PREFACE

In a bid to standardise higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, discipline specific, generic elective, ability* and *skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility to choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry acquired credits. I am happy to note that the University has been accredited by NAAC with grade 'A'.

UGC (Open and Distance Learning Programmes and Online Learning Programmes) Regulations, 2020 have mandated compliance with CBCS for U.G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the *six* semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English / Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

Netaji Subhas Open University

Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject: Honours in Chemistry (HCH)
Course : Physical Chemistry-I
Course Code : CC - CH - 09

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UG : Chemistry
(HCH)

Course : Physical Chemistry - I
Course Code - CC - CH - 09

Unit 1 ❑ Kinetic Theory and Gaseous State

Structure

1.1 Objective

After completion of the study of this unit the learner will be able to—

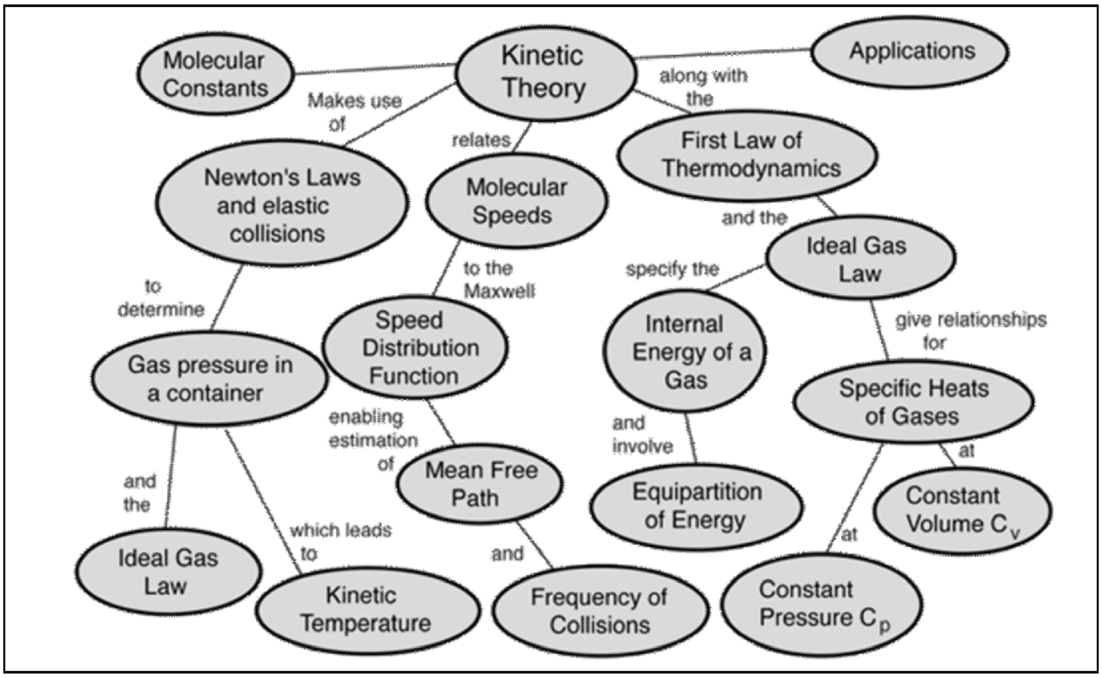
(i) understand the concept of ideal gas, real gas and their pressure and temperature.
(ii) learn the concept of collision diameter, collision number, mean free path of gas molecules.

(iii) understand Maxwell's distribution of speed and energy of gas molecules.
(iv) calculate average, root mean square, most probable speed of gas molecules.
(v) explain compressibility factor, Boyle temperature etc.
(vi) understand the different equation of states for real gases.

1.2 Introduction

The kinetic theory of gases attempts to explain the macroscopic properties of a gas in terms of microscopic properties of the individual gas molecules and the forces between them. The kinetic theory of gases has a long history. In its modern form, kinetic theory of gases began with the work of D. Bernoulli, clausius and most importantly Maxwell, who first used statistical methods to compute the properties of gases, recognizing that the random motions of the gas molecules could be best described by a distribution function.

In the second part of this unit, we will see that the ideal gas equation is not applicable for general atmospheric gas which are termed as real gases. So, the behaviour of real gases are need to be explained in terms of their own equation of states. However, it is not a straight forward task. We will see that many scientists have come up with their own versions of equation of states for real gases and those equations are applicable under certain conditions.



1.3 Kinetic theory of gases assumptions

The basic philosophy of kinetic theory of gas is to interpret quantitatively the observed or experimental properties of a macroscopic or bulk gaseous system in terms of microscopic or molecular point of view. As the static and dynamical behaviour of a molecule cannot be measured directly, one has to guess its properties which requires certain assumptions or postulates.

The model— The gas molecules in ceaseless-chaotic motion and hence we call it the kinetic theory of gas (KTG).

Assumptions of Kinetic Theory of Gases (KTG)

1. The gas consists of very small size particles known as molecules. The molecules of same gas have the same masses. There is no interaction among gas molecules, except during elastic collisions with themselves or with walls of container and they move independently.
2. Size of individual molecule is considered point mass or volume of each molecule is negligible.
3. When the molecules collide with the wall there is change of momentum. Rate of change of momentum per unit time per unit area gives pressure of the gas.
4. The average kinetic energy of the gas depends only on the absolute temperature of the system. The kinetic theory has its own definition of temperature, not identical with the thermodynamic definition.

1.4 Concept of pressure and temperature

According to KTG, the gas molecules make elastic collisions with the wall of the container. Due to this collision, there will be change in momentum. Rate of change in momentum per unit time per unit cross-sectional area gives pressure exerted on the wall. Based on the postulates of KTG, an equation can be derived $P = \frac{1}{3}\rho c_{rms}^2$, that relates the pressure with density of the gas and root mean square speed.

The basic equation, $P = \frac{1}{3}\rho c_{rms}^2$,is independent of the shape of the container. Although we will use a cubic box for derivation of the expression, we properly use the symmetry of the container then we will find that the derivation is simpler than that of cubic box.

The derivation have been performed in the thermodynamic limit when number of particles $N \rightarrow \infty$, the volume of the container $V \rightarrow \infty$, but the number density $\frac{N}{V}$ is finite. Moreover, quantum effect is not considered. This will be satisfied in a limit of inter-particle separation $\left(\frac{V}{N}\right)^{1/3}$ is much greater than deBroglie's wavelength $\lambda_d = \frac{h}{\sqrt{2\pi m k_B T}}$, where h is the Planck constant, k_h is the Boltzmann constant. If any of these assumptions are not obeyed our conclusion will not be valid.

The Kinetic Interpretation of the Pressure of a gas

We know gas exerts pressure. How this pressure is developed and how much is that ?

For analysis, we take a gas in a cylindrical container, at one end of which there is a frictionless piston, which can move along either direction. The molecules inside are in ceaseless random motion and continuously bombard on the piston. Each time the piston receives a certain momentum for each collision, it picks up speed. Let there be vacuum outside.

Receiving a certain amount of momentum from each collision, the piston starts moving out of the box. In order to keep it from moving out, we must therefore hold the piston with a certain force F. The magnitude of the Force applied normally per unit area of the piston which is just sufficient to keep the piston at its position is defined as the pressure (P) of the gas.

The tactics of the calculation involve three steps :

1. The calculation of the change in momentum that occurs when one molecule strike a wall.
2. The calculation of the total number of collisions with a wall of given area in a given interval.
3. The conversion of the total change in momentum to a force per unit area

Calculation

How much momentum transferred normally per second on the wall by bombarding molecules ?

(i) Let us fix the reference frame so that the x-axis of the coordinate system is perpendicular to the piston.

(ii) C_x is the velocity component of a molecule along the +ve X-axis collides with the wall on the right and is deflected back along its path, its momentum changes from mC_x before collision to $-mC_x$ after the collision (when it is travelling in the opposite direction).

(iii) The momentum therefore changes by $2mC_x$ on each collision (the y and z component are unchanged) .

(iv) The number of molecules that collide with the wall in the time interval 1 sec or in a time interval Δt, travels a distance $C_x.1$ or $C_x.$ Δt along x axis and if the wall has area A, then all the particles in a volume A × $C_x.1$ or A × $C_x.$ Δt is $\left(\frac{nN_A}{V}\right)AC_x\ \Delta t$.

(v) On average, at any instant half the particles are moving to the right, and half moving tho the left. Therefore the average number of collisions with the wall during the interval Δt is $\frac{1}{2}nN_AAC_x\frac{\Delta t}{V}$.

The total momentum change in that interval is the product of this number and the change is = $\frac{nN_AAC_x\Delta t}{2V}\times 2mC_x = \frac{nN_AmAC_x^2\Delta t}{V}$. The product of the molecular mass m and Avogadro's constant molar mass M of the molecules, so Momentum change = $\frac{nMC_x^2A\Delta t}{V}$.

(vi) Force is the rate of change of momentum divided by the interval Δt during which it occurs ;

Rate of change of momentum = $\frac{nMC_x^2A}{V}$

Force per unit area is Pressure = $\frac{nMC_x^2}{V}$

(vii) Let there be unit volume, n_1 molecules with x-component velocity C_{x1}, n_2 molecules with x-component velocity C_{x2}, Since not all the molecules travel with the same velocity, so the

$$C_x^2 >= \frac{n_1C_{x1}^2 + n_2C_{x2}^2 + ...}{n_1 + n_2 + ...}$$

So, the pressure equation P = 2m $(n_1C_{x1}^2 + n_2C_{x2}^2 + ...)$, including average of

C_x^2 is given by $= < C_x^2 > = \frac{\sum n_i C_{xi}^2}{n}$

$$P = \frac{nM < C_x^2 >}{V}$$

Molecules are moving about y direction with mean squared velocity, $< C_y^2 >$ and also up and down in z direction with $< C_z^2 >$. Due to isotropic movement,

$$< C_x^2 > = < C_y^2 > = < C_z^2 >$$

And if $< C^2 > = < C_x^2 > + < C_y^2 > + < C_z^2 > = 3 < C_x^2 >$

$$< C_x^2 > = \frac{1}{3} < C^2 >$$

$$P = \frac{1}{3V} nM < C^2 > = \frac{1}{3}\frac{nM}{V} C^2_{rms5} = \frac{1}{3}\rho C^2_{rms}$$

Question

Consider a collection of 6.023×10^{23} numbers of ideal gas molecules of molar mass 32 $gmol^{-1}$ kept in a cubic container of volume 1L. Temperature of the system is 300K. Using the basic equation of KTG, find the pressure. Does it change if it is a spherical container instead of cubic one.

From KTG, the pressure is given by,

P $= \frac{1}{3}\rho C^2_{rms}$, where rms speed is given by, $C_{rms} = \sqrt{\frac{3RT}{M}}$ Putting $R = 8.314 \times 10^7$ $ergmol^{-1} K^{-1}$ $M = 32$ g mol^{-1}; T = 300K ; $C_{rms} = 48.356\times10^3 cm\ s^{-1}$.

Then the Pressure will be,

$$P = \frac{1}{3}\rho C^2_{rms} = \frac{1}{3}\frac{mN}{V} C^2_{rms}, m = \frac{32gmol^{-1}}{6.0^{23}\times10^{-1}}, N = N_A$$

$= 24.42 \times 10^6$ dynes cm^{-2}

Basic equation of KTG is independent of the container. Hence, it remains unchanged.

Concept of Temperature from Kinetic Theory of gas

From the basic KTG equation

$$P = \frac{1}{3}\frac{mN}{V}C_{rms}^2$$

$$PV = \frac{2}{3}N\frac{1}{2}mC_{rms}^2 = \frac{2}{3}N < \varepsilon >$$

where $< \varepsilon > = \frac{1}{2}mC_{rms}^2$ is the average kinetic energy

Now comparing with the ideal gas law **PV = Nk$_B$T** where k_B is the Boltzmann constant and T is the absolute temperature.

$$\frac{2}{3}N < \varepsilon > = Nk_BT$$

$$< \varepsilon > = \frac{3}{2}k_BT$$

$$T = \frac{2}{3}\frac{< \varepsilon >}{k_B}$$

The average molecular kinetic energy is proportional to the ideal gas law's absolute temperature. Temperature is the manifestation of average kinetic energy.

Derivation of empirical gas laws from basic equation of KTG

1. Boyle's Law

From the basic equation of KTG, pressure is given by $P = \frac{1}{3}\frac{mN}{V}C_{rms}^2$

This equation can be rearranged as $P = \frac{2N}{3V}\frac{1}{2}mc_{rms}^2 = \frac{2N}{3V} < \varepsilon >$

As the temperature is a measure of average kinetic energy, when temperature is kept constant, average kinetic energy is also constant. For fixed amount of gas and fixed temperature, volume of the gas is inversely proportional to applied pressure *i.e.* $V \alpha \frac{1}{P}$

2. Charles' law

From basic equation of KTG, pressure is given by

$$P=\frac{1}{3}\frac{mNc_{rms}^2}{V}=\frac{2N}{3V}\frac{1}{2}mc_{rms}^2=\frac{2N}{3V}<\varepsilon>$$

$$\text{Or } V=\frac{2N}{3P}<\varepsilon>$$

For fixed amount of gas and pressure, volume is proportional to temperature.

1.5 Collision of gas molecules

Molecular Collisions and the Mean Free Path

Due to the random erratic motion, the molecules of a gas suffer continuous collisions among themselves and with the walls of the container. We count the number of collisions among the molecules.

A molecular collision may be a two body (i.e. binary; two molecule collide) or many body. But since the probability that the centres of three or more molecules comes at aparticular point in space at a particular instant is very small, we consider only the binary collisions. The calculation of the binary molecular collisions is important because:

1. It helps calculating the rate of chemical reactions in the gas phase.
2. It helps calculating the mean free path of the molecules in a gas.

