamics states that the increase in internal energy is equal to the total heat added plus the work done on the system by its surroundings. If the containing walls pass neither matter nor energy, the system is said to be isolated and its internal energy cannot change. The first law of thermodynamics may be regarded as establishing the existence of the internal energy. The internal energy is one of the two cardinal state functions of the state variables of a thermodynamic system.

XII. CARNOT THEOREM

No engine operating between two reservoirs (at temperatures T_H and T_C) is more efficient than a Carnot engine operating between them.

A. Proof

Since a Carnot engine is reversible, it can be run backward as a refrigerator. Use the non-Carnot engine to run the Carnot engine backward. Let us denote the heat exchanges of the non-Carnot and Carnot engines by Q_H , Q_C , and Q_H , Q_C , respectively. The net effect of the two engines is to transfer heat equal to $Q_H - Q_H = Q_C - Q_C$ from T_H to T_C . According to Clausius statement, the quantity of transferred heat cannot be negative, i.e. $Q_H \geq Q_H$. Since



1 of 1

24/10/16 16:22

FIG. 2. Temperature versus Entropy Diagram for Nitrogen Gas.

the same quantity of work W , is involved in this process, we conclude that

$$\frac{W}{Q_H} \leq \frac{W}{Q'_H} \rightarrow \eta_{Carnot} \geq \eta_{not} - \eta_{Carnot} \quad (46)$$

B. Corollary

: All reversible (Carnot) engines have the same universal efficiency $\eta(T_H, T_C)$, since each can be used to run the other one backward. The Thermodynamic Temperature Scale: As shown earlier, it is at least theoretically possible to construct a Carnot engine using an ideal gas (or any other two parameter system) as working substance. We now find that independent of the material used, and design and construction, all such cyclic and reversible engines have the

same maximum theoretical efficiency. Since this maximum efficiency is only dependent on the two temperatures, it can be used to construct a temperature scale. Such a temperature scale has the attractive property of being independent of the properties of any material (e.g. the ideal gas). To construct such a scale we first find out how $\eta(T_H, T_C)$ depends on the two temperatures. Consider two Carnot engines running in series, one between temperatures T_1 and T_2 , and the other between T_2 and T_3 ($T_1 T_2 T_3$). Denote the heat exchanges, and work outputs, of the two engines by Q_1, Q_2, W_{12} , and Q_2, Q_3, W_{23} respectively. Note that the heat dumped by the first engine is taken in by the second, so that the combined effect is another Carnot engine (since each component is reversible) with heat exchanges Q_1, Q_3 , and work output $W_{13} = W_{12} + W_{23}$. The three heats are related by

$$Q_2 = Q_1 - W_{12} = Q_1[1 - \eta(T_1, T_2)] \quad (47)$$

$$Q_3 = Q_2 - W_{23} = Q_2[1 - \eta(T_2, T_3)] = Q_1[1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)] \quad (48)$$

$$Q_3 = Q_1 - W_{13} = Q_1[1 - \eta(T_1, T_3)] \quad (49)$$

Comparison of the final two expressions yields

$$[1 - \eta(T_1, T_3)] = [1 - \eta(T_1, T_2)][1 - \eta(T_2, T_3)] \quad (50)$$

This property implies that $[1 - \eta(T_1, T_2)]$ can be written as a ratio of the form $\frac{f(T_2)}{f(T_1)}$ which by convention is set to $\frac{T_2}{T_1}$, i.e.

$$1 - \eta(T_1, T_2) = \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \quad (51)$$

$$\eta(T_H, T_C) = \frac{T_H - T_C}{T_H} \quad (52)$$

The above equation defines temperature up to a constant of proportionality, which is again set by choosing the triple point of water, ice, and steam to 273.16°K .

XIII. ENTROPY

: The following theorem allows us to construct another function of state using the second law.

XIV. CLAUSIUS THEOREM:

For any cyclic transformation (reversible or not), $\oint dQ/T \leq 0$ where dQ refers to the heat increment supplied to the system at temperature T .

A. Proof:

We can subdivide the cycle into a series of infinitesimal transformations in which the system receives energy in the form of heat dQ and work in equilibrium at each interval. Direct all the heat exchanges of the system to one part of a Carnot engine, which has another reservoir at a fixed temperature T_0 . Since the sign of dQ is not specified, the Carnot engine must operate a series of infinitesimal cycles in either direction. To deliver heat dQ to the system at some stage, the engine has to extract heat dQ_R from the fixed reservoir. If the heat is delivered to a part of the system which is locally at a temperature T ,

$$dQ_R = T_0 \frac{dQ}{T} \quad (53)$$

After the cycle is completed, the system and the Carnot Engine return to their original states. The net effect of the combined process is extracting heat $Q_R = \oint dQ$ from the reservoir and converting it to external work W . The work

$W = Q_R$ is the sum total of the work elements done by the Carnot engine, and the work performed by the system in the complete cycle. By Kelvins statement of the second law, $Q_R = W \leq 0$, i.e.,

$$T_0 \int \frac{dQ}{T} \leq 0 \rightarrow \int \frac{dQ}{T} \leq 0 \quad (54)$$

since T_0 . Note that T in above equation refers to the temperature of the whole system only for quasi-static processes in which it can be uniquely defined throughout the cycle. Otherwise, it is just a local temperature (say at a boundary of the system) at which the Carnot engine deposits the element of heat

XV. PRINCIPLE OF INCREASING ENTROPY

Consider a closed system consisting of a series of (open) macroscopic subsystems with equal numbers of molecules. Assume that each subsystem is in equilibrium internally but not with each other. As argued in the previous lecture each subsystem will have (to a good approximation) a Gibbs distribution which in the simplest case is specified by the subsystem mean energy. Assume that these mean energies are not all the same. From the Gibbs distribution we can deduce the entropy of each subsystem using the formula derived in the first lecture. Now if we further assume, as we did in the last lecture, that the joint probability distribution for the entire closed system is the product of all the individual Gibbs distributions then it follows that the total entropy of the system is the sum of the subsystem entropies i.e. entropy is an additive macroscopic variable like energy.

As time proceeds it is empirically observed that the total system entropy monotonically increases and in equilibrium a maximum is achieved in which the mean energies are all equal. This is commonly known as the second law of thermodynamics and is a central organizing principle in thermodynamics. It is important to note that this principle is appropriate only for a closed i.e. isolated system. In an open system entropy may be added from the system to the environment resulting in a local decrease but an overall total increase. The second law is an empirical fact of macroscopic systems and no violation has ever been observed. Actually proving it is so from first principles is non-trivial. Indeed the second law implies an arrow in time which is absent from the classical dynamical equations since these are invariant under a reversal of time. This has been a topic of endless fascination since statistical mechanics was first proposed by Boltzmann and it is fair to say still remains not fully understood. When we deal with non-equilibrium systems later in the course we shall revisit this issue.