1.6 Collision Diameter

The kinetic theory of gases treats molecules as point masses. When two such molecules approach each other, a point is reached at which the mutual repulsion between the molecules becomes so strong that it causes reversal of the direction of their motion. The distance between the centres of the two molecules at the point of their closest approach is known as collision diameter. It is represented by sigma (σ). Evidently, a gaseous molecule can be regarded as a rigid (or hard) sphere of diameter σ.

If the distance between the centres of two molecules is less than σ, there would be a collision between them. Thus, collision is an event in which the centres of two identical molecules come within a distance σ from each other.

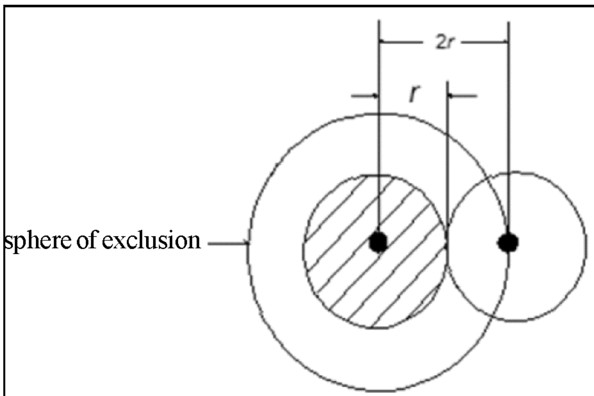


Fig.(a) Actual Collision

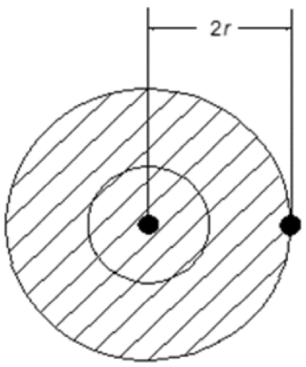


Fig.(b) Sphere of exclusion

Collision Cross-section

The model of gaseous molecules as hard, non-interacting spheres of diameter σ can satisfactorily account for gaseous properties such as the transport properties (viscosity, diffusion, thermal conductivity), the mean free path and the number of collisions the molecules undergo. It can easily be visualised that when two molecules collide, the effective area of the target is $\pi\sigma^2$. The quantity $\pi\sigma^2$ is called the collision cross-section of the molecule into which the centre of another molecule cannot penetrate.

1.7 Collision Number

In a gas the number of molecules with which a single molecule will collide per unit time is given by $\sqrt{2}\pi\sigma^2 < c > \rho$ and $< c >$ is the average speed of the gas molecules. where ρ is the number density *i.e* number of molecules per unit volume of the gas. This expression gives the number of collisions suffered by a single molecule per unit time per unit volume of the gas. This is known as the collision number. $Z_1 = \sqrt{2}\pi\sigma^2 < c > \rho$.

The total number of molecules colliding per unit time per unit volume of the gas is, therefore, given by $\sqrt{2}\pi\sigma^2 < c > \rho^2$. Since each collision involves two molecule, the number of bimolecular collisions per unit volume of the gas is given by

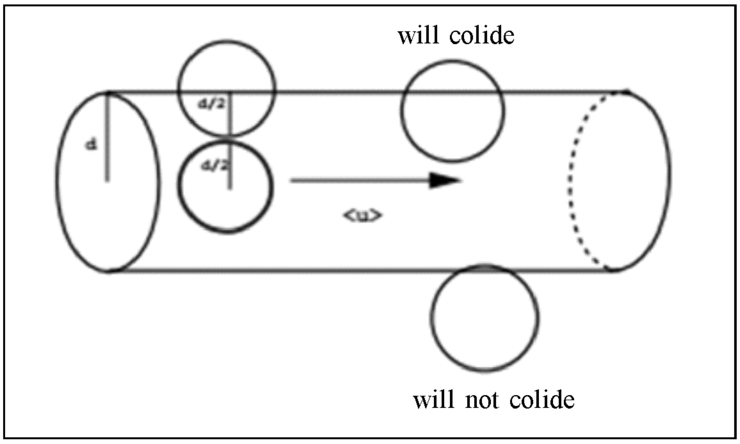
$$Z_{11} = \frac{1}{2}\left(\sqrt{2}\pi\sigma^2 < c > \rho^2\right). = \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \rho^2 \;....$$

$= \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \frac{(P)^2}{(kT)^2}$ since number density from ideal gas law $\rho = \frac{N}{V} = \frac{P}{kT}$

Units of collision number is s^{-1}.

1.8 Collision Frequency

The number Z_{11} in the above equation gives collision frequency of the gas.. Thus collision frequency is the number of molecular collisions occurring per unit time per unit volume of the gas.



The number of collisions of molecules of type 1 with type 2 given by $Z_{12} = \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \rho_1\rho_2$ where ρ_1 and ρ_2 are the number of densities of the molecules 1 and 2 respectively. The number density ρ is equal to $\frac{P}{kT}$,

For ideal gas PV = nRT n is number of mole, $PV = \frac{N}{N_A}RT = N = \frac{R}{N_A}T = Nk_BT$

$P = \frac{NkT}{V}$, hence $\rho = \frac{N}{V}$. Thus $P = \rho kT$ and $\rho = \frac{P}{kT}$

$Z_1 = \sqrt{2}\pi\sigma^2 < c > \rho = \sqrt{2}\pi\sigma^2 < c > \frac{P}{kT}$ collision number.

Collision Frequency

Since the number of collision is counted twice, the number of binary collision between different molecules of two different gases A and B per unit volume per sec is given by

$$Z_{11} = \frac{1}{2}\sqrt{2}\pi\sigma^2 < c > \rho^2$$

$$Z_{11} = \frac{\pi\sigma^2 < c >}{\sqrt{2}} \cdot \frac{P^2}{(kT)^2}$$ units of collision frequency $s^{-1}m^{-3}$.

Frequency of binary collision between molecules of different gases

Let us consider a mixture of two different gases containing respectively n_A and n_B number of molecules per unit volume at temperature T and pressure P. Molecular masses m_A and m_B. Molecular diameter σ_A, σ_B. As collision between the molecules of A and B gases may occur at any angle, the average angle of collision considered as 90°. If average velocities then for 90° collision the average relative velocity of A with respect to B is given by.

$$< c_{rel} >= \sqrt{\langle c_A \rangle^2 + \langle c_B \rangle^2} = \sqrt{\frac{8kT}{\pi}\left(\frac{1}{m_a} + \frac{1}{m_B}\right)} = \sqrt{\frac{8kT}{\pi\mu}}$$

Where $\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B}\mu_m = \frac{m_1 m_2}{m_1 + m_2} = \frac{M_A M_B}{N_A^2} \times \frac{N_A}{M_A + M_B} = \frac{M_A M_B}{N_A(M_A + M_B)}$ and is called reduced mass of the two colliding molecules.

To find out the number of collisions of $(\sigma_A + \sigma_B)/2$ from the centre of the given A molecule with B molecules per sec. instead of considering both the types of molecules are moving. All the B molecules are stationary and A molecules are moving, it is equivalent to consider that B molecules are stationary and A molecules are moving with velocity $<c_{rel}>$.

Hence all the B molecules present in the cylinder of radius$(\sigma_A + \sigma_B)/2$ and length $c_{rel.av} =< c_{rel} >$ suffer collisions with the A molecule passing along the axis of the cylinder in a sec. Therefore, the number of collisions suffered by one A molecule per sec with B molecules.

$$= \pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \langle c_{rel} \rangle n_B$$

$$= \pi\left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8kT}{\pi\mu}} n_B = \pi(\sigma_A + \sigma_B)^2 \frac{1}{4}\sqrt{\frac{8kT}{\pi\mu}} n_B$$

$$= (\sigma_A + \sigma_B)^2 \sqrt{\frac{8\pi^2 kT}{16\pi\mu}} n_B$$

$$= (\sigma_A + \sigma_B)^2 \sqrt{\frac{\pi kT}{2\mu}} n_B$$

So the total number of collisions between A and B molecules per unit volume per sec

$$= (\sigma_A + \sigma_B)^2 \sqrt{\frac{\pi kT}{2\mu}} n_B n_A$$

Since the number of collision is counted twice , the number of binary collision between different molecules of two different gases A and B per unit volume per sec is given by

$$Z_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)^2 \sqrt{\frac{nkT}{2\mu}} n_B n_A$$

Z_{AB} (w,r,t to radius) = $n_A n_B (r_A + r_B)^2 \pi \sqrt{\frac{8kT}{\pi\mu_{AB}}} = n_A n_B (r_A + r_B)^2 \sqrt{\frac{8\pi kT}{\mu_{AB}}}$

Variables that affect collisional frequency

- **Temperature:** As is evident from the collisional frequency equation, when temperature increases, the collisional frequency increases.
- **Density**: From a conceptual point, if the density is increased, the number of molecules per volume is also increased. If everything else remains constant, a single reactant comes in contact with more atoms in a denser system. Thus if density is increased, the collisional frequency must also increase.
- **Size of Reactants**: Increasing the size of the reactants increases the collisional frequency. This is directly due to increasing the radius of the reactants as this increases the collisional cross section. This in turn increases the collisional cylinder. Because radius term is squared, if the radius of one of the reactants is doubled, the collisional frequency is quadrupled. If the radii of both reactants are doubled, the collisional frequency is increased by a factor of 16.

Question

A cylinder containing hydrogen at 400 K, 1 atm is placed in an evacuated chamber. If a hole of area 0.03mm^2 is made in the cylinder. Calculate the number of molecules leaking through the hole per second. Take the average velocity of the molecules as 0.725 of the rms speed.

Solution :

For hydrogen,

$PV = Nk_BT$

$$n = \frac{N}{V} = \frac{P}{kT} = \frac{1.01325 \times 10^5}{1.38 \times 10^{-23} \times 400}$$

$$1.83 \times 10^{25} \text{ molecules}/\text{m}^3$$

$$V_{rms} = \left[\frac{3kT}{m}\right]^{1/2} = \left[\frac{3 \times (1.38 \times 10^{-23}) \times 400}{3.32 \times 10^{-27}}\right]^{\frac{1}{2}} = 2233.3 \text{ m}/\text{s}$$

$$\overline{v} = 0.725 \times 2233.3 = 1619.14 \text{ m}/\text{s}$$

Rate of flux of molecules per unit area

$$= \frac{1}{4} n\overline{v} = \frac{1}{4} \times 1.83 \times 10^{25} \times 1619.14 = 2.96 \times 10^{28} \text{ molecules}/\text{m}^3\text{s}$$

Rate of hydrogen leakage through the hole

$$= 2.96 \times 1028 \times 0.03 \times 10^{-6} = 8.88 \times 10^{20} \text{ molecules}/\text{s}.$$

Mean Free Path

The mean free path is defined as the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the speed of a particle and the time between collisions.

λ is defined as the mean distance travelled by a gas molecule between two successive collisions.

$$\lambda = \frac{<c>}{Z_1} = \frac{<c>}{\left(\sqrt{2}\right)\pi\sigma^2 <c> P/kT} = \frac{kT}{\left(\sqrt{2}\right)\pi\sigma^2 P}$$

Following are the features of mean free path :

1. Mean free path is inversely proportional to the macroscopic collision cross section.
2. The unit of mean free path is the unit of length.
3. Mean free path does not depend upon the molecular speed.
4. Mean free path increases as pressure is decreased.

Question

For Oxygen gas at 25°C calculate (i) the mean free path at 1 atm pressure (ii) the mean free path at 10^{-3} mm Hg pressure (iii) the number of collisions per second per molecule (iv) the number of collisions per cubic metre per second and (v) the number of collisions per cubic metre per second (vi) the number of moles of collisions per dm^3 per second. In parts (iii), (iv) and (v) the pressure is 1 atm. The collision diameter of oxygen molecule (σ) is 361 pm.

Solution

(i) 1 atm = 1.01325×10^5 N m^{-2} T = 25°C = 298 K

σ = 361 pm = 361×10^{-12} m = 3.61×10^{-10}m.

$$= \frac{kT}{(\sqrt{2})\pi\sigma^2 P} = \frac{(1.38\times10^{-23}\,\text{JK}^{-1})298\text{K}}{1.4142\times3.1416\times(3.61\times10^{-10}\,\text{m})^2\times1.01325\times10^5\,\text{Nm}^{-2}}$$

= 7.02×10^{-8}m = 70.2 nm

$$\text{(ii)}\quad P = 10^{-3}\text{ mm Hg} = \frac{(10^{-3}\text{ mm Hg})(1.01325\times10^5\,\text{Nm}^{-2}\text{atm}^{-1})}{760\text{ mm Hg atm}^{-1}} = 0.1333\text{N m}^{-2}$$

$$\therefore \lambda = \frac{(1.38\times10^{23}\,\text{JK}^{-1})298\text{K}}{1.414\times3.1416\times(3.61\times10^{-10}\,\text{m})^2(0.1333\text{Nm}^{-2})}$$

$$Z_1 = \sqrt{2}\pi\sigma^2 < c > \rho = \sqrt{2}\pi\sigma^2 < c > \frac{P}{kT}$$

$$< c > = \sqrt{\frac{8RT}{\pi M}} = \left[\frac{8\times8.314\text{JK}^{-1}\text{mol}^{-1}\times298\text{K}}{3.1416\times(32\times10^{-3}\,\text{kgmol}^{-1})}\right]^{\frac{1}{2}} = 444\text{ms}^{-1}$$

$$Z_1 = \sqrt{2}\pi\sigma^2 < c > \rho = \sqrt{2}\pi\sigma^2 < c > \frac{P}{kT} = \frac{1.4142\times(3.146\times3.61\times10^{-10}\,\text{m})\times1.01325\times10^5\,\text{Nm}^{-2}}{1.38\times10^{-23}\,\text{JK}^{-1}\times298\text{K}}$$

= 6.32×10^9 s^{-1}.

(iv) $$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \rho^2 = \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \frac{(P)^2}{(kT)^2}$$

$= 7.77\times10^{34}\ m^{-3}s^{-1}$.

(v) Number of moles of collision per dm^3 per second

$$= \frac{7.77\times10^{34} m^{-1}s^{-1}\times10^{-3}m^3dm^{-3}}{6.022\times10^{23}mol^{-3}}$$

$= 1.29\times10^{8}$ mol $dm^{-3}s^{-1}$

Question

Calculate the average translational kinetic energy of an ideal gas per molecule $<\varepsilon_1>$ and $<E_1>$ per mole at 25°C

$$<\varepsilon_1> = \frac{3}{2}kT = 6.17\times10^{-23}J \text{ per molecule}$$

$$<E_1> = \frac{3}{2}RT = 3.716\times10^{3}J\ \ mol^{-1}$$

1.9 Nature of distribution of velocities

The molecules in a gas due to their random motion are continuously colliding with each other. Their speeds are, therefore, constantly changing. For quantitative description of the behaviour of gases, we make use of three different types of molecular speeds, viz. average speed, most probable speed and root mean square speed.

Average speed (<c>) It is the arithmetic mean of the different speeds of all the molecules present in a given mass of a gas.

$$< c > = \frac{n_1c_1 + n_2c_2 + n_3c_3 + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots} = \frac{1}{N}\sum_{i=1}^{N} n_ic_i$$

As n is continuously varying function of c, the above equation is = $\frac{1}{N}\int_0^{\infty} cdn_c = \int_0^{\infty}\frac{cdn_c}{N}$

m = mass of a gas molecule
M = molar mass of the gas

Substituting $\frac{dn_c}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^2 \exp\left(-\frac{mc^2}{2kT}\right)dc$ (solution done afterwards)

$$C_{avg} = \sqrt{\frac{8RT}{\pi M}}.$$

Most Probable speed (C_{mps}) The speed possessed by maximum number of molecules of the gas is termed the most probable speed.

The most probable speed correspond to the maximum (peak) of the distribution curve.

$$\frac{dn_c}{Ndc} = \frac{1}{N}\frac{dn_c}{dc} = \frac{d\left(\frac{dn_c}{N}\right)}{dc} = \frac{d}{dc}4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} c^2 \exp\left(-\frac{Mc^2}{2RT}\right)$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}}\left[\exp\left(\frac{-Mc^2}{2RT}\right)\times 2c + c^2 \times \exp\left(\frac{-Mc^2}{2RT}\right)\left(\frac{-M}{2RT}\times 2c\right)\right]$$

$$= 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} \times 2c \times \exp\left(-\frac{Mc^2}{2RT}\right)\left[1 - \frac{Mc^2}{2RT}\right]$$

$$= \text{Slope at the peak} = 0 \quad \left[1 - \frac{Mc^2}{2RT}\right] = 0$$

$$C_{mps} = \sqrt{\frac{2RT}{M}}$$

Root Mean square speed (C_{rms}). It is the square root of the mean of the squares of the different speeds of the gas molecules.

$\left(c^2\right)^{\frac{1}{2}} = \sqrt{<c^2>} =$ Reading from back square then mean then root

$= \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ...}{N}}$ where $N = n_1 + n_2 + n_3 + ...$

$$<c^2> = \frac{1}{N}\int_0^\infty c^2 dn_c = \int_0^\infty \frac{c^2 dn_c}{N}$$

Formula to obtain average for any quantity $\langle q\rangle = \frac{1}{N}\int_0^\infty (q)dn_c = \int_0^\infty \frac{q dn_c}{N}$

Substituting $\frac{dn_c}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} c^2 \exp\left(-\frac{mc^2}{2kT}\right)dc$ (solution done afterwards)

$$C_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

Relationship between Different types of speed

(i) Most probable speed = $\sqrt{\frac{2}{3}} \times$ Root mean square speed = $0.816 \times C_{rms}$

(ii) Average speed = $\sqrt{\frac{8}{3\pi}} \times$ Root mean square speed = $0.9213 \times C_{rms}$

The three are related, C_{avg} in the middle as name suggest, C_{rms} maximum

$$C_{mps} : \langle C_{avg} \rangle : C_{rms} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

Question

Compute the most probable speed, the mean speed, and the root-mean-square speed for oxygen at 0°C.

Mass of an oxygen atom $= \frac{32}{6.023\times10^{23}} = 5.31\times10^{-23}\text{g}$

$$C_{mps} = \left[{}^{2kT}\!/_{m}\right]^{1/2} = \left[\frac{2\times1.38\times10^{-23}\times273.15}{5.31\times10^{-23}}\right]^{1/2}$$

11.91m/s.

$$C_{avg} = \left[{}^{8kT}\!/_{\pi m}\right]^{1/2} = \left[\frac{8\times1.38\times10^{-23}\times273.15}{5.31\times10^{-23}}\right]^{1/2} = 13.41\text{m/s.}$$

$$C_{rms} = [3kT/m]^{1/2} = 14.59\,{}^{m}\!/_{s}$$

Question :

Calculate the rms speed for hydrogen at 400 K. What is the mean translation kinetic energy of a molecule of hydrogen?

Solution :

Mass of an hydrogen molecule, m

$$= \frac{M}{N_0} = \frac{2}{6.023 \times 10^{26}} = 3.32 \times 10^{-27}\,\text{kg}$$

$$v_{rms} = \left[\frac{3KT}{m}\right]^{1/2} = \left[\frac{3 \times (1.38 \times 10^{-23}) \times 400}{3.32 \times 10^{-27}}\right]^{\frac{1}{2}} = 2233.3\,\text{m/s}$$

$$KE_{mean} = \frac{1}{2} m\overline{v}^2 = \frac{3}{2} KT = \frac{3}{2} \times 1.38 \times 10^{-28} \times 400$$

$$= 8.28 \times 10^{-21} \frac{J}{\text{molecule}}$$

1.10 Maxwell-Boltzmann distribution of molecular velocities

The rms velocity of the molecules of gas is related to the gas temperature, $c\infty\sqrt{T}$. Let us consider a volume of gas at a constant temperature, the molecules of which are moving at different velocities. The instantaneous velocity vector of each molecule is revolved into components v_x, v_y and v_z. Let us imagine a velocity space so that the space area of a sphere represents, at an instant, all molecules of equal velocities.

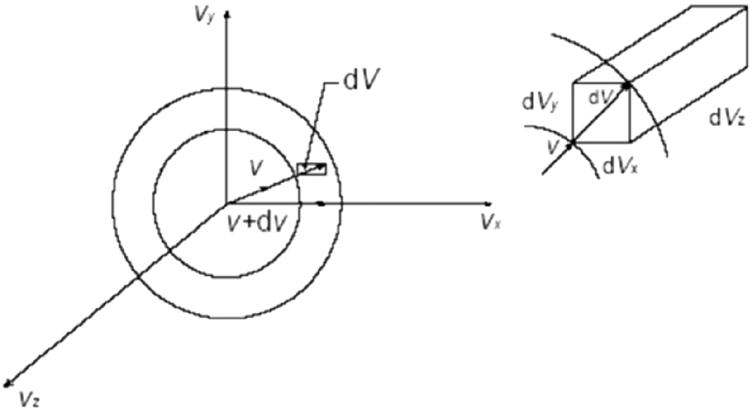


Fig. Velocity Space

Each molecule has a representative point in velocity space. The number of molecules whose velocities lie between *v* and *v* + *dv* would be represented by the spherical strip of thickness *dv*, and be denoted by dN_v. Since the total number of molecules *N* is very large, the strip *dv*, although small, still contains a large number of molecules. Let dN_{vx} represent the number of molecules whose x -component velocities lie between v_x and $v_x + dv_x$. Then the fraction $(dN_{v_x})/N$ is a function of the magnitude of v_x and the distance dv_x,

or, $\frac{dN_{v_x}}{N} = f(v_x)dv_x$

Where f (V_x) is called the distribution function for x-component of velocity.

Boltzmann has shown that the probability for a molecule to have an energy ε is was proportional to $e^{-\varepsilon/kT}$. We can equate the probability with f (v) $dv_x = Ae^{\frac{-mu^2}{2kT}}$ dv_x = where A is constant of proportionality. The constant can be evaluated by requiring that the total probability must be unity. Thus,

$$\int_{-\infty}^{\infty} f(V_x) = A\int_{-\infty}^{\infty} e^{-mu^2/2kr} = 1$$

The range of integration of velocity component v_x is $-\infty$ to $+\infty$ since velocity has magnitude and direction.

Setting $\frac{m}{2kT} = a$,

$$\int_{-\infty}^{\infty} e^{-av_x^2}dv_x = \left(\frac{\pi}{a}\right)^{\frac{1}{2}} = \left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}}$$

$$A\left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}} = 1$$

$$A = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}$$

$f(V_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2kT}}\,dv_x$ is called the Maxwell's distribution of molecular velocities in one dimension.

Similarly,

$$\frac{dN_y}{N} = f\left(v_y\right)dv_y$$

$$\frac{dN_z}{N} = f\left(v_z\right)dv_z$$

The probability of finding molecules having x-components of velocity within the range v_x and $v_x + dv_x$ and y-component of velocity within the range v_y and v_y+dv_y simultaneously given by

$$\frac{dNv_xv_y}{N} = A^2e^{-\beta\left(v_x^2+v_y^2\right)}dv_xdv_y$$

Likewise in 3d space

$$\frac{1}{N}\frac{dNv_xv_yv_z}{dv_x\,dv_y\,dz_z} = A^3e^{-\beta^{c^2}}$$ where $c^2 = v_x^2 + v_y^2 + v_z^2$ Note for 1 dimension : A^1

The volume enclosed within a spherical shell of radius is given by

ΔV = (Volume of large sphere radius c+dc) - (Volume of the small sphere of radius c)

$$= \frac{4}{3}\pi\ (c+dc)^3 - \frac{4}{3}\pi c^3$$

$$= \frac{4}{3}\left[c^3 + 3c^2\,(dc)^2 + 3c\,(dc)^3\right]$$

$$= \frac{4}{3}\pi\,3c^2dc\left[1+\left(\frac{dc}{c}\right)+\frac{1}{3}\left(\frac{dc}{c}\right)^2\right]$$

$\approx 4\ c^2dc$ as $\frac{dc}{c}$ <<1, we can neglect the higher terms.

Hence the probability of finding molecules having speed within the range c and c+dc.

$$\frac{I}{N}\frac{dNv_xv_yv_z}{dv_x\ dv_y\ dz_z}=\frac{dN_c}{N}=A^3\ 4\pi c^2dc=4\pi\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}}c^2\exp(-mc^2/2k_BT)$$

This is known as Maxwell Boltzmann velocity distribution function.

NOTE

$\Gamma(n)=\int_o^\infty x^{n-1}e^{-x}dx\ (n>0)$ is called Gamma function, the value of which are given in where.

Table Values of gamma function

$$\Gamma(n)=\int_o^\infty x^{n-1}e^{-x}dx\ (n>0)$$

n Γ (n)	Γ (n)	n	
$\frac{1}{2}$	$\sqrt{\pi}$	3	2
1	1	$\frac{7}{2}$	
$\frac{15}{8}\sqrt{\pi}$			
$\frac{3}{2}$	$\sqrt{\frac{\pi}{2}}$	4	
6			
2	1	$\frac{9}{2}$	$\frac{105}{16}\sqrt{\pi}$
$\frac{5}{2}$	$\frac{3}{4}\sqrt{\pi}$	5	24

Maxwell's speed distribution in one dimension

$\frac{dNv_x}{N}=\left(\frac{m}{2\pi k_8T}\right)^{\frac{1}{2}}e^{\frac{-mv_x^2}{2k_8T}}\ dv_x$ where $\frac{dNv_x}{N}$ is the probability or fraction of molecules having velocity within the range u and u+du, N is the total number of molecules, m is the mass of a single molecule, is the Boltzmann constant and T is the Temparature in Kelvin.

This equation can also be expressed as $\frac{dNv_x}{N} = \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-\frac{M_x^2}{2RT}}$ where $M = N_a m$ is the molar mass and R is the universal gas constant.

Some important points to note

1. Thus curve is a Gaussian curve and Maxwell's velocity distribution in one dimension is a Gaussian distribution or normal distribution.
2. With the increase in temparature height of the peak decreases and the probability of finding molecule having higher velocity increases. But the area under the curve which represent the total probability remains the same and is equal to 1. With the increase in temparature average kinetic energy increases and consequently molecules move with higher velocity.
3. When the temparature tends to zero Kelvin, the distribution curve will be along the $f(v_x)$ axis, Since at Zero kelvin disorder is minimised and only single state is populated. But as T .. ∞, probability distributions will be along the v_x axis.
4. With the increase in molar mass of the gas molecules, the height of the peak increases, and probability of finding molecules having higher velocity decreases. But the area under the curve, which represents the total probability (= 1) remains the same.
5. This distribution curve is symmetric about $v_x = 0$. Average velocity in one dimension is zero. It does not mean that all the molecules are at rest. As there is no intermolecular interaction, both directions (+ × and ×) are equally probable.
6. To find the average velocity along a particular direction say +× direction

$$<V_{x+}> = \int_0^\infty v_x f(v_x) dv_x = \int_0^\infty v_x \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{mv_x^2}{2k_BT}} dv_x$$

Let $\frac{mv_x^2}{2k_8T}$ = z, then $v_x dv = \frac{kT}{m}dz$. Again $V_x = 0$, z = 0, u and z -

$$<Vxt> = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \int_0^\infty \frac{k_8T}{m} e^{-z}\, dz = \left(\frac{m}{2\pi k_8 T}\right)^{\frac{1}{2}} \frac{kt}{m}\times\Gamma(1) = \sqrt{\frac{kT}{2\pi m}}$$

$$\text{or, } \frac{1}{4}\sqrt{\frac{8kT}{\pi m}} = \frac{1}{4} < c >$$

Where <c> is average speed in three dimension.