XVI. THIRD LAW OF THERMODYNAMICS

We have just found that the thermal efficiency of all Carnot engines operating between the same two heat reservoirs is universal: η is the same for all such heat engines. Thus, η does not depend on the specific design of the engine. Instead, it can only depend on the properties of the reservoirs. Because the only relevant property is temperature, it must be that η is a function of just two variables, the temperatures of both reservoirs. It follows that if Q_1 denotes the heat absorbed from a hot reservoir of temperature T_1 , and Q_2 is the heat rejected to a cold reservoir of temperature T_2 , then

$$\frac{Q_1}{Q_2} = f(T_1, T_2), \quad (55)$$

where f is a universal function, the same for all Carnot engines.

We can obtain some information about the form of f by forming a composite engine out of two Carnot engines, one (R) operating between reservoirs at temperatures T_1 and T_2 , the other (R) operating between reservoirs at temperatures T_2 and T_3 . We assume $T_1 > T_2 > T_3$. The first engine absorbs a quantity Q_1 of heat W from the reservoir at T_1 , and rejects a quantity Q_2 of heat to the reservoir at T_2 ; for this engine, we have $\frac{Q_1}{Q_2} = f(T_1, T_2)$. The second engine absorbs a quantity Q_2 of heat from the reservoir at T_2 , and rejects a quantity Q_3 of heat to the reservoir at T_3 ; for this engine, we have $\frac{Q_2}{Q_3} = f(T_2, T_3)$. If we design our engines so that R' absorbs the same quantity of heat as R rejects, then $Q_2 = Q_2$, and we have $\frac{Q_1}{Q_3} = f(T_1, T_2) \cdot f(T_2, T_3)$. We now consider the composite engine, operating between the reservoirs at T_1 and T_3 , absorbing a quantity Q_1 of heat from the hot reservoir, and rejecting a quantity Q_3 of heat to the cold reservoir. Because the W composite engine is also a Carnot engine (it is reversible and it operates between the reservoirs at T_1 and T_3), we have $\frac{Q_1}{Q_3} = f(T_1, T_3)$. This means that f must satisfy the

functional relation

$$f(T_1, T_3) = f(T_1, T_2)f(T_2, T_3) \quad (56)$$

The only possible solution is $f(T_1, T_2) = \frac{\theta(T_1)}{\theta(T_2)}$, where $\theta(T)$ is a universal function of temperature. This function is called the thermodynamic temperature. To summarize, the ratio of heat absorbed to heat rejected by any Carnot engine operating between the same two reservoirs is given by

$$\frac{Q_1}{Q_2} = \frac{\theta(1)}{\theta(2)} \quad (57)$$

where $\theta(1) \sim \theta(2)$ are the thermodynamic temperatures of the hot and cold reservoirs, respectively. The great generality of this result is most remarkable.

We still have to determine the relation between θ and T . Because this relation is universal, it is the same for all Carnot engines operating between the same two reservoirs. It therefore suffices to consider one particular type of Carnot engine. We shall choose a Carnot engine whose working substance is an ideal gas. Calculating the thermal efficiency for this engine will allow us to deduce the form of the relation $\theta(T)$.

The four stages of the Carnot cycle are

1. $A \rightarrow B$: The ideal gas is compressed from a volume V_A to a volume V_B , at a constant temperature T_2 . The work done on the gas is $W(A \rightarrow B) = nRT_2 \ln(\frac{V_A}{V_B})$. This is equal to Q_2 , the heat rejected to the cold reservoir.

2. $B \rightarrow C$: The gas is compressed adiabatically to a smaller volume V_C . During this transformation, the temperature increases from T_2 to T_1 according to the relation $TV^{\gamma-1}$ is constant which implies $\frac{T_1}{T_2} = (\frac{V_B}{V_C})^{\gamma-1}$.

3. $C \rightarrow D$: The gas is expanded to a volume V_D , at a constant temperature T_1 . The heat absorbed from the hot reservoir is $Q_1 = nRT_1 \ln(\frac{V_D}{V_C})$.

4. $D \rightarrow A$: The gas is expanded adiabatically to the larger volume V_A . During this transformation, the temperature decreases from T_1 to T_2 according to the relation $TV^{\gamma-1}$ is constant which implies $\frac{T_1}{T_2} = (\frac{V_A}{V_B})^{\gamma-1}$. Finally, we find that the ratio of heat absorbed to heat rejected is equal to

$$\frac{Q_1}{Q_2} = \frac{nRT_1 \ln(\frac{V_D}{V_C})}{nRT_2 \ln(\frac{V_A}{V_B})} = \frac{T_1}{T_2} \quad (58)$$

To summarize, we have found that the thermal efficiency of any Carnot engine operating between a hot reservoir at T_1 and a cold reservoir at T_2 is given by

$$\eta = 1 - \frac{T_2}{T_1} \quad (59)$$

irrespective of the specific design of the engine. Notice that this is equal to the thermal efficiency of the Stirling engine, which was calculated.

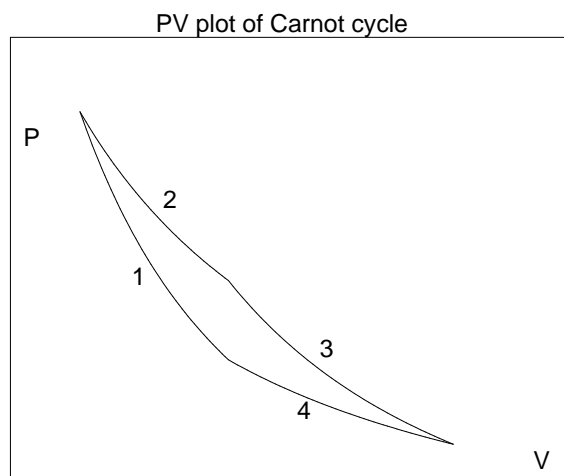


FIG. 3.

XVII. THERMODYNAMICS VARIABLES

When considering physical systems, it is often very useful to stay aware of whether the property being considered is intensive or extensive. An intensive variable is one that does not depend on the volume of the system, and an extensive variable is one that does. Intensive variables are sometimes called the bulk properties of the system. For example, consider the following expression of the ideal gas law

$$p = \rho RT \quad (60)$$

Say we had a box with each of the properties p , ρ and T , and we subdivided the box, it would not change the values of these properties, so each of these properties is intensive. However,

$$\rho = \frac{m}{V} \quad (61)$$

Subdividing the box, into small boxes with smaller V would lead to a corresponding reduction in the mass in each subdivided box m . Thus, m and V are extensive variables.