Some Important points to note

1. For a particular gas and at a constant temparature the distribution curve varies with speed as

$f(c)\,dc = \frac{dN_c}{N} \sim c\, e^{-c2.}$ The polynomial part dominates at low speed and exponential part dominates at high speed region. Hence f(c) first increase linearly, it reached maximum value, then decreases exponentially.

2. With the increase in temparature height of the peak decreases and the probability of finding molecule having high speed increases. But the area under the curve which represents the total probability density remains the same and is equal to 1. With the increase in temparature, average kinetic energy increases and consequently molecules move with higher and higher speed.

3. When temparature tendz to zero Kelvin, the distribution curve along the f(c) axis. But as T ... probability distribution will be along the x-axis.

4. With the increase in Molar mass of the gas molecules, the height of the peak increase and the probability of finding molecules having higher and higher speed decreases. But the area under the curve, which represents the total probability (=1) remains the same.

5. $<c> = \int_0^\infty c\,f(c)dc = \int_0^\infty \left(\frac{m}{kT}\right)\sqrt{\frac{1}{2}}\times\sqrt{\frac{kT}{m}}\times\frac{2kT}{m}\int_0^\infty z^{\frac{1}{2}}e^{-z}dz$

$$= \sqrt{\frac{2k_8T}{m}}\Gamma\left(\frac{3}{2}\right) = \sqrt{\frac{2kT}{m}}\frac{1}{2}\sqrt{\pi} = \sqrt{\frac{\pi k_B T}{2m}}$$

Here $\frac{mc^2}{2k_BT}$ by z and hence $dc = \sqrt{\frac{kT}{2m}}\, z^{-\frac{1}{2}}$ again when c = 0, z = 0.

6. $<c^2> = \int_0^\infty c^2 f(c)\,dc$ Note $<\text{quantity}> = \int_0^\infty \text{quantity} \times f(c)\,dc$

Note $f(c)\,dc = \frac{dNc}{N} = \left(\frac{m}{2k_BT}\right)_c e^{-\frac{mc^2}{2k_BT}} dc$

$$= \int_0^\infty \left(\frac{m}{k_BT}\right) c^3 e^{-\frac{mc^2}{2k_BT}} dc$$

$$= \frac{m}{2k_BT} \times \left(\frac{2k_BT}{m}\right)^{\frac{3}{2}} \times \frac{k_BT}{2m} \int_0^\infty ze^{-z} dz$$

$$= \left(\frac{2k_BT}{m}\right) \times \Gamma(2)$$

$$= \frac{2k_BT}{m},$$

here $\frac{mc^2}{2k_BT}$ by z and hence $dc = \sqrt{\frac{kT}{2m}} z^{-\frac{1}{2}}$ dz, again when c = 0, Z = 0.

Hence the root mean square speed is given by $c_{rms} = \sqrt{\frac{2k_BT}{m}}$

7. Variance of speed in two dimension is given by

$$\sigma_c^2 = <c^2> - <c>^2 = \frac{2k_BT}{m} - \frac{\pi k_BT}{2m} - \frac{k_BT}{m}(4 - \pi) = 0.43 \frac{K_BT}{m}$$

8. Standard deviation of speed in two dimension is given by

$$= \sigma_c = \sqrt{< c^2 > - < c >^2} = \sqrt{\frac{kT}{2m}(4 - \pi)} = 0.656 \sqrt{\frac{k_BT}{m}}$$

9. The speed at which probability of finding molecules is maximum is called the most probable speed. To find the most probable speed we set the condition.

$$\frac{\partial f(c)}{\partial c} = 0$$

$$\frac{\partial}{\partial c}\left[\left(\frac{mc}{k_BT}\right)e^{-\frac{mc^2}{2k_BT}}\right]=0$$

$$\frac{\partial}{\partial c}\left[c\times e^{-\frac{mc^2}{2k_BT}}\right]=0$$

Then either $e^{-\frac{mc^2}{2k_BT}} = 0 \Rightarrow c.$ which corresponds minimum value of f(c) and/or $\frac{mc^2}{[1-k_BT]}=0=0 \Rightarrow c = \pm\sqrt{\frac{k_BT}{m}}$, But speed cannot be negative. Hence most probable speed in two dimension is $c=\sqrt{\frac{k_BT}{m}}$

Height of the peak can be obtained or determined by putting $c = c_{mp}$ in the expression f(c)

This gives,

$$f(c) = c_{mp} = \frac{m}{k_BT}\times c_{mp}\times e^{-mc_{mp}^2}/2k_BT = \frac{m}{k_BT}\sqrt{\frac{k_BT}{m}}\times c\frac{mc^2}{2k_BT} = \sqrt{\frac{m}{k_BT}}\times\frac{1}{\sqrt{c}}$$

From this expression, it is clear that height of the peak decreses with increase in temparature and it increase with increase in molar mass.

1. At what temparature Maxwell's speed distribution plot of Cl_2 will be identical to that of N_2 at 27° C?

From Maxwell's speed distribution in three dimension.

$$f(c)\ dc = \frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} c^2\, e^{-\frac{mc^2}{2k_BT}}dc$$

Where f(c) dc is the probability of finding molecules having speed within range c and c+dc. It is clear that f(c) is a function of $\frac{m}{T}$, where m is the atomic mass of the gas molecule, and T is the temparature.

This distribution will be identical to Cl_2 and N_2 if $\frac{mcl_2}{Tcl_2}=\frac{mN_2}{TN_2}$

$$T_{Cl_2} \frac{mCl_2}{mN_2} = TN_2 = \frac{71}{28} = 300K = 760.71K = 487.71°C$$

"The exponential term in the expression for Maxwell velocity distribution can never be positive."

Explain

The Maxwell's distribution law of molecular speed is given by,

$$\frac{I}{N}\frac{dN_c}{dc} = f(c) = 4\pi\left(\frac{m}{2\pi k_8 T}\right)^{\frac{3}{2}} c^2 \; e^{-\frac{mc^2}{2k_BT}}$$

Where $\frac{I}{N}\frac{dN_c}{dc}$ is the probability of finding gas molecules having speed range in between c and $c + dc$, m is mass of gas molecules, T is the Temparature.

If exponential term be positive then probability of finding molecules having speed within the range c+dc tends to infinity as $c \pm \infty$, which is absurd. Hence it must be negative.

Summary

1. Maxwell's speed distribution in 1 dimention

$$f(c)\,dc = \frac{dN_{v_x}}{N} = \left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} e^{-mv_x^2/2k_BT} dv_{x_z}$$

$= \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} e^{-Mv_x^2/2RT} dv_x$, m is the mass of a gas molecule, k_b Boltzmann constant (1.38×10^{-23} JK^{-1}), T temparature, M is molar mass of the gas molecules, R is the Universal.

2. Maxwell's speed distribution in 2D

$$f(c)\,dc = \frac{dN_c}{N} = \left(\frac{M}{2k_bT}\right)_c e^{-mc^2/2k_BT}\,dc$$

$$= \left(\frac{M}{2RT}\right)_c e^{-Mc^2/2RT}\,dc$$

m is the mass of a gas molecule, k_B Boltzmann constant (1.38×10^{-23} J^{K-1}), T temparature, M is molar mass of the gas molecules, R is the Universal gas constant.

3. Maxwell's speed distribution in 3D

$$f(c)\ \frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} c^2\, e^{-\frac{mc^2}{2k_B T}} dc$$

$$f(c)\ \frac{dN_c}{N} = 4\pi\left(\frac{m}{2\pi RT}\right)^{\frac{3}{2}} c^2\, e^{-\frac{Mc^2}{2RT}}\, dc$$

m is the mass of a gas molecule, k_B Boltzmann constant (1.38×10^{-23} J^{K-1}), T temparature, M is molar mass of the gas molecules, R is the Universal gas constant.

4. Average speed <c>

(a) In 1D, <c> = 0

(b) In 2D, $<c> = \sqrt{\frac{\pi k_B T}{2m}} = \sqrt{\frac{RT}{2M}}$

(c) In 3D, $<c> = \sqrt{\frac{8 k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$

5. Root mean square (RMS) speed

(a) In 1D, $C_{rms} = \sqrt{\frac{k_n T}{m}} = \sqrt{\frac{RT}{M}}$

(b) In 2D, $<c> = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$

(c) In 3D, $<c> = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$

6. Most Probable speed C_{mps}

(a) In 1D, $C_{mps} = 0$

(b) In 1D, $C_{mps} = \sqrt{\frac{k_B T}{2m}} = \sqrt{\frac{RT}{2M}}$

(c) In 3D, $C_{mps} = \sqrt{\frac{2K_B T}{m}} = \sqrt{\frac{2RT}{M}}$

7. Average kinetic energy $<\varepsilon>$

(a) In 1D, $<\varepsilon> = \frac{1}{2}k_BT$

(b) In 2D, $<\varepsilon> = k_BT$

(c) In 3D, $<\varepsilon> = \frac{3}{2}k_BT$

8. Height of the peak in speed distibution.

(a) In 1D $\sqrt{\frac{m}{2\pi k_BT}} = \sqrt{\frac{M}{2\pi RT}}$

(b) In 2D $\sqrt{\frac{m}{k_BTe}} = \sqrt{\frac{M}{RTe}}$

(a) In 3D $\frac{1}{e}\sqrt{\frac{2m}{\pi k_BT}} = \frac{1}{e}\sqrt{\frac{2M}{\pi RT}}$

1.11 Maxwell's Kinetic Energy distributions

According to kinetic theory of gas, molecules are in ceaseless and chaotic motion and they move with an arbitary speed ranging from zero to infinity, Consequently, its Kinetic energy is also random and ranging from zero to infinity. There will be a kinetic energy distribution similar to speed distribution. Here we will investigate what is the probability of finding molecules having kinetic energy within the range $\varepsilon + d\varepsilon$. This is obtained from Maxwell's kinetic energy distribution function which is special case of Maxwell's distribution.

Also the fraction of molecules having the kinetic energy greater than or equal to a certain value can be realised. Only those reactant molecules having kinetic energy greater than or equal to the activation energy can undergo a chemical change.

Maxwell's kinetic energy distribution in one dimension

Maxwell's velocity distribution formula in ID

$$f(u)\,dc = \frac{dN_u}{N} = \frac{dN_u}{N} = \left(\frac{m}{2\pi k_BT}\right)^{\frac{1}{2}} e^{-mvu^2/2k_BT}du$$

$$= \left(\sqrt{\frac{M}{2\pi RT}}\right)^{\frac{1}{2}} e^{-Mu^2/2RT} du\,,$$

where $\frac{dN_u}{N}$ is the probability or fraction of molecules having velocity within the range u and u+du. N is the total number of molecules, u is velocity in = x direction.

Now the kinetic energy of the molecule $\varepsilon = \frac{1}{2}mu^2$. Then $du = \pm\sqrt{\frac{d}{2m\varepsilon}}$. Putting these values we get Maxwell's kinetic energy distribution formula in one dimension and it is given as

$$f(\varepsilon)\, d\varepsilon = \frac{dN_\varepsilon}{N} = 2\left(\frac{m}{2\pi k_B T}\right)^{\frac{1}{2}} \frac{1}{\sqrt{2m\varepsilon}} e^{-\varepsilon/k_B T}\, dc.$$

Where $f(\varepsilon)\, d\varepsilon = \frac{dN_\varepsilon}{N}$ is the probability or fraction of molecules having kinetic energy within the range ε and ε+dε. Here the factor 2 is multiplied to incorporate the ± sign. This implies even if the velocity is positive or negative, kinetic energy is always positive.

There are some important points to note

1. Unlike velocity distribution kinetic energy distribution is independent of mass of the molecules and it is a function of temperature only.
2. When ε is very small, f(ε) varies with $\frac{1}{\sqrt{\varepsilon}}$. When ε is much greater compared to the thermal energy $\langle k_B T \rangle$, f (ε) decreases exponentially. As it does not passes through a maximum, there is nothing so called most probable energy.
3. When temparature tends to infinity the distribution will be along the horizontal axis that will be along the ε–axis. If the temparature is zero kelvin then the distribution curve will be along the vertical axis that is along the P (ε) –axis.