The distinction is important, because often we want to know how much we have of a particular thing. The nature of the thing is defined by one or two of the intensive variables p , ρ and T (note that from 1, we only need two to define the third). The amount we have is defined by the mass m . In atmospheric sciences, when we consider the ideal gas equation

$$p = \rho RT \quad (62)$$

where p is an intensive variable and mass $m = \rho V$ is the extensive variable, where m normally refers to either the mass of dry air or the mass of water vapor. The convention used in Wallace and Hobbs, one that is commonly employed is to use the lower case for intensive quantities and the upper case for extensive quantities. Thus, for example, the internal energy per unit mass is given the symbol u and the internal energy is given the symbol U . In atmospheric sciences, we very often think about intensive quantities, because we reference them to a parcel of air in which the mass of the air (but not the volume) does not change with time. Thus

$$u = \frac{U}{m} \quad (63)$$

In the notes here, I will express intensive variables that are referenced with respect to volume in bold lower case, i.e. the internal energy per unit volume is u

XVIII. MAXWELLS GENERAL RELATION

we observed that quantities such as the isothermal compressibility, the coefficient of thermal expansion, and the molar heat capacities describe properties of physical interest. Each of these is essentially a derivative $(\partial X / \partial Y)_{r.r...}$, in which the variables are either extensive or intensive thermodynamic parameters. With a wide range of extensive and intensive parameters from which to choose, in general systems, the number of such possible derivatives is immense. But there are relations among such derivatives, so that a variety of relations among different variables are possible.

We have noted that both $S(U, V, N)$ and $U(S, V, N)$ contain complete thermodynamic information. We will use the fundamental thermodynamic identity

$$dU = Tds - pdV + \mu dN \quad (64)$$

as an aid to memorizing the of temperature, pressure, and chemical potential from the consideration of equilibrium conditions. by calculating the appropriate partial derivatives we have

$$\left(\frac{dU}{dS}\right)_{V,N} = T, \quad (65)$$

$$\left(\frac{dU}{dV}\right)_{S,N} = -P, \quad (66)$$

and

$$\left(\frac{dU}{dN}\right)_{S,N} = \mu, \quad (67)$$

We can also write the fundamental thermodynamic identity in the entropy representation:

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (68)$$

from which we find

$$\left(\frac{dS}{dU}\right)_{V,N} = \frac{1}{T}, \quad (69)$$

$$\left(\frac{dS}{dV}\right)_{U,N} = \frac{P}{T}, \quad (70)$$

and

$$\left(\frac{dS}{dN}\right)_{U,N} = -\frac{\mu}{T}, \quad (71)$$

By calculating the second partial derivatives of these quantities we find the Maxwell relations. Maxwell relations can be used to relate partial derivatives that are easily measurable to those that are not. Starting from

$$\left(\frac{dS}{dN}\right)_{U,N} = T, \quad \left(\frac{dU}{dV}\right)_{S,N} = -P, \quad (72)$$

we can calculate

$$\frac{d^2U}{dVdS} = \left(\frac{dT}{dV}\right)_{S,N}, \quad \frac{d^2U}{dVdS} = -\left(\frac{dp}{dS}\right)_{V,N}, \quad (73)$$

Now since under appropriate conditions

$$\frac{d^2U}{dVdS} = \frac{d^2U}{dSdV}, \quad (74)$$

then

$$\left(\frac{dT}{dV}\right)_{S,N} = \left(\frac{dp}{dS}\right)_{V,N}, \quad (75)$$

This result is called a Maxwell relation. By considering the other second partial derivatives, we find two other Maxwell relations from the energy representation of the fundamental thermodynamic identity. These are:

$$\left(\frac{dT}{dN}\right)_{S,V} = \left(\frac{d\mu}{dS}\right)_{V,N} \quad - \left(\frac{dp}{dN}\right)_{S,V} = \left(\frac{d\mu}{dV}\right)_{S,N} \quad (76)$$

Similarly, in the entropy representation, starting from

$$dS = \frac{dU}{T} + \frac{p}{T}dV - \frac{d\mu}{T}dN \quad (77)$$

and the results

$$\left(\frac{dS}{dU}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{dS}{dV}\right)_{U,N} = \frac{p}{T}, \quad \left(\frac{dS}{dN}\right)_{U,N} = -\frac{\mu}{T} \quad (78)$$

we find the Maxwell relations:

$$\left(\frac{dS}{dV}\right)_{T,N} = \left(\frac{dp}{dT}\right)_{V,N}, \quad \left(\frac{dS}{dN}\right)_{T,V} = \left(\frac{d\mu}{dT}\right)_{V,N}, \quad \left(\frac{dp}{dN}\right)_{T,V} = \left(\frac{d\mu}{dV}\right)_{T,N} \quad (79)$$

XIX. EQUILLIBRUM BETWEEN PHASES

collection of molecules is in equilibrium with its surroundings if there is no net transfer of energy or matter across the boundaries to the environment. Individual molecules may constantly be zinging across the boundaries, or bumping into neighbors and transferring heat, due to thermal motion. But if we average over millions of molecules, the number of molecules leaving the volume of interest ("control volume") gets cancelled out by an equal number returning to the control volume, so the net motion across the boundary is zero. This situation is analogous to chemical reaction equilibrium – when equilibrium is reached, the rate of the forward reaction is equal to the rate of the reverse reaction, and there is no net measurable change in the concentration of reactants or products with time. In each case, the equilibrium is dynamic, meaning that forward and reverse reactions are constantly occurring. However, the overall measurable properties of the system do not change with time, and we consider the system at equilibrium.

Consider the situation where Phase I and Phase II are pure components A and B (phases are liquid, solid, or gas). Imagine that you put A + B together in a closed vial, shook the vial vigorously, then waited an "infinitely" long time, keeping the vial at constant temperature. At infinity, you should observe 2 separate phases (e.g., a layer of salt crystals at the bottom of a layer of water; oil layered on top of water, or liquid/gas). [Note – if you do not observe 2 phases at infinite time, then you did not add enough of the component in the missing phase...i.e., you did not reach its solubility limit. Go back and add more until you see two phases at infinity...] You then carefully withdraw a small sample of Phase II and determine the concentration of A in it. This concentration is defined as the "solubility" of A in B – it is the most A that will ever dissolve in B at that temperature. You also withdraw a small amount of Phase I and measure the concentration of B in it. This gives you the solubility of "B" in "A" at that temperature. How do you know you are at equilibrium? It is not always easy to tell! Systems come to equilibrium over anywhere from a few minutes to a few days. equilibrium is determined by careful sampling, always keeping the vial at a constant temperature. When the concentrations no longer change with time (may require many many points to determine you have a flat line within statistical significance), you are at equilibrium.

If "A" (Phase I) is a liquid and "B" (Phase II) is a gas, the equilibrium concentration of A in B is usually reported as a vapor pressure of A, and is often designated as a "saturation" vapor pressure. Antoine's equation is a common correlation of the vapor pressures of various compounds as a function of temperature. Gasses (such as oxygen and nitrogen) are typically only sparingly soluble in liquids and their solubilities are typically reported as Henry's Law coefficients. Liquid/liquid solubilities are often reported as volume percents (vol). [For example, when water and oil are mixed, a small amount of water dissolves in the oil, as in the homework problem]. The solubilities of solids in liquids are often reported as weight percents (wt). There is no set, standard reporting structure, so just look at units carefully.

Now consider that Phase I and Phase II are pure components A + B and a small amount of component "C" is added. Component C distributes throughout the two phases according to its relative solubility in each phase. Visualize a container filled with an oil/water mix (AB), to which a brilliant blue hydrophilic dye ("C") is added. The water phase will appear deep blue, but the oil phase will appear only faintly blue. Hydrophilic means "water-loving," and the dye partitions into the aqueous phase. [Note that such dyed, oil/water-filled devices were a commercial fad not too long ago as "instant ocean" (usually, the "oceans" contained a tiny air bubble to allow for thermal expansion/contraction).] A key factor in understanding phase equilibria is to realize that there are two possible routes to determining the concentrations of the dye (aka, component "C") in each of the two phases. Both methods give you a parameter known as the partition coefficient – the relative solubility in one phase compared to the other.

XX. CLASIUS-CLAPEYRON EQUATION

The Clausius-Clapeyron equation relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapour pressure with temperature. Or, in the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure.

Let us imagine a vapour in equilibrium with its liquid held in a cylinder by a piston, at a constant temperature namely the temperature at which the liquid and vapour are in equilibrium that is to say, the boiling (or condensation) point for that pressure. We imagine the piston to be pulled out, at constant temperature; liquid evaporates and the pressure remains constant. If the piston is pushed in, vapour condenses, at constant temperature and pressure. During this process the pressure and temperature remain constant, so the Gibbs free energy of the system is constant.

Let G_1 be the specific Gibbs free energy for the liquid and G_2 be the specific Gibbs free energy for the vapour. Suppose that a mass dm of the liquid vaporizes, so that the Gibbs free energy for the liquid decreases by $G_1 dm$ and the Gibbs free energy for the vapour increases by $G_2 dm$. But the Gibbs free energy for the system is constant. This therefore shows that, when we have a liquid in equilibrium with its vapour (i.e. at its boiling point) the specific Gibbs

free energies of liquid and vapour are equal. (The same is true, of course, for the molar Gibbs free energies.) That is:

$$H_1 - TS_1 = H_2 - TS_2 \quad (80)$$

$$T(S_2 - S_1) = H_2 - H_1 \quad (81)$$

in which the enthalpy and entropy are specific. The left hand side is the specific latent heat of vaporization, and we already knew from Chapter 9 that this was equal to the difference in the specific enthalpies of liquid and vapour.

The equality of the specific Gibbs free energies of liquid and vapour can also be written

$$U_1 - TS_1 + PV_1 = U_2 - TS_2 + PV_2, \quad (82)$$

$$T(S_2 - S_1) = U_1 - U_2 + P(V_2 - V_1) \quad (83)$$

This shows that the latent heat of vaporization goes into two things: To increase in the internal energy upon vaporization (especially the increase of potential energy as the molecules are pulled apart from each other) and the PdV work done against the external pressure as the volume increases. Thus we could divide the latent heat into an internal latent heat and an external latent heat.

In the foregoing, we imagined that some liquid vaporized as we withdrew the piston. Now let us imagine that we cause some liquid to vaporize as we add some heat at constant volume. The specific Gibbs free energies of liquid and vapour both increase, but they increase by the same amount because, as we have seen, when a liquid and its vapour are in equilibrium at the boiling point, their specific Gibbs free energies are equal. Thus

$$-S_1dT + V_1dP = -S_2dT + V_2dP \quad (84)$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \quad (85)$$

The left hand side is the rate of increase of vapour pressure with temperature, while $S_2 - S_1$ is equal to L/T , where L is the specific latent heat of vaporization. Thus we arrive at the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad (86)$$

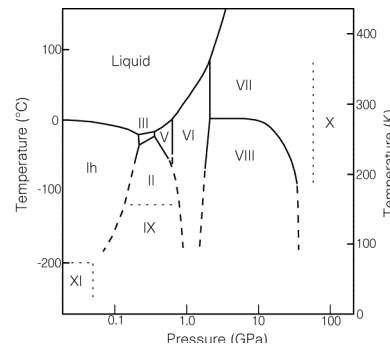
XXI. PHASE TRANSFORMATION OF A SINGLE SUBSTANCE

Boiling, freezing, and the conversion of graphite to diamond examples of phase transitions changes of phase without change of chemical composition. In this chapter we describe such processes thermodynamically, using the tendency of systems at constant temperature and pressure to minimize their Gibbs energies.

A phase of a substance uniform throughout in chemical composition and physical state: solid, liquid, and gas phases of a substance; its various solid phases (the white and black allotropes of phosphorus, graphite and diamond, monoclinic and orthorhombic sulfur, etc.)

A phase transition the spontaneous conversion of one phase to another occurring at a characteristic temperature at a given pressure. The transition temperature, T_{trs} the temperature at which two phases are in equilibrium at the prevailing pressure. We must distinguish between the thermodynamic description of a phase transition and the rate at which the transition occurs. A transition, which is spontaneous according to thermodynamics, may occur too slowly to be significant in practice. Example: graphite and diamond at normal T and p the molar Gibbs energy of graphite is lower than that of diamond there is a thermodynamic tendency for diamond to change into graphite. However, for the transition to occur, the C atoms must change their locations, which a very slow process in a solid, unless T is very high. The rate to reach equilibrium is a kinetic problem outside the range of thermodynamics. In gases and liquids, the molecules are mobile and phase transitions occur rapidly, but in solids thermodynamic instability may be frozen in. Thermodynamically unstable phases that persist because the transition is kinetically hindered metastable phases The phase diagram of a substance a map that shows the regions of temperature and pressure at which its various phases are thermodynamically most stable.

The boundaries between regions (phase boundaries) show the values of p and T at which the two neighboring phases are in equilibrium. The pressure of vapor in equilibrium with its liquid vapor pressure. The liquid-vapor phase boundary shows the variation of the vapor pressure with temperature. The solid-vapor phase boundary shows the variation of the sublimation vapor pressure with temperature.



1 of 1

23/10/16 18:41

FIG. 4.