4. Average kinetic energy distribution (in one dimension)
Average kinetic energy is given as

$$<\varepsilon> = \int_0^\infty \varepsilon \ f(\varepsilon)\ d(\varepsilon)$$

$$= \int_0^\infty \varepsilon \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} e^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_0^\infty \varepsilon^{\frac{1}{2}}\ e^{-\frac{\varepsilon}{K_B T}} d\varepsilon$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_0^\infty \sqrt{k_B T}\ z^{\frac{1}{2}}\ e^{-z}\ k_B T\ dz$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} (k_B T)^{\frac{3}{2}} \times \left(\frac{3}{2}\right)$$

$$= \frac{k_B T}{\sqrt{\pi}} = \frac{1}{2} k_B T$$

Here we have substituted $\frac{\varepsilon}{k_B T}$ by *z* and hence $d\varepsilon = k_B T dz$. Again when = 0, and as → ∞ then z → ∞

5. $<\varepsilon^2>$ from Kinetic energy distribution (in one dimension)

$$<\varepsilon^2> = \int_0^\infty \varepsilon^2 f(\varepsilon) d\varepsilon \int_0^\infty \varepsilon^2 \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} e^{-\frac{1}{2}}\ e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_0^\infty \varepsilon^{\frac{3}{2}}\ e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_0^\infty (k_B T)^{\frac{3}{2}}\ z^{\frac{3}{2}}\ e^{-z}\ k_B T\ dz$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} (k_B T)^{\frac{5}{2}} \int_0^{\infty} z^{\frac{3}{2}e^{-z}} dz$$

$$= \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} (k_B T)^{\frac{5}{2}} \Gamma\left(\frac{5}{2}\right)$$

$$= \frac{k_B^2 T^2}{\sqrt{\pi}} - \frac{3}{2} \times \frac{1}{2} \times \sqrt{\pi}$$

$= \frac{3}{4} k_B^2 T^2$ Here we substituted $\frac{\varepsilon}{k_B T}$ by z and hence dε. Again when $\varepsilon = 0$, $z = 0$ and as $\varepsilon \to \infty$ and as $z \to \infty$

6. Variance in energy (in one dimension)

$$\sigma_\varepsilon^2 = <\varepsilon^2> - <\varepsilon>^2$$

$$= \frac{3}{4} k_B^2 T^2 - \frac{1}{4} k_B^2 T^2 = \frac{1}{2} k_B^2 T^2$$

7. Standard deviation in energy (in one dimension)

$$\sigma_\varepsilon^2 = \sqrt{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}$$

$$= \frac{1}{\sqrt{2}} k_B T$$

8. Fraction of molecules having kinetic energy $\varepsilon \geq \varepsilon'$ is given by

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} f(\varepsilon)\, d\varepsilon = \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_{\varepsilon'}^{\infty} \varepsilon^{-\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

Let $\varepsilon = k_n T x^2$, then $d\varepsilon = 2k_B T\, x dx$. When $\varepsilon = \varepsilon'$, $x = \sqrt{\frac{\varepsilon'}{k_B T}}$ and as $\varepsilon \to \infty$ then $z \to \infty$ Therefore

$$\frac{N(\varepsilon')}{N} = \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \frac{1}{\sqrt{k_B T x}} - e^{-x^2} \times 2k_B T \times dx$$

$$\frac{N(\varepsilon')}{N}=\frac{2}{\sqrt{\pi}}\int_{\sqrt{\frac{\varepsilon'}{k_BT}}}^{\infty} e^{-x^2}dx=\operatorname{erfc}\left(\sqrt{\frac{\varepsilon'}{k_BT}}\right)$$

In a special case when $\varepsilon' >> k_BT$, erfc $\left(\sqrt{\frac{\varepsilon'}{k_BT}}\right) \to 0$ and hence $\frac{N(\varepsilon')}{k_BT} \to 0$

With the increase in temparature average kinetic energy increases and hence fraction of molecules having kinetic energy $\varepsilon \geq \varepsilon'$ increases. This is significant when we consider rate of a gas phase reaction. For a reactant molecule to be transformed into a product it has to cross the activation energy barrier. Hence the rate of reaction should be proportional to that fraction of reactant molecules which has energy $\varepsilon \geq E_{act}$, the activation energy. Consequently the rate of reaction increases with increase in pressure.

Fraction of molecules having Kinetic energy $\varepsilon \geq \varepsilon'$ in two dimensions.

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} f(\varepsilon)\, d\varepsilon$$

$$= \left(\frac{1}{k_BT}\right)\int_{\varepsilon'}^{\infty} e^{-\frac{\varepsilon}{k_BT}}\, d\varepsilon$$

$$\frac{N(\varepsilon')}{N} = \frac{1}{k_BT}\left[\frac{e^{-\frac{\varepsilon}{k_BT}}}{-\frac{1}{k_BT}}\right]_{\varepsilon'} = e^{-\frac{\varepsilon'}{k_BT}}$$

Fraction of molecules having Kinetic energy $\varepsilon \geq \varepsilon'$ in three dimensions.

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} f(\varepsilon)\, d\varepsilon$$

$$= 2\pi\left(\frac{1}{\pi k_BT}\right)^{\frac{3}{2}}\int_{\varepsilon'}^{\infty} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_BT}}\, d\varepsilon$$

Let $\varepsilon = k_B T x^2$, then $d\varepsilon = 2K_B T\ x dx$. When $\varepsilon = \varepsilon', x = \left(\sqrt{\frac{\varepsilon'}{k_B T}}\right)$ and $\varepsilon \rightarrow \infty$ and as $z \rightarrow \infty$ Therefore

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = 2\pi\left(\frac{1}{\pi k_B T}\right)^{\frac{3}{2}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \left(k_B T x^2\right)^{\frac{1}{2}} e^{-x^2} \times 2\, k_B T \times dx$$

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{\frac{3}{2}} \left(k_B T\right)^{\frac{3}{2}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \left(2x^2\right) e^{-x^2} dx$$

$$= \frac{2}{\sqrt{\pi}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \left(2x^2\right) e^{-x^2} dx$$

$$= -\frac{2}{\sqrt{\pi}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} x d\left(e^{-x^2}\right) \quad \text{[Integrating by parts]}$$

$$= -\frac{2}{\sqrt{\pi}}\left[\left(xe - x^2\right)^{\infty} \sqrt{\frac{\varepsilon'}{k_B T}} - \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \frac{dx}{d\left(e^{-x^2}\right)} e^{-x^2} d\left(e - x^2\right)\right]$$

$$= \frac{2}{\sqrt{\pi}}\left[-\sqrt{\frac{\varepsilon'}{k_B T}}\, e^{-\frac{\varepsilon'}{k_B T}} - \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} e^{-x^2} dx\right]$$

$$= 2\sqrt{\frac{\varepsilon'}{\pi k_B T}}\, e^{\frac{\varepsilon'}{k_B T}} + \operatorname{erfc}\left(\sqrt{\frac{\varepsilon'}{k_B T}}\right)$$

In a special case when $\varepsilon' >> K_B T$, then the second term involving co-error function becomes zero and we get { erfc $\left(\sqrt{\frac{\varepsilon'}{k_B T}}\right) \to 0$

$$\frac{N(\varepsilon')}{N} = 2\sqrt{\frac{\varepsilon'}{\pi k_B T}}\, e^{-\frac{\varepsilon'}{k_B T}}$$

Question

Show that the average kinetic energy of the molecules of a gas at equilibrium, at a fixed temparature T is kT $\frac{3}{2}$

Using the rule of averaging, the average energy <ε> is

$$<\varepsilon> = \int_0^\infty \varepsilon \frac{dN_\varepsilon}{N} = \frac{1}{N}\int_0^\infty \varepsilon dN_\varepsilon$$

$$= 2\pi\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{\varepsilon}{kT}} \varepsilon^{\frac{3}{2}}\, d\varepsilon$$

$$= 2\pi\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \int_0^\infty e^{-\frac{\varepsilon}{kT}} \varepsilon^{\frac{3}{2}-1}\, d\varepsilon$$

$$= 2\pi\left(\frac{1}{\pi kT}\right)^{\frac{3}{2}} \frac{\left(\frac{3}{2}\right)\left(\frac{3}{2}\right)\sqrt{\pi}}{\left(\frac{1}{kT}\right)^{\frac{3}{2}}} = \frac{3}{2}kT$$

The Gamma Function

The Gamma function introduced by Euler in the 1700s is the gamma function, and is defined by integral.

$$\Gamma(n) = \int_0^\infty e^{-x}\, x^{n-1} dx \; n > 0$$

Note that the integral is a function x and n, and the resulting integral is a function of n.

If $n \geq 2$, we can integrate $\Gamma(n)$ by parts : using e^{-x} dxdv and x^{n-1} as u

$$\left[\int udv = uv - \int vdv\right]$$

$$\Gamma(n) = \left[-x^{n-1}e^{-x}\right]_0^\infty + (n-1)\int_0^\infty x^{n-2}\, e^{-x}\, dx$$

$$\Gamma(n) = 0 + (n\text{-}1) \int_0^\infty x^{n-2}e^{-x}\, dx$$

$\Gamma(n)$ = (n-1) $\Gamma(n\text{-}1)$

We can now write $\Gamma(n\text{-}1)$ = (n-2) $\overline{)(n-2)}$ and so on, finally

$\Gamma(n)$ = (n-) (n-2).............$\Gamma(1)$

$$\Gamma(n) = (n\text{-}1)! \qquad \therefore \Gamma(1) = \int_0^\infty e^{-x}dx = 1$$

Up to this point the equation $\Gamma(1) = \int_0^\infty e^{-x}dx = 1$ is restricted to integer values of $n \geq 2$; but we can also decline factorials for other values of n. For n = 1, $\Gamma(1)$ = 0!, which is interesting.

For other values of n (non-integers). For n = $\frac{1}{2}\int_0^\infty e^{-x}\, x^{-\frac{1}{2}}\, dx$

Let $x = u^2$ then x^{-12} dx = 2du

$$\Gamma\left(\frac{1}{2}\right) = 2\int_0^\infty e^{-n^2}du = \sqrt{\pi}$$

Degrees of Freedom

Degree of freedom of a molecule may be defined as number of independent parameters which must be specified to describe the state or position of the molecule completely. Formula = 3N, N is the number of atoms.

For a monoatomic gas, there will be 3 degrees of freedom, all of which are translational.

For a diatomic molecule, gas, there will be six degrees of freedom. Out of these three will be translational, two will be rotational and one will be vibrational.

For a triatomic molecule, there will be nine degrees of freedom, of which three will be translational. That means there will be six degrees of freedom for the vibrational and rotational modes.Linear (CO_2), there are two rotational degrees of freedom, four vibrational degrees of freedom. For Nonlinear tri-atomic molecule (H_2O) there will be three rotational and three vibrational degrees of freedom.

In general, the number of vibrational degrees of freedom of a molecule containing N atoms

i) A linear molecule has (3N-5) vibrational degrees of freedom.

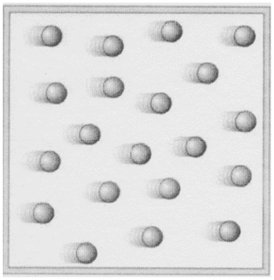
ii) A non-linear molecule has (3N-6) vibrational degrees of freedom.

1.12 Equipartition of Energy

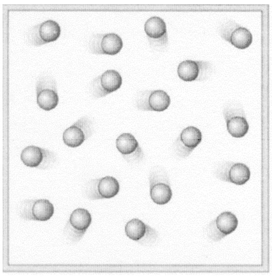
The theorem of equipartition of energy states that molecules in thermal equlibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is

$\frac{1}{2}$ kT per molecule	k = Boltzmann's constant	$\frac{3}{2}$kT	For three translational degrees of freedom, such as in an ideal monoatomic gas.
$\frac{1}{2}$ RT per mole	R = gas constant	$\frac{3}{2}$RT	

To give a rather contrived example, consider a container in which we have placed a number of ping-pong balls. Initially the balls are stationary. Imaging we now throw some energy randomly into our box, which will be shared out amongst the ping-pong balls in some way such that they begin to move about. While you might not realise it, intuitively you know what this motion will look like. For example, you would be very surprised if the particle motion looked like this :



You would probably predict something more like this :



i.e. completely random motion of the ping-pong balls. This is exactly the same result as predicted by the equipartition theorem–the energy is shared out evenly amongst the x,y, and z translational degrees of freedom.

The equipartition theorem can go further than simply predicting that the available energy will be shared evently amongst the accessible modes of motion, and can make quantitative predictions about how much energy will appear in each degree of freedom. Specifically, it states that each quadratic degree of freedom will, on average, possess an energy $\frac{1}{2}$kT. A 'quadratic degree of freedom' is one for which the energy depends on the square of some property. Consider the kinetic and potential energies associated with translational, rotational and vibrational energy.

$\frac{1}{2}mv_z^2$ $\left(\frac{1}{2}mv_y^2\right)$ $\left(\frac{1}{2}mv_z^2\right)$

Law of equipartition of energy : Statement

According to the law of equipartition of energy, for any dynamic system in thermal equilibrium, the total energy for the system is equally divided among the degree of freedom. The kinetic energy of a single molecule along the x-axis, the y-axis and the z-axis is given as

$\frac{1}{2}mv_x^2$, along the x-axis

$\frac{1}{2}mv_y^2$, along the y-axis

$\frac{1}{2}mv_z^2$, along the z-axis

When the gas is at thermal equilibrium, the average kinetic energy is denoted as

$\left(\frac{1}{2}mv_x^2\right)$, along the x-axis

$\left(\frac{1}{2}mv_y^2\right)$, along the y-axis

$\left(\frac{1}{2}mv_z^2\right)$, along the z-axis

According to the kinetic theory of gases, the average kinetic energy of a molecule is given by,

$$\frac{1}{2}mv^2_{rms} = \frac{1}{2}k_BT$$

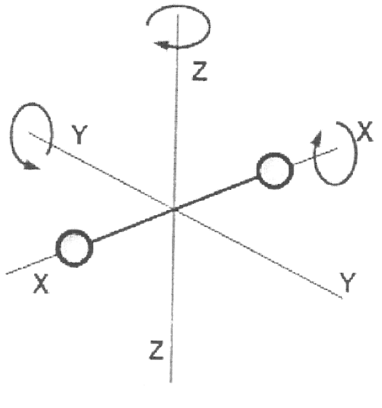
Where V_{rms} is the root mean square velocity of the molecules, k_b is the Boltzmann constant and T is the temparature of the gas.

The mono-atomic gas has three degrees of freedom, so the average kinetic energy per degree of freedom is given by KE $= \frac{3}{2}k_BT$

If a molecule is free to move in space, it needs three coordinates to specify its location, thus, it possesses three translation degrees of freedom. Similarly, if it is constrained to move in a plene, it possesses two translational degrees of freedom and if it is a straight line, it possesses one translational degree of freedom. In case of a tri-atomic molecule, the degree of freedom is. And the kinetic energy of the per molecule of the gas is given as,

$$6 \times N \times \frac{1}{2}k_BT = 3 \times \frac{R}{N}Nk_BT = 3RT$$

Molecules of a mono-atomic gas like argon and helium has only one translational degree of freedom. The kinetic energy per molecule of the gas is given by



$$3 \times N \times \frac{1}{2}k_BT = 3 \times \frac{R}{N}Nk_BT = \frac{3}{2}RT.$$

The diatomic gases such as O_2 and N_2 which have three translational degrees of freedom can rotate only about their centre of mass. Since, they have only two independent axis of rotation, as the third rotation is negligible, due to its 2-D structure. Thus, only two rotational degrees of freedom are considered. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of translational energy t and rotational energy.