XXII. CALCULATION OF VAPOUR PRESSURE

At ambient temperatures, the vapor pressure of a compound can vary by an order of magnitude, so the dependence on temperature is important. It is illustrative to imagine what the molecules of a substance achieve to establish an equilibrium vapor pressure by examining a kinetic-molecular description. The molecules in the liquid will be thermally jostling each other and will be continuously exchanging energies. At a given temperature, the energies of the molecules in the liquid will have a distribution of energies according to the Maxwell-Boltzmann distribution. Some of these molecules will have sufficient energy to overcome the intermolecular forces of attraction. Those molecules on the surface of the liquid with energies greater than the intermolecular forces will escape the liquid. The concentration (partial pressure or vapor pressure) of the molecules above the liquid will steadily increase and the rate of collisions will also increase. A fraction of these colliding molecules will lose sufficient energy so that if they come in contact with the liquid surface, they will become trapped again. When the rate of escape (evaporation) from the liquid equals the rate of entrapment (condensation), the partial pressure of the gas above the pure liquid is called the equilibrium vapor pressure, P .

$$P = e^{\frac{\text{energy}}{RT}} \quad (87)$$

and also

$$\ln P = -\frac{\text{energy}}{RT} + \text{constant} \quad (88)$$

XXIII. CHAPTER. 3

XXIV. THERMODYNAMIC POTENTIALS

Evolution of non-equilibrium systems towards equilibrium is governed by the second law of thermodynamics. For example, in the previous section we showed that for an adiabatically isolated system entropy must increase in any spontaneous change and reaches a maximum in equilibrium. What about out of equilibrium systems that are not adiabatically isolated and which may also be subject to external mechanical work? It is usually possible to define other thermodynamic potentials that are extremized when the system is in equilibrium.

Enthalpy is the appropriate function when there is no heat exchange ($dQ = 0$), and the system comes to mechanical equilibrium with a constant external force. The minimum enthalpy principle merely formulates the observation that stable mechanical equilibrium is obtained by minimizing the net potential energy of the system plus the external agent. For example, consider a spring of natural extension L_0 and spring constant K , subject to the force exerted by a particle of mass m . For an extension $x = LL_0$, the internal energy of the spring is $\frac{Kx^2}{2}$, while there is a change of mgx in the potential energy of the particle. Mechanical equilibrium is obtained by minimizing $\frac{Kx^2}{2} - mgx$ at an extension $x_{eq} = \frac{mg}{K}$. The spring at any other value of the displacement initially oscillates before coming to rest at x_{eq} due to friction. For general displacements x , at constant generalized forces J , the work input to the system is $dW \leq J\delta x$ and

$$\delta H \leq 0, \quad H = E - Jx \quad (89)$$

is the enthalpy. The variations of H in equilibrium are given by

$$dH = dE - d(Jx) = Tds + Jdx - x.dJ - J.dx = Tds - x.dJ \quad (90)$$

Note that above equation refers to variations of H on approaching equilibrium as some parameter that is not a function of state is varied (e.g. the velocity of the particle joined to the spring in the above example). Therefore it describes a relation between equilibrium coordinates. To differentiate the two cases, I will denote the former non-equilibrium variations by δ .

The coordinate set (S, J) is the natural choice for describing the enthalpy, and it follows from eq. that

$$x_i = -\left(\frac{dH}{J_i}\right)_S \quad (91)$$

Similarly Variations of the enthalpy with temperature are related to heat capacities at constant force.

XXV. PROBABILITY

The probability of an event is its relative frequency in the long run. If an event occurs x times out of n , then its probability will converge on X/n as n becomes infinitely large. For example, if we flip a coin many times, we expect to see half the flips turn up heads. Note that when n is small, the observed relative frequency of an event will not be a reliable reflection of its probability. However, as the number of observations n increases, the observed frequency becomes a more reliable reflection of the probability. For example, if a coin is flipped 10 times, there is no guarantee that it will turn up as exactly 5 heads every time. However, if the coin is flipped 10,000 times, chances are pretty good that the proportions of heads will be pretty close to 0.5.

XXVI. MICROSTATE

Classical thermodynamics describes macroscopic systems in terms of a few variables (functions of state): temperature, pressure, volume. But such a system is really made of atoms, so a much richer description must be possible in principle: we could specify the quantum state of all the atoms of the microstate. Of course as the atoms interact this state changes very rapidly—perhaps 10^{35} times a second. But the observed macrostate doesn't change. Many different microstates all correspond to the same macrostate.

A Microstate is defined as a state of the system where all the parameters of the constituents (particles) are specified. Many microstates exist for each state of the system specified in macroscopic variables (E, V, N, \dots) and there are many parameters for each state. We have 2 perspectives to approach in looking at a microstate :

XXVII. MACROSTATE

A Macrostate is defined as a state of the system where the distribution of particles over the energy levels is specified. The macrostate includes what are the different energy levels and the number of particles having particular energies. It contains many microstates.

In the equilibrium thermodynamic state, we only need to specify 3 macroscopic variables (P,V,T) or (P,V,N) or (E,V,N), where P : pressure, V : Volume, T : Temperature, N : Number of particles and E : Energy. The equation of state for the system relates the 3 variables to a fourth, for e.g. for an ideal gas.

$$PV = NKT \quad (92)$$

In statistical mechanics, the equilibrium tends towards a macrostate which is the most stable. The stability of the macrostate depends on the perspective of microstates. We adopt the a priori assumption which states the macrostate that is the most stable contains the overwhelming majority of microstates. This also gives the probabilistic approach in physics.

Studynama.com

Introduction

I. BOLTZMANN ENTROPY RELATION

In statistical mechanics, Boltzmann's equation is a probability equation relating the entropy S of an ideal gas to the quantity W , numbers are real microstates corresponding to a given macrostate:

$$S = k_B \log W \quad (1)$$

where k_B is the Boltzmann constant (also written with k), which is equal to 1.38065×10^{-23} J/K.

Canonical Distribution Law

Consider a system A in contact with a heat reservoir A' at temperature T . The whole system $(A + A')$ is isolated. Hence, its total energy is conserved (the number of particles is also conserved). The system A can be found in any energy E and the A' in corresponding $(E^0 - E)$. We are interested in the probability of finding the system A in a state having energy E_i . When A is definitely in a state of energy E_i . The number of states accessible to the whole system is simply the number of states accessible by the system A' which is equal to $\Omega'(E^{\text{deg}} - E_i)$ when its energy lies in some narrow range δE around $E^0 - E_i$.

$$So, P(E_i) = C\Omega'(E^0 - E_i) \quad (2)$$

Since, A' is a heat reservoir, we may take

$$E_i \ll E^0$$

$$So, \quad \Omega'(E^0 - E_i) = e^{\ln \Omega'(E^0 - E_i)} \quad (3)$$

$$= e^{\ln \Omega'(E^0) - E_i \frac{\partial \ln \Omega(E^0)}{\partial E}} \quad (4)$$

$$= e^{\ln \Omega'(E^0)} e^{-\beta E_i} \quad (5)$$

Thus

$$P(E_i) = C e^{\beta E_i}$$

Where, C is some constant of proportionality which is to be determined by the condition $\sum_i P(E_i) = 1$

The exponential factor $e^{-\beta E}$ is called the Boltzmann factor. An ensemble of systems of which can exchange energy with a reservoir (but not particle) are said to be canonical ensemble, and the corresponding probability distribution is called a canonical distribution.

Partition Function

We know the classical distribution Function can be written as

$$n_i = g_i e^{-\beta \epsilon_i - \mu} \quad (6)$$

$$n_i = e^{\beta \mu} (g_i e^{-\beta \epsilon_i}) \quad (7)$$

where $\beta = (k_B T)^{-1}$.