Application of Equipartition of Energy-Specific Heat of a Gas

Following the equipartition principle, the mean total energy of a molecule having f degrees of freedom is : $\varepsilon = \frac{f}{2}kT$

and the total energy of N molecules is

$$U = N\dot{\varepsilon} = \frac{f}{2}NkT = \frac{f}{2}n\dot{R}T$$

or, the molal internal energy, and molal specific heat at constant volume

$$C_v = \left[\frac{\partial u}{\partial T}\right]_y = \frac{f}{2}\dot{R}$$

For an ideal gas

$$C_P - C_v = \bar{R}$$

$$C_p = \frac{f}{2}\dot{R}\frac{f}{2}\dot{R} + \dot{R} = \frac{f+2}{1}\dot{R}$$

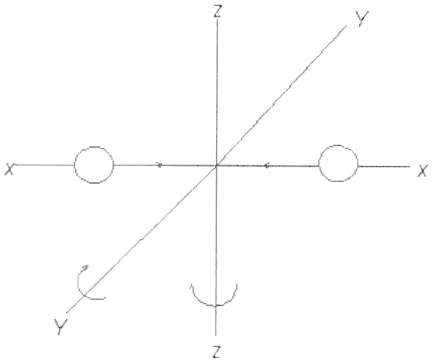
and

$$\gamma = C_p / C_v = \frac{f+2}{f}$$

It is to be noted that C_v, C_p and γ are all the constant and independent temparature. For a monatomic gas which has only translational kinetic energy, f = 3. Thus,

$$U = \frac{3}{2}\dot{R}T, C_v = \frac{3}{2}\dot{R}\,C_p \text{ and } \gamma = \frac{5}{3} = 1.67$$

A diatomic molecule is commonly pictured as having the dumbbell structure. Its moment of inertia about y and z axes is very greater than that about x axis, and the latter is neglected.



The molecule has thus two rotational degrees of freedom. Since the atoms can also vibrate along the line joining them, the molecule has two vibrational degrees of freedom, one for kinetic energy and the other for potential energy, because the vibrational energy is partly kinetic and partly potential. A diatomic molecule is thus expected to have seven degrees of freedom (3 for translation, 2 for rotation and 2 for vibration). Thus

$$f = 7,\ C_V = \frac{7}{2}R \text{ and } \gamma = \frac{9}{7} = 1.29$$

These values do not tally with experimental results.

Table Experimentally measured values of C_p and γ of different gases at room temparature

Gas	γ	C_p/R
He	1.66	2.50
Ne	1.64	2.50
A	1.67	2.51
Kr	1.69	2.49
Xe	1.67	2.50
H_2	1.40	3.47
O_2	1.40	3.53
N_2	1.40	3.50
CO	1.42	3.50
NO	1.43	3.59
Cl_2	1.36	4.07
CO_2	1.29	4.47
NH_3	1.33	4.41

Much better agreement is achieved if f = 5. Then

$$u = \frac{5}{2}\bar{R}, C_v = \frac{5}{2}\bar{R}, c_p = \frac{7}{2}\bar{R}, \text{ and } \gamma = \frac{7}{5} = 1.40$$

This implies that at room temparature, the diatomic molecules possess either rotational or vibrational energy, but not both. At higher temparature, however, both of these modes become achieve. At very low temparature, c_v approaches $\frac{3}{2}\bar{R}$ suggesting that only translational motion is present.

Minimum degree of freedom for a single molecule is f = 3, thus $\gamma = 1 + 2/3 = 1.67$. For heavy molecules the degree of freedom is large thus 2/f in the expression of γ approaches to 0 value. Hence γ must be between 1 and 1.67.

Molecular basis of Specific heats

Specific heat of substance is defined as the quantity of heat required to raise the temparature of one gram of the substance through one degree kelvin.

Molar heat at constant volume-Heat energy required to raise the temparature of one mole of a gas through 1°C keeping the volume of the gas constant, is called heat capacity at constant volume.

Molar heat at constant pressure-Heat energy required to raise the temparature of one mole or a gas through 1°C keeping the pressure of the gas constant, is called heat capacity at constant pressure.

Question :

Assuming a tri-atomic molecule to be a triangular structure with each atom at one apex, determine the specific heat ratio of a gas consisting of tri atomic molecules, with the help of equipartition principle.

Solution :

Each atom is free to vibrate along the line joining in to another atom. Each molecule has six vibrational degrees of freedom apart from three translation degree of freedom and three rational degrees freedom. Therefore, the total internal energy according to the principle of equipartition of energy is :

$$U = U_{trace} + U_{rot} + U_{vib}$$

$$= N\left[\frac{3}{2}k_B + \frac{3}{2}k_B + \frac{6}{2}k_B\right]$$

$$= 6Nk_BT = 6nRT$$

$$U = 6\bar{R}T$$

$$C_v = 6\dot{R}$$

$$h = 7\dot{R}T$$

$$C_P = 7\dot{R}$$

$$\gamma = \frac{C_P}{C_v} = \frac{7}{6} = 1.167$$

Question :

At what temparature is the mean translational K.E. of a molecule equal to that of a singly charged ion of the same mass that has been accelerated from rest through a potential difference of (a) 1 volts, (b) 500 volts? Neglect relativistic effect.

Solution :

$$\bar{\epsilon} = \frac{3}{2}KT = \frac{3}{2} \times 1.38 \times 10^{-23} \times T\,\text{J/molecule}$$

Energy of a singly charged of the same mass as that of the molecules, accelerated from rest through a potential difference of 1 volt is given by :

$$\bar{\epsilon} = 1.6021 \times 10^{-19}\,\text{J}$$

$$\frac{3}{2} \times 1.38 \times 10^{-23} \times T = 1.6021 \times 10^{-19}$$

T = 7730K ....(Ans. a)

Similarly, for (b)

$$T = \frac{1.6201 \times 10^{19} \times 500}{\frac{3}{2} \times 1.38 \times 10^{-23}} = 3.86 \times 10^{6}\,\text{K} \text{ ....(Ans.b)}$$

1.13 Real gases

A gas which does not obey general gas equation and all other gas laws strictly but tends towards ideally at low pressure and high temparature is known as Real gas.

Ideal gas	Real gas
1. Obey PV = RT under all conditions of Temparature and Pressure	Obeys gas laws at high temparature and low pressure.
2. Volume occupied by gas molecule is negligible to the total volume of gas	Volume occupied by gas molecule is not negligible
3. Attractive forces between gas molecules are negligible	Attractive forces between gas molecules are appreciable.

Deviations from Ideal behaviour

All known gases are real gases. Amagat, Andrew and other scientists studied the behaviour of various gases under different conditions of temparature and pressure. They found that all gases shoe devaiations from ideal behaviour and deviations are considerable at high pressure and low temparatures. Further, it has been found that the most easily liquefiable and highly soluble gases shows larger deviations.

Deviations from Boyle's law

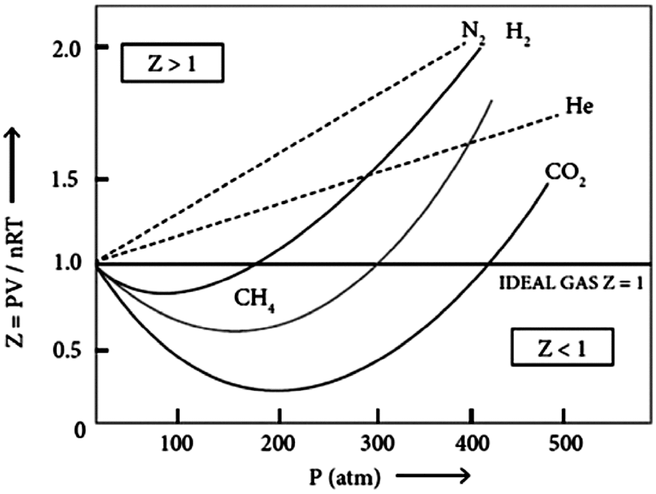
It was discovered as early as 1881 that Boyle's law was not strictly obeyed by gases at high pressure.

Deviations from Charles's law

Amagat Andrew and others found the Charles Law is valid only at low pressures. As the pressure increase several deviations set in. The gases which are more easily liquefiable show larger deviations.

1.14 The van der Waals Equation

How can the ideal gas law be modified to yield an equation that will represent the experimental date more accurately? Beginning from correcting obvious defect in the ideal gas law, namely the prediction that under finite pressure the



volume of the gas is zero at the absolute zero temparature : $V=\frac{RT}{P}$. On cooling, real gases liquefy and ultimately solidify; after liquefication the volume does not change very much. We can arrange the new equation so that it predicts a finite volume for the gas at 0 K by adding a positive constant b to the ideal volume : V $=b+\frac{RT}{P}$, T = 0 K molar volume obtained is b, b is comparable with molar volume of the liquid or solid.

The equation predicts as pressure becomes infinite the molar volume approaches the limiting value b. This prediction is more in line with the experience.

Comparing $\frac{V_{real}}{V_{ideal}}$ = Z (compressibility factor)

$Z=1+\frac{bP}{RT}$. Z = f (linear function of P), with positive slope, $\frac{b}{RT}$

The equation can fit the behaviour of Hydrogen gas but it is not possible to fit the curve of nitrogen.

In the low pressure region the data is well represented by the above equation. It can thus be concluded that the assumption that the molecules of a gas have a finite size is sufficient to explain the values of Z greater than unity, Aparently this size effect is the dominating one in producing deviations from ideality in hydrogen at 0°C. It is also clear that some other effect produce the deviation fro ideality in gases such as nitrogen and methane. Since the size effect cannot explain their behaviour in the low pressure range.

The other effect

First, the energy here known as the heat of vaporisation, must be supplied to take a molecule out of the liquid and put it into vapour. This energy is required because the forces of attraction is strong if the molecules are close together, as they are in a liquid, and very weak if the molecules are far apart, as they are in a gas. The problem is to find an appropriate way to modify the gas equation taking into account the effect of these weak attractive forces.

The pressure exerted by a gas on the walls of a container acts in an outward direction. Attractive forces between the molecules tend to pull them together, thus diminishing the outward thrust against the wall and reducing the pressure below that exerted by the ideal gas. This reduction in pressure should be proportional to the force of attraction between the molecules of the gas.

Consider two small volume elements V_1 and V_2 in a container of gas. Suppose each volume element contains one molecules and that the attractive force between the two volume element contains is some small value f. If another molecule is added to V_2, keeping one molecule in V_1, the force acting between the two elements should be 2f; addition of a third molecule to V_2 should increase the force to 3f, and so on. The force of attraction between the two volume elements is therefore proportional to c_2, the concentration of molecules in volume v_2.

If at any point in the argument, the number of molecules in v_2 is kept constant and molecules are added to v_1. Thus, the force acting between the two elements can be written as : force ∞. Since the concentration in a gas is everywhere the same, $c_1 = c_2$ and so, force ∞ But $c = \frac{n}{V} = \frac{1}{V}$. Consequently, force ∞ $\frac{1}{V^2}$

The equation is re-written as $P = \frac{RT}{V-b}$ Because of the attractive forces between the molecules, the pressure is less than that given by the above equation by an amount proportional to $\frac{1}{V^2}$, so a term is substracted from the right-hand side to yield.

$P = \frac{RT}{V-b} - \frac{a}{V^2}$, where a isa positive constant roughly proportional to the energy of vaporisation of the liquid.

Two things should be noted about the introduction of the $\frac{a}{V^2}$ term. First, forces acting on any volume element in the interior of the gas balance out to zero; only those element of volume near the wall of the container experience an unbalanced force that tends to pull them towards the centre. Thus the effect of the atttractive force is felt only at the wall of the container experience an unbalanced force that tends to pull them towards the center. Thus the effect of the attractive forces is only felt at the walls of the vessel.

Second, the derivation assumed an effective range of action of the attractive forces of the order of centimeters; in fact the range of these forces is of the order of nanometers.

Van der Waals was first to recognize the influences of molecular size and intermolecular forces on the pressure of a gas. These weak forces of attraction are called van der waals forces. The van der waals equations are usually written in the equivalent but less instructive forms.

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \text{for 1 mole}$$

$$\left(P+\frac{n^2a}{V^2}\right)(V-nb) = nRT \text{ for n moles}$$

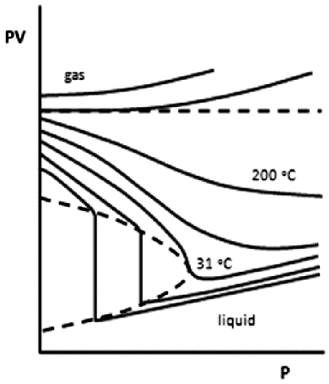
Compressibility Factor, $\frac{V_{real}}{V_{ideal}} = Z$

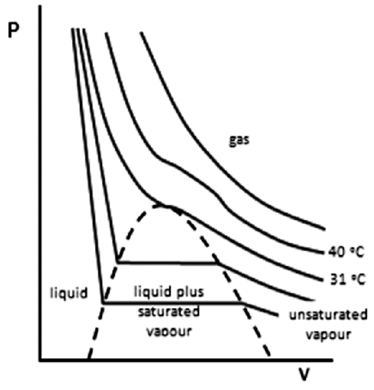
A convenient way of showing deviations of gases from ideal behaviour is to plot compressibility factor $Z=\frac{PV}{nRT}$ **against the Pressure.**

The characteristics obtained from Z vs P plot

1. All the curves approach the ideal value as the pressure approaches to zero. Thus at low pressures all gases behave ideally.
2. At moderate pressures, there is a negative or under effect deviation. Hydrogen does not show negative deviation. However negative deviation for Hydrogen is observed at low temparature.
3. At very high pressure, there is positive deviationand the gases do not even approximately obey the Boyel's law.

Amagat's plots and Andrew's





Above about 50° C Boyle's law closely obeyed the behaviour of the gas and below about 30° C in fact Andrews found that the critical temparature for CO_2 was 30.9° C. Above this temparature carbon dioxide could not be liquefied by pressure alone while below this temparature and increase in pressure would finally result in liquid Carbon dioxide. At the critical point of the gas and liquid are in equilibrium.

1.15. Other Equations of State

Following are some of the real gas equations :

1. van der Waals equation of state for real gas

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT$$

2. Where $\frac{a}{v^2}$ is accounting for the force of cohesion and b is accounting for volume of the molecules termed as co-volume.

3. Berthelot equation of state.

$$p=\frac{RT}{v-b}-\frac{a}{T-v^2}$$

4. Dieteriei equation of state

$$p=\frac{RT}{v-b}e^{-a/RT}$$

5. Redlich-Kwong equation of state

$$p=\frac{RT}{v-b}-\frac{a}{T^{1/2}v(v+b)}$$

6. Saha-Bose equation of the state

$$p=\frac{RT}{v-b}e^{-a/RT}\ln\left(\frac{v-2b}{v}\right)$$

Where a and b are constants which can be evaluated from the **critical data.**

1. The **van der Waals,** Berthelot and Dieterici equations of state are of limited accuracy.
2. The **Redlich-Kwong** equation gives good results at high pressures and is fairly accurate for temparatures above the critical value.
3. **Saha-Bose** equation of state is quite accurate for densities less than about 0.8 times the critical density.

One more widely used equation of state with good accuracy is the **Beattic-Bridgeman** Equation :

$$p=\frac{RT(1-e)}{v^2}(v+B)-\frac{A}{v^2}$$

where $A=A_0\left(1-\frac{a}{v}\right)$ $\quad B=B_0\left(1-\frac{b}{v}\right)$ $\quad e=\frac{c}{VT^3}$

There are five constants, A_0, B_0, a, b, and c to be determined experimentally for each gas.

Viral Expression

The relation between pv and p in a term of power series may be expressed as

$$P\bar{v}=A\left(1+B'P+C'P^2+D'P^2+...........\right)$$

For any gas

$$\lim_{p\to\infty}P\bar{v}=A=\dot{R}T$$

$$\therefore \ \frac{P\bar{v}}{RT} = 1 + B'P + C'p^2 + D'P^3 + \ldots\ldots\ldots$$

An alternative experssion is

$$\frac{P\bar{v}}{RT} = 1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \ldots\ldots\ldots$$

Both expressions in are known as virial expansions or virial equations of state, first introduced by the Dutch physicist, Kammerlingh onnes B′, C′ B, C........etc. are called virial coefficients. B′ and B are called second virial coefficients, C′ and C are called third viral coefficients, and so on. For a given gas, these coefficients are functions of temparature only.

The ratio $\frac{P\bar{v}}{RT}$ is called the compressibility factor, Z. for an ideal gas z=1. The magnitude of Z for a certain gas at a particular and temparature gives an indication of the extent of deviation of the gas from the ideal gas behaviour.

The virial expansions become

$$Z = 1 + B'P + C'P^2 + D'p^3 + \ldots\ldots\ldots\ldots\ldots\ldots$$

and

$$Z = 1 + \frac{B}{V} + \frac{C}{\bar{v}^2} + \frac{D}{\bar{v}^3} + \ldots\ldots\ldots$$

The relations between B′, C′ and B,C ....can be derived as follows

$$\frac{PV}{RT} = 1 + B'p + C'p + D'p^3 + \ldots\ldots\ldots$$

$$= 1 + B'\left[\left(\frac{R\bar{T}}{v}\right)\left(1 + \frac{B}{\bar{v}} + \frac{C}{\bar{v}^2} + \ldots\ldots\right)\right] +$$

$$C'\left[\left(\frac{R\bar{T}}{v}\right)^2\left(1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \ldots\ldots\right)^2\right] + \ldots\ldots\ldots$$

$$1+\frac{BRT}{\bar{v}}+\frac{BRT+C'\left(RT\right)^2}{\bar{v}^2}+$$

$$\frac{B'RTC+C'\left(RT\right)^2 D'\left(RT\right)^3}{\bar{v}^3}+........$$

Comparing this equation and rearranging

$$B'= B'\frac{B}{\bar{R}T}, C'=\frac{C-B^2}{\left(\bar{R}T\right)^2}, D'=\frac{D-3BC+2B^3}{\left(\bar{R}T\right)^3},.......$$

$$Z=\frac{P\bar{v}}{\bar{R}T}=1+B'p+C'p^2+.........$$

Therefore

$$=1\frac{B}{\bar{R}T}P+\frac{C-B^2}{\left(\bar{R}T\right)^2}p^2+...........$$

The terms B/$\bar{V}$, C/$\bar{V}^2$ etc. of the viral expansion arise on account of molecular interaction. If so such interactions exist (at very low pressures) $B=0$, $C=0$ etc. $Z=$ 1 and $P\bar{v}-\bar{R}T$. It may be observed from Eq that the compressibility factor is a function of temparature and pressure of a gas.

A graph for variation of pressure versus Z with constant temparature can be plotted from which value of Z for a pair of pressure and temparature states can be estimated. Further using the equation PV = ZRT, the volume of the gas can be obtained.

Question

Determine Boyle temparature from van der Waal's equation

Solution

$$\left[\frac{\partial(pv)}{\partial p}\right]_{\substack{r=0\\p=0}} = 0 = \frac{B}{RT}$$

$$\therefore \quad B = 0$$

or, $T_B = \frac{a}{bR}$

Since $B = b - \frac{a}{RT}$

The second virial coefficient describes the contribution of the pair-wise potential to the pressure of the gas. The third virial coefficient depends on interactions between three molecules, and so on and so forth.

Liquefaction

Liquefaction is the transformation of a gaseous substance into its liquid state. This change is the outcome of change in physical conditions like temparature, pressure, and volume. Thomas Andrew was the first person to study the change of state from gases to liquids in Carbon Dioxide. It was later discovered that most real gases behave like Carbon Dioxide (CO_2) and change from gases to liquids if optimum physical changes in temparature and pressure and achieved.

In his experiment on CO_2, Andrews came to a conclusion that at high temparatures, despite high pressure, the gases cannot be liquefied. Also with the increase in temparature, the gases show significant deviation from the ideal behavior. In the case of carbon dioxide, at 30.98° C, the gas started changing into a liquid.

1.16 Critical Temparature, Volume, and Pressure

Andrews in his experiment observed that above a specific temparature, the gas sample couldn't be liquefied, howsoever high the pressure becomes. The critical temparature is the temparature at which a gas changes into liquid. With the increase in temparature, the pressure required to liquefy a gas also increases. This temparature was the highest temparature at which a gas appears in the form of liquid. It is critical temparature of Tc.

Critical constants play an essential role in the change of states of matter. Critical constants are critical pressure, temparature, and volume. The volume of one mole of a gas volume liquefied at critical temparature is known as the critical volume (V_c) while the pressure required to liquefy the gas at critical temparature is called as the Critical pressure (p_c).

Calculation of Critical constants

At the critical pint, the maximum and minimam coalesce, it is thus a point inflexion. At inflexion point.

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

$$P = \frac{RT}{V - b} - \frac{a}{v^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{RT}{(V - b)^2} + \frac{2a}{V^3}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{RT}{(V - b)^3} - \frac{6a}{V^4}$$

At the critical point T = Tc when both differentials are zero. Hence,

$$\frac{RT_C}{(V_e - b)^2} = \frac{2a}{Vc^3} \text{ and } \frac{RT_C}{(V_c - b)^3} = \frac{6a}{Vc^4} \text{ Dividing}$$

$$\frac{(V_c - b)}{2} = \frac{V_C}{3} \text{ or } V_e = 3b$$

Substituting the value of Vc=3b in $\frac{RT_C}{(V_c - b)^2} = \frac{2a}{V_C^3}$ or in equation $\frac{RT_C}{(V_c - b)^3} = \frac{6a}{V_C^4}$

$$T_C = \frac{2a(V_C - b)^2}{RV_C^3} \text{ or } T_C = \frac{8a}{27Rb}$$

From $P = \frac{RT}{V - b} - \frac{a}{V^2}, PC = \frac{RT_C}{(V_C - b)^2} - \frac{a}{V_c^2} = \frac{8a}{27b}\frac{1}{(3b - b)} - \frac{a}{9b^2}$

$$P_C = \frac{a}{27b^2}$$

Thus $b = \frac{V_C}{3}$ and $a = 3P_c V_C^2$

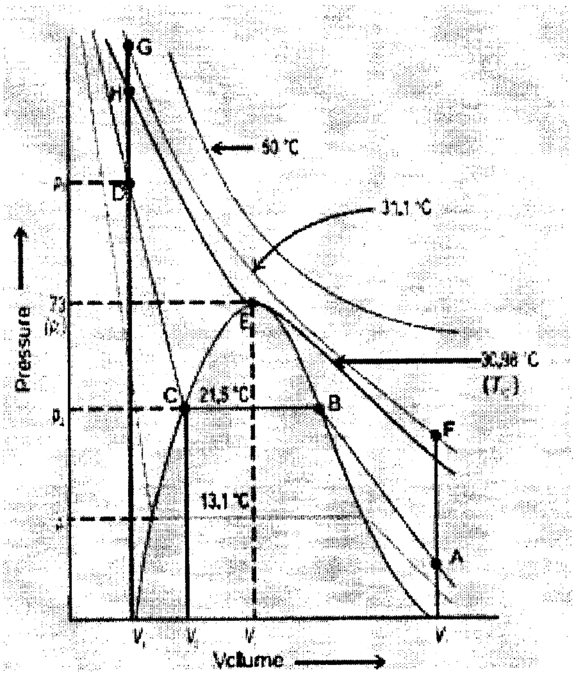
$$R = \frac{8P_c V_c}{3T_C}$$

At critical state, $Z = 3/8 = 0.375$

Isotherm of Carbon Dioxide

The graph between the Pressure and Volume at a given constant temparature is the isotherm. On studying the isotherm of Carbon dioxide we get to know the different intervals of temparatures at which a gas can show signs of liquefaction.

On studying the isotherm above we get to know the physical change of state temparature wise. Volume and pressure play a vital role in the change of state. In the above isotherm, we study the liquefaction of Carbon dioxide.



We see that the gasous state of carbon dioxide change to liquid at 30.98° C. The curve changes at a lower temparature, while at the higher temparature it does not show any change. At 30.98° C, the gas shows considerable deviation from the ideal gas behaviour.

Equillibrium state

Here we notice that the curve at increased pressure signifies compressibility of liquid CO_2 while the step line pertains to the isotherm of the liquid, slightest of compression results in a sharp rise in the pressure, thus indicating the amount of compressibility of CO_2. On attaining 21.5° Carbon dioxide behaves like a gas until point B.

The point B shows signs of liquid CO_2. The gas now exists in the dual form i.e both liquid and gas. At this stage compressing further does not affect the pressure on the gas, rather it result in condensation. At poiint C, all the CO_2 gas has condensed and further compression results in the rise in pressure.

From the above isotherm it is clear that at point A, CO_2 exists in the gaseous state while at point D it exists in a liquid state. At point D the compression of the liquid CO_2 is almost impossible. At point C an equilibrium state between the two states of matter is seen.

We further find that the behaviour of all the gases is similar to CO_2 and this is because of the constant temparature or isothermal compression. This similar behaviour shown by gases, in compression, at constant temparature is known as isothermal compression.

Gases to liquids

1. The critical temparature of the gas is the highest temparature at which the first occurence of liquefaction of gas is seen. The critical temparature signifies the force of attraction between the molecules. The higher the critical temparature, higher is the intermolecular force of attraction and easier is the liquefaction of the gas.
2. Gases require cooling and compression both for liquefaction. Now what gases need cooling and compression both for liquefaction? The gases which display a positive deviation from compressibility factor (Z) are permanent gases and they need both cooling and compression for the change in state.

   We already know that the compressibility factor is the ratio of the original volume of a gas to the molar volume, now if the value of Z is in positive or greater than 0 then it shall need both cooling and compression for the change of state.

Effect of Compression and Cooling

Compression is the process of increasing pressure on the molecules of the gas. It brings the molecules close to each other. As soon as the molecules come in the vicinity of each other the reduced temparature slows the random movement of the molecules. This dual action of compression and cooling instigates intermolecular interactions. With the start of this intermolecular interaction, the molecules gradually and closely move toward each other leading to a change in the state.

Limitations of van der waals Equation

1. van der Waal's constant a and b are empirical constants and their value depend upon the nature of the gas. Thus generality is lost.
2. The P-V-T relationship shows appreciable deviations when the pressure is too high or the temparature is too low. This is because value of a, b vary with temparature, pressure.
3. The values of critical constants calculated from van der Waals equation do not agree with the experimental values.
4. According to van der Waals equation, $\frac{RT_c}{P_cV_c} = 2.67$ for all gases. However the values found experimentally higher.
5. According to van der Waals equation, the isotherms should be continuous at all temparatures. However, the experimental isotherms are found to be discontinuous below the critical temparature.

1.17 Law of Corresponding States

The general shapes of the vapour dome and the constant temparature lines on the p-v plane are similar for all substances. However, scales may be different for different substances. This similarity can be utilized with application of dimensionless properties called reduced properties.

A reduced property is the ratio of the existing property (X) to the critical property (X_c) of the substance. Thus where the subscript r and c refer to the reduced and critical properties, respectively. Various primary properties in terms of reduced property are given in Table.