Since $\sum_i n_i (= N)$ is the total number of particles, we have

$$N = e^{\beta \mu} \sum_i g_i e^{-\beta \epsilon_i} \quad (8)$$

On combining Eqs() and () we find that the probability of finding a particle in the i th energy level is given by

$$P_i = \frac{n_i}{N} = \frac{g_i e^{-\beta \epsilon_i}}{\sum_i g_i e^{-\beta \epsilon_i}} \quad (9)$$

The quantity in the denominator of Eq.(9) denotes the sum over states and is called the partition function. it is generally denoted by the symbol Z , i.e.

$$Z = \sum_i g_i e^{-\beta \epsilon_i} \quad (10)$$

Partition Function For An Ideal Monoatomic Gas

Consider an ideal monoatomic gas contained in a box. We know that all gaseous particles are identical and their motion is completely random. This means that they cannot be distinguished from each other. Let the number of particles be N . We now wish to obtain the partition function of this system of ' N non-localised, indistinguishable, independent particles in terms of the single particle partition function. We know that in such case, there is no potential energy due to interaction. Moreover, at moderate temperature the higher energy electronic states and nuclear states of individual particles are not excited and we have to consider only the translational motion of any one molecule.

Single Particle Partition Function

Let us consider one particle in a cubical box of side L , i.e. having volume $V = L^3$. The box is placed in thermal contact with a heat reservoir at a constant temperature T . Since the particle has translational degrees of freedom only, the energy eigenvalues of the possible single particle quantum states are

$$\epsilon_i = \frac{\pi^2 \hbar^2}{2mV^{2/3}} (n_x^2 + n_y^2 + n_z^2) \quad (11)$$

where each of n_x , n_y and n_z may have values in the range 1 to ∞ . Hence, the single particle partition function is given by

$$Z_s = \sum_i \exp(-\beta \epsilon_i) = \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp[-\alpha (n_x^2 + n_y^2 + n_z^2)] \quad (12)$$

where

$$\alpha = \frac{\beta \pi^2 \hbar^2}{2mV^{2/3}} \quad (13)$$

To evaluate the triple sum in Eq. (12), we note that n_x , n_y and n_z are independent. Therefore, we can write

$$Z_s = \left(\sum_{n_x} e^{-\alpha n_x^2} \right) \left(\sum_{n_y} e^{-\alpha n_y^2} \right) \left(\sum_{n_z} e^{-\alpha n_z^2} \right) \quad (14)$$

and it is sufficient to evaluate

$$Z_u = \sum_{n_u=1}^{\infty} \exp -\alpha n_u^2 \quad (15)$$

Where u is a floating index for x, y and z .

We know that the values of n_x , n_y and n_z which give rise to appreciable values of energy are very large. Also, a change in the values of n_x , n_y and n_z by one produces a negligibly small change in the value of energy. So the discrete sum can be replaced by integral, with a lower limit of zero and an upper limit of infinity. Therefore

$$Z_u = \int_0^{\infty} \exp -\alpha n_u^2 dn_u \quad (16)$$

This is a standard gamma function integral and has value $\frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$. Hence $Z_x = Z_y = Z_z = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$

$$Z_s = \frac{1}{8} \left(\frac{\pi}{\alpha} \right)^{3/2} \quad (17)$$

On substituting for α , we get the single particle partition function:

$$Z_s = g \left(\frac{m}{2\beta \pi \hbar^2} \right)^{3/2} V \quad (18)$$

This equation gives the partition function associated with translational degrees of freedom of a particle in a box.

The Rigorous Form Of Equipartition of Energy

According to equipartition theorem, when a system is in thermal equilibrium with a heat bath at temperature T, the mean contribution of each quadratic term to the total energy is $kT/2$.

Proof: To prove this theorem, let us take the general case of a system, the classical description of which requires f co-ordinates q_1, \dots, q_f and f corresponding momenta p_1, \dots, p_f . Therefore, the energy U of the system is a function of these coordinates. It is quite possible that this energy is of the form

$$U = \epsilon_i(p_i) + U'(q_1, \dots, q_f; p_1, \dots, p_{i-1}, p_{i+1}, \dots, p_f) \quad (19)$$

where ϵ_i is a function of a particular momentum p_i only and U' does not depend on p_i . Now, the probability of finding the system in a microstate, in which energy associated with p_i is ϵ_i , is given by

$$P'(p_s, q_s) dp_s dq_s = C' \exp[-\beta U(p_s, q_s)] dp_s dq_s \quad (20)$$

where $U(p_s, q_s)$ is the energy of the systems as a function of momenta and coordinates of the constituent particles. Hence, p_s represents p_1, \dots, p_{3N} , the momentum components of all the N particles in the system, and q_s represents q_1, \dots, q_{3N} . Therefore, the average value of ϵ_i becomes

$$\bar{\epsilon}_i = \frac{\int \epsilon_i [-\beta(\epsilon_i + U')] dp_1 \dots dq_f}{\int [-\beta(\epsilon_i + U')] dp_1 \dots dq_f} \quad (21)$$

The value of C' has been determined using normalization condition. Equation (20) can be rewritten as

$$\bar{\epsilon}_i = \frac{\int \epsilon_i e^{-\beta \epsilon_i} dp_i \int e^{-\beta U'} dp_1 \dots dq_f}{\int e^{-\beta \epsilon_i} dp_i \int e^{-\beta U'} dp_1 \dots dq_f} \quad (22)$$

as ϵ_i is a function of p_i only, and U' is not a function of p_i . The prime on some integral signs means that these integrals in the numerator and denominator are equal, they cancel out. Therefore, we get

$$\bar{\epsilon}_i = \frac{\int \epsilon_i e^{-\beta \epsilon_i} dp_i}{\int e^{-\beta \epsilon_i} dp_i} \quad (23)$$

When $\bar{\epsilon}_i$ is a quadratic function of p_i , it can be written as

$$\epsilon_i = b p_i^2 \quad (24)$$

Where b is a constant. Equation (23) now becomes

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} e^{-b\beta p_i^2} b p_i^2 dp_i}{\int_{-\infty}^{\infty} e^{-b\beta p_i^2} dp_i} \quad (25)$$

substituting the values of these integrals, we obtain

$$\bar{\epsilon}_i = \frac{b \times \sqrt{\pi/4} \times (kT/b)^{3/2}}{\sqrt{\pi/2} \times (kT/b)^{1/2}} \quad (26)$$

or

$$\bar{\epsilon}_i = \frac{1}{2} kT \quad (27)$$

Maxwell-Boltzmann Distribution

Consider an isolated sample of an ideal gas. Let it consists of n molecules and let its volume be V . It is a dynamic system. All particles are in random motion, continuously colliding with each other as well as with the walls of the containing vessels. But, the system being isolated, its energy must remain constant with time. Let the energy of the system be denoted by u . We can divide the energy into k intervals, where k is very large. Let the mean energy of different intervals be denoted by $u_1, u_2, u_3, \dots, u_k$ respectively. Each molecule of the system must have

energy corresponding to one of the above mentioned k intervals. if the number of particles in the energy intervals denoted by mean values $u_1, u_2, u_3, \dots, u_k$ etc. be $n_1, n_2, n_3, n_4, \dots, n_k$ respectively, then:

$$u = \sum_{i=1}^k n_i u_i \quad (28)$$

Also

$$n = \sum_{i=1}^k n_i \quad (29)$$

These equations specify the constraints on the system, which may be restated as follows (1) Total number of particles is equal to n , that is :

$$n = \sum_{i=1}^k n_i = \text{constant} \quad (30)$$

$$dn = \sum_{i=1}^k dn_i = 0 \quad (31)$$

(ii) Total energy of the system is equal to u , that is :

$$u = \sum_{i=1}^k u_i n_i = \text{constant} \quad (32)$$

$$du = \sum_{i=1}^k u_i dn_i = 0 \quad (33)$$

Here u_i , the energy in the i th interval (compartment) is also a constant.

Since the system must satisfy both the relations given by the equations (30) and (32), therefore we can write:

$$\sum_{i=1}^k [\alpha dn_i + \beta u_i dn_i] = 0 \quad (34)$$

Here α and β are the constants, whose values are to be determined.

The thermodynamical probability of the macrostate $(n_1, n_2, n_3, n_4, \dots, n_k)$ is given by

$$W(n_1, n_2, n_3, n_4, \dots, n_k) = n \prod_{i=1}^k \frac{(g_i)^{n_i}}{n_i} = W \quad (35)$$

On simplifying we get

$$W = \sum_{i=1}^k n_i \ln g_i \quad (36)$$

Applying stirling formula, we get

$$\ln W = n \ln n - n + \sum_{i=1}^k n_i \ln g_i - \sum_{i=1}^k n_i \ln n_i + \sum_{i=1}^k n_i \quad (37)$$

$$\ln W = n \ln n + \sum_{i=1}^k n_i \ln g_i - \sum_{i=1}^k n_i \ln n_i \quad (38)$$

Differentiating both sides we

$$0 = 0 + \sum_{i=1}^{i=k} dn_i \ln g_i - \sum_{i=1}^{i=k} [dn_i \ln n_i - n_i \frac{1}{n_i} dn_i] \quad (39)$$

$$0 = \sum_{i=1}^{i=k} dn_i \ln g_i - \sum_{i=1}^{i=k} dn_i \ln n_i - \sum_{i=1}^{i=k} dn_i \quad (40)$$

$$0 = \sum_{i=1}^{i=k} (\ln g_i - \ln n_i) dn_i \quad (41)$$

Using the method of Lagrangian method of undetermined multipliers

$$0 = \sum_{i=1}^{i=k} [\ln g_i - \ln n_i - \alpha - \beta u_i] dn_i \quad (42)$$

Because all values of dn_i are independent of each other, therefore equation is valid only when:

$$\ln g_i - \ln n_i - \alpha - \beta u_i = 0 \quad (43)$$

$$\ln\left(\frac{g_i}{n_i}\right) = \alpha + \beta u_i \quad (44)$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta u_i} \quad (45)$$

$$n_i = g_i e^{\alpha + \beta u_i} \quad (46)$$

This is the expression for the Maxwell Boltzmann law of energy distribution.

Bose Einstein Distribution Law

Consider a system of n bosons. In the most probable state of the system, let $n_1, n_2, n_3, n_4, \dots, n_k$ particles be possessing mean energies $u_1, u_2, u_3, \dots, u_k$ respectively. The phase space of the system can be divided into k compartments each corresponding to one energy interval. Thus, i th compartment contains n_i particles each having u_i energy. let $g_1, g_2, g_3, \dots, g_k$ be the cells in the compartment numbered 1, 2, 3, ..., k respectively. The thermodynamical probability of distribution of n particles in k compartments are

$$W = \prod_{i=1}^{i=k} \frac{(n_i + g_i - 1)}{(g_i)(n_i)} \quad (47)$$

on simplification we get

$$\ln W = \sum_{i=1}^{i=k} [(n_i + g_i - 1) \ln(n_i + g_i - 1) - (g_i - 1) \ln(g_i - 1) - n_i \ln n_i] \quad (48)$$

Differentiating and noting that g_i is constant, we get

$$d(\ln W) = \sum_{i=1}^{i=k} [\ln(n_i + g_i - 1) - \ln(n_i)] dn_i \quad (49)$$

or

$$d(\ln W) = \sum_{i=1}^{i=k} [\ln(n_i + g_i) - \ln(n_i)] dn_i \quad (50)$$

In most probable state, the value of thermodynamical probability is maximum

$$d(\ln W) = 0 \quad (51)$$

$$\therefore \sum_{i=1}^{i=k} [\ln(n_i + g_i) - \ln(n_i)] dn_i = 0 \quad (52)$$

Using the method of lagrangian method of undetermined multipliers we get

$$\sum_{i=1}^{i=k} [\ln(n_i + g_i) - \ln(n_i) - \alpha - \beta u_i] dn_i = 0 \quad (53)$$

As the variation in dn_i for different compartments is independent of each other, therefore the above relation can be written as

$$\ln(n_i + g_i) - \ln(n_i) - \alpha - \beta u_i = 0 \quad (54)$$

$$n_i = \frac{g_i}{e^{\alpha + \beta u_i} - 1} \quad (55)$$

This is the expression for Bose Einstein Distribution Law

One of the fundamental challenges in Theoretical Physics is to understand the properties of many-body systems in terms of the underlying interactions among their constituent particles. In the case of self-bound composite system governed by non-relativistic or relativistic quantum mechanics, dramatic simplifications must be incorporated in the theoretical approaches to render the many-body problem tractable. This is exactly the case for describing the structure and dynamical properties in the nuclear many-body system. Atomic nucleus fall in the category of the complex quantum many-body fermionic systems which exhibits a variety of phenomena. These phenomena are a result of interplay between single particle and collective excitations.

As the dimensions of the mathematical equations describing the system grow rapidly with system size, they can only be solved using numerical techniques for the very simplest of nuclei containing just a few particles. To describe nuclei that contain up to a few hundred nucleons, it is necessary to make approximations and to model the dynamics of these microscopic quantum mechanical object's behavior, based on the knowledge of the underlying many-body problem. Our understanding of some of the key components of this force between nucleons has been gained through studying some empirical properties of nuclei and has led to the development of a set of theoretical models that successfully describe the trends and detailed properties of a wide class of nuclei.

The development of models for nuclear structure has been started since the early days of nuclear physics about 70 years ago. The production of more and more new isotopes, with the advent of state-of-the-art experimental facilities has revived the interest in nuclear structure models in recent years. The advancements in experimental techniques using radioactive ion beam facilities have provided significant opportunities for the exploration of the exotic nuclei that populate nuclei beyond the β stability valley. Our ability to probe their structure properties has led to the discovery of several unexpected features that provide new challenges for nuclear theory and the models in vogue. Such features include halos, neutron skins and the evolution of shell structure that leads to changes in the magic numbers away from the region of stability.

The large variety of new modeling initiatives have been pursued for better understanding of nuclear structure across the nuclear chart. These initiatives are broadly categorized into three different approaches: microscopic self-consistent mean-field (SCMF), shell-model theories and macroscopic models with a touch of quantum shell structure. Nuclear SCMF models with density dependent interactions are in many respects analogs of density-functional theory which give a very successful description of many-electron systems.

The SCMF methods concentrate on self-consistent determination of the nuclear mean field, employing effective interactions. Nuclear density functional theory is outlined in refs. for non-relativistic models and in for relativistic ones. Attempts have been made to map nuclear many-body theory onto mean-field models for finite nuclei using the local-density approximation. These yield in a straightforward manner reasonable results for energies and radii,

but for more quantitative purposes, energy density functionals with phenomenologically determined parameters are far more accurate. The form of the effective energy functional is motivated from ab initio theory, but the actual parameters (around 10) are adjusted by extensive fits to nuclear structure data.

The nuclear SCMF models have been used extensively since the 1970s. However, there were still several restrictions imposed on the SCMF models which limited the range of applications and left room for macroscopic-microscopic models. The main restrictions were related to the symmetries of the wave functions which limited application of the model to ground-state properties of even nuclei only. The situation changed in the 1990s when nearly symmetry-unrestricted SCMF calculations became possible with advances in computer technology. Thanks to this development, studies of rotational bands in heavy nuclei could be systematically performed, in particular, the SCMF models encountered great success in the studies of superdeformed rotational bands in isotopes around Dy and Hg. This result was not obvious, since the energy density functionals that were used were not at-all adjusted to this kind of a phenomenon. To give another example, systematic calculations of superheavy nuclei were also performed, throwing doubt on some of the conclusions drawn from macroscopic models. At the same time, intense experimental developments greatly increased our knowledge of nuclei far from stability. This in turn had an impact on SCMF based on effective interactions, which were improved in several ways over the last decade. The success of the SCMF method has now reached a point where one has to introduce correlations beyond the mean field to improve further on the quality of the description. Several developments along this line have been started in recent years and the first applications seem to be very promising.

Microscopic description of nuclear reactions and dynamics at low energy where quantum effects play a significant role is an equally challenging field in nuclear physics. The bulk properties of nuclei are described by the static mean-field approach. A straightforward extension to study reaction dynamics is represented by the time-dependent mean-field methods. There are two basic mean-field approaches to study reactions, the time-dependent Hartree-Fock (TDHF) and the time-dependent Hartree-Fock- Bogoliubov (TDHFB). The TDHFB describes systems with pairing correlations. There have been many applications of TDHF method, e.g., in nuclear and heavy-ion dynamics . TDHF theory has been applied to the study of heavy ion collisions at energies around the Coulomb barrier. The interplay between nuclear structure and reaction mechanisms is crucial at energies around the Coulomb barrier where Coulomb and nuclear interactions compete.

TDHF theory presents the advantage of treating both structure and reaction dynamics within the same formalism and provides a self-consistent mean-field description of the many-body dynamics. Early TDHF calculations in nuclear physics incorporate various symmetries and simplified Skyrme interactions to reduce computational times . Recent increases of computational power allow realistic TDHF calculations in 3-dimensions with full Skyrme energy density functional (EDF) including spin-orbit terms .

Further, TDHF approach is widely used in nuclear physics to provide a description of collective states with applications that include the study of small amplitude excitations, i.e., in the limit of harmonic oscillations, such as, giant resonances and Gamow-Teller resonances , as well as large amplitude motion. The large amplitude limit within the TDHF approach covers a range of phenomena such as fission and fusion properties , rotational bands and deep inelastic scattering in heavy mass systems . Such microscopic approaches are well suited to the kind of open-ended problem posed in the case of nuclear collisions, where the complex many-body nature of the processes makes it impossible to know in advance the relevant observables and reaction channels. Many of the TDHF calculations were performed in the coordinate-space representation to describe nuclear fusion and heavy-ion collision dynamics .

The TDHF is a good tool to describe excited state and collective motion in nuclei, however, they can not deal with an important correlation in nuclei, i.e., pairing correlations. The TDHF theory can be extended to the one applicable to superfluid nuclei and inclusion of the pairing correlation TDHFB theory. However, it requires enormous computational resources because the number of orbitals to treat is, in principle, infinite. Only recently, a few attempts of the TDHFB have been done for realistic applications, but either with a spherical restriction or with a small model space .

An alternative and feasible approach is the Canonical-basis time-dependent Hartree-Fock-Bogoliubov (Cb-TDHFB) approach which has been proposed recently in the three-dimensional coordinate-space representation. This approach is used to study excited states and dynamics of atomic nuclei. The Cb-TDHFB is a simplified approach of the full TDHFB theory, treating pairing energy functional with BCS-like approximation which is assumed to be diagonal in the canonical basis. Implementing the theory with a real-space and real-time method, one can describe nuclear excitations and dynamics taking account of deformation effects and pairing correlations even for heavy nuclei. The Cb-TDHFB approach, formulated in the canonical-basis representation and an approximation for the pair potential, leads to a simple theory that requires the computational cost much smaller than the full TDHFB calculation.

Microscopic descriptions of the large amplitude collective motion such as fusion and fission phenomena have been long-standing issues in nuclear theory. The fusion and fission dynamics are important not only in fundamental sciences but also have applications to such as nuclear energy generation and transmutation of radioactivity. One of the major ingredients in the microscopic treatment of these phenomena is the evaluation of the collective inertia. In most of the studies, cranking approximation is employed that is a very crude approximation. The application of full

adiabatic TDHFB approach to evaluate inertia becomes exceedingly problematic for heavy nuclei. We consider that Cb-TDHFB theory provides a promising starting point. In view of rapid development of computational techniques, parallel computations with massively parallel supercomputer will be a key factor to realize the above mentioned goals.

This dissertation is organized as follows. In chapter 2, we discuss main formalism of self consistent mean-field theory in nuclei, which includes HF, HFB, TDHF, TDHFB and RPA approaches. In chapter 3, we discuss a basic idea and re-derive the Cb-TDHFB equations. In chapter 4, we discuss Adiabatic time-dependent Hartree-Fock-Bogoliubov (ATDHFB) theory. In chapter 5, we discuss the Finite amplitude method for solving the random-phase approximation (RPA) in the self-consistent and density-functional theory. The method is based on numerical evaluation of the residual interaction utilizing the finite amplitude of single-particle wave functions. Finally, the summary and future perspective of the present work are given in Chapter 6.

Studynama.com