Table : Reduced Properties

Sl. No	Reduced Property	Symbol
1.	Reduced Pressure	$P_r = \frac{P}{P_c}$
2.	Reduced Temparature	$T_r = \frac{T}{T_c}$
3.	Reduced specific Volume	$vr = \frac{v}{v_c}$

The relations among the reduced properties, P_r, T_r, v_r and v_r is known as the law of correspondings states.

The specific volume or moral volume of different gases are different under same pressure and temparature. However, it is found from experimental data that at the same reduced pressure and reduced temparature, the reduced volumes of different gases are approximately the same. Therefore, for all substances

$$v_r = f\,(P_r, T_r)$$

Now,

$$V_r = \frac{v}{v_c} = \frac{ZRTP}{Z_cRT_cP} = \frac{z}{z_c}.\frac{T_r}{P_r}$$

where is called the critical compressibility factor.

From above two equations Eqs.

$$Z = f\,(p_r, T_r Z_e)$$

Experimental values fo Z_c for most substances fall within a narrow range of 0.20-0.30. Therefore, Z_c may be taken to a constant.

$$Z = f\,(p_r, T_r)$$

where T_r is plotted as a function of reduced pressure and Z, a single plot, known as the **generalized compressibility chart,** is found to be satisfactory for a great variety of substances. Although necessarily approximate, the plots are extremely usuful is situations where detailed data on a particular gas are lacking but its critical properties are available.

Law of corresponding states for van der Waal's gas

For a van der Waals gas,

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

where a,b, and R are the characteristic constants of the particular gas.

$$pv^3-(pb+RT)\,v_2+av\text{-}ab=0$$

It is therefore a cubic profile in v and for given values of p and T has three roots of which only one need be real.

1. For low temparatures, three positive real roots exist for a certain range of pressure.
2. As the temparature increases the three real roots approach one another.
3. At the critical temparature all the roots become equal. Above this temparature only one real root exists for all values of p.
4. The critical isotherm T_c at critical state on the p-v plane, where the three real roots of the van der Waals Equation coincide, not only has zero slope, but also its slope changes at the critical state (point of inflecttion), so that the first and second derivatives of p with respect to v at $T = T_c$ are each equal to zero. Therefore,

$$\left(\frac{\partial p}{\partial v^2}\right)_{T=T_c}=\frac{2.RT}{(v_c-b)^3}-\frac{6a}{v_c^4}=0$$

From these two equation, by rearanging and dividing.

$$b=\frac{1}{3}\,v_e$$

Substituting the value of b in

$$R=\frac{8a}{9T_cv_c}$$

Substituting the value of b and R

$$\left(p_c+\frac{a}{v_c^2}\right)\left(\frac{2}{3}v_c\right)=\left(\frac{\partial p}{\partial v}\right)_{T=T_c}=\frac{8a}{9T_cv_c}.T_c$$

$$a=3P_cv_c^2$$

Therefore, the value of R becomes $R=\frac{8}{3}\frac{p_cv_c}{T_c}$

The values of a,b, and R have thus been expressed in terms of critical properties, substituting these in van der Waals equation of state.

$$\left(p+\frac{3P_cv_c^2}{v^2}\right)\left(v-\frac{1}{3}v_c\right)=\frac{8}{3}\frac{P_cv_c}{T_c}T$$

or, $$\left(\frac{p}{p_c}+\frac{3v_c^2}{v^2}\right)\left(\frac{v}{v_e}-\frac{1}{3}\right)\frac{8}{3}\frac{T}{T_c}$$

Using the reduced parameter

$$\therefore \left(P_r+\frac{3}{v_r^2}\right)(3v-1)=8T_r$$

In the reduced equation of state the individual coefficients a,b and R for a particular gas have disappeared. So this equation is an expression of the law of corresponding states because it reduced the properties of all gases to one formula.

Similarly, two different substances are considered to be in 'corresponding states'. If their pressure, volumes and temparatures are of the same fraction or multiplies of the critical pressure, volume and temparature of those substances.

Values of constants 'a' and 'b' for van der Waals and Redlich-Kwong are given below Table

Table : Values of a and b

	Van der Waals		**Redlich-Kwong**	
substances	a	b	a	b
	bar $\left(\frac{m^2}{kmol}\right)^2$	$\left(\frac{m^3}{kmol}\right)$	bar $\left(\frac{m^3}{kmol}\right)^2 K^{\frac{1}{2}}$	$\left(\frac{m^3}{kmol}\right)$
Air	1.368	0.0367	15.989	0.02541
Butane (C_4H_{10})	13.86	0.1162	289.55	0.08060
Carbon monoxide (CO)	1.474	0.0395	17.22	0.02737
Methane (CH_4)	2.293	0.0428	32.11	0.02965
Nitrogen (N_2)	1.366	0.0386	15.33	0.02677
Oxygen (O_2)	1.369	0.317	17.22	0.02197

	Van der Waals		Redlich-Kwong	
substances	a	b	a	b
	bar $\left(\frac{m^2}{kmol}\right)^2$	$\left(\frac{m^3}{kmol}\right)$	bar $\left(\frac{m^3}{kmol}\right)^2 K^{\frac{1}{2}}$	$\left(\frac{m^3}{kmol}\right)$
Propane (C_3H_8)	9.349	0.0901	182.23	0.06242
Refrigerant 12	10.49	0.0971	208.59	0.06731
Sulfur dioxide (SO_2)	6.883	0.0569	144.80	0.03945
Water (H_2O)	5.531	0.0305	142.59	0.02111
Source : calculated from critical data				

The generalized compressibility chart in terms of reduced properties is shown in generalized compressibility chart. It is very useful in predicting the properties of substances for which more precise data are not available.

1.18 Intermolecular forces

Among seveal distinct types of molecular and interatomic forces van de Waals "forces include those interactions which are neither due to formation of chemical bond nor due to electrostatic interactions between ions in an ionic crystal. The van der Waals "interaction does not include interaction due to hydrogen bond formation. In includes those attractive forces which neutral molecules experience.

The van der Waals force includes–

i) dipole-dipole interaction : Keesom force

ii) dipole-included dipole interaction; Debye force and

iii) included dipole-induced dipole interaction : London force (dispersion force)

Dipole-dipole interaction :

This interaction originates due to electrical asymmetry of the molecules. Polar molecules in the gaseous state are under the influence of two opposing forces. Thermal motion tries to keep the molecules in most random state whereas dipole-dipole interaction tends to orient them in the direction of having lowest energy. The equilibrium arrangement is something in between the most random state and the most ordered state depending upon the temparature and dipole moment of the molecules.

The interaction energy per pair of molecules due to orientation of the diploar molecules in presence of one another was deduced by W.H. Keesom and is represented as

$$U_1 = \frac{2\mu^4}{3(4\pi\varepsilon_0)^{\frac{1}{2}} kTr^6}$$ where r = distance between two dipolar molecules.

μ = dipole moment of the molecule.

$$= \frac{A_1}{-r^6} \text{ where } A_1 = \frac{2\mu^4}{3(4\pi\varepsilon_0)^{\frac{1}{2}} kT}$$

ii) Dipole included dipole interaction :

Whenever a polarisable atom or molecule comes near a polar molecule, it is polarised by the field of the polar molecule, i.e. the polar molecules induces dipole moment to the molecule.

The induced dipole moment μinduced ∞F where F is the field strength. μinduced α_0= F where α_0 is called the polarisability of the molecule and α has the dimension of volume. The induced dipole is instantaneous and it changes with molecular motion. Hence the interaction energy between a dipole and a polarisable molecule is independent of temparature. P Debye calculated the interaction energy between a dipole and a polarisable molecule considering the average of all orientation of the dipole i.e. all angle of approach and the interaction energy is obtained as

$$U_1 = \frac{2\mu^2\alpha}{-(4\pi\varepsilon_0)^{\frac{1}{2}} kTr^6} \text{ where } A_2 = \frac{2\mu^2\alpha}{-(4\pi\varepsilon_0)^2}$$

iii) Induced dipole-induced dipole interaction i.e. Dispersion interaction : or London Forces. These forces exist between non-polar atoms like inert gases and non-polar molecules He, Ar, N_2. H_2 etc. Existence of these forces is evident from the fact that these gases can be liquefied by applying sufficiently high pressures at low temparature.

The atom is electrically neutral as centre of gravity of positive and negative charges are at the samepoint. The nonpolar character is due to spherical distribution of electron surrounding the nucleus. The movement of electrons is very fast, it is considered that every moment the charge centre lies on any one side of the nucleus.

Then every instant the atom acts as a dipole due to seperation of charge centres and the transient dipole changes. With favourable orientation, transient attraction develops between the neighbouring atoms. The interaction called dispersion interaction.

$$U_2 = -\frac{3}{4}hv_o\left(\frac{\alpha}{4\pi\varepsilon_0}\right)^2\frac{1}{r^6} = \frac{A_4}{r^6}$$

For simple molecules hv_o is equal to ionisation energy.

Due to high dispersion energy of I_2 is solid at toom temparature but F_2 is a gas.

Total dispersion energy per pair of molecules sepoerated by a distance r given by

$$U_{attraction} = \frac{A_3}{-r^6}$$

Repulsive potential $\frac{B}{r^n}$, n usually is 12.

Total interaction energy $= \frac{A_3}{-r^6} + \frac{B}{r^n}$

Factors affecting the strength of London Forces

i) Atomic and molecular size

Atoms and molecules with large size have large surface area. Their electron clouds thus become diffused and disorted.

ii) Molecular weight

Boiling point of Octane is more than hexane. Large weight, Large surface area. London forces are stronger.

iii) Molecular shape

iv) Temparature

v) Pressure

vi) Number of electrons in atoms (inert gases) and molecules.

Lennared-Jones Potential

Proposed by Sir John Edward Lennard-Jones, the Lennard-Jones potential describes the potential energy of interaction between two non-bonding atoms or molecules based on their distance of seperation. The potential equation accounts for the difference between attractive forces (dipole-dipole, dipole-induced dipole, and London interactions) and repulsive forces.

Introduction

Imagine two rubber balls seperated by a large distance. Both objects are far enough apart that they are not interacting. The two balls can be brought closer together with minimal energy, allowing interaction. The balls can continuously be brought closer together until they are touching. At this point, it becomes difficult to further decrease the distance between the two balls. In order to bring the balls any closer together, increasing amounts of energy must be added. This is because eventually, as the balls begin to invade each other's space, they repel each other; the force of repulsion is far greater than the force of attraction.

1. Both balls are an infinite distance apart and are not interacting

2. The balls are brought closer together with minimal energy input to a certain distance, r. At this distance, the balls have on attractive force between them.

3. The attractive force between the two objects brings the objects ever further together until they reach an equillibrium distance apart at which their minimum bonding potential is reached.

4. To further decrease the distance between both objects, aditional energy is required because as the balls overlap, repulsive forces act and push both balls further apart. At these distances, the force of repulsion is greater than the force of attraction.

This scenario is similar to that which takes place in neutral atoms and molecules and is often described by **Lennard-Jones potential.**

The Lennard-Jones potential

The Lennard-Jones model of two 'parts'; a steep repulsive term, and smoother attractive term, representing the London dispersion forces. Apart from being an important model in itself, the Lennard-Jones potential frequently forms one of 'building blocks' of many force fields. It is worth mentioning that the 12-6 Lennard-Jones model is not the most faithful representation of the potential energy surface, but rather its use is widespread due to its computational expediency. The Lennard-Jones Potential is given by the following equation :

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

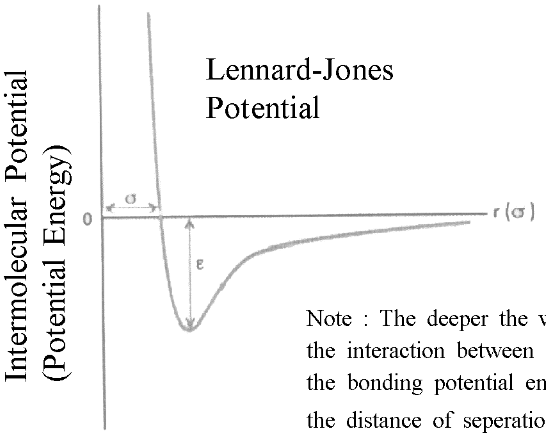
$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}}$$

Where V, is the intermolecular potential between the two atoms or molecules. is the well depth and a measure of A how strongly the two particles attract each other. σ is the distance at which the intermolecular potential between the two particles is zero (Figure 1) and σ gives a measurement of how close two nonbonding particles can get and is thus referred to as the **van der Waals** radius. It is equal to one-half of the internuclear distance between nonbonding particles.

r is the distance of seperation between both particles (measured from the center of one particle to the center of the other particle).

$A = 4,\ \sigma^{12}\ B = 4\ \sigma^{6}$

Minimum value of $\Phi 12\,(r)$ at $r = r_{\text{min}}$



Note : The deeper the well depth (e), the stronger the interaction between the two particles. When the bonding potential energy us equal to zero, the distance of seperation, will be equal to σ

Figure B
Eqyation 1

: The LJ potential describes both the attraction and repulsion between monitonic practicles. The first part of the equation, describes $(\sigma/r)^{12}$ describes the repulsive forces between particles while the latter part of the equation, $(\sigma/r)^6$ denotes attraction.

Question

The and σ values for Xenon (X_e) are found to be 1.77 kJ/mol and 4.10 angstroms, respectively. Determine the van der Waals redius for the Xenon atom.

Solution

Recall that the van der Waals radius is equal to one-half of the intermolecular distance between monbonding particles. Because σ

gives a measure of how close two non-bonding particles can be, the van der Waals radius for Xenon (Xe) is given by :

$r = \sigma/2 = 4.10$ Angstroms/2 = 2.05 Angstroms

Bonding Potential

The Lennard-Jones potential is a function of the distance between the centers of two particles. When two non-bonding particles are an infinite distance apart, the possibility of them coming together and interacting is minimal. For simplicity's sake, their bonding potential energy is considered zero. However, as the distance of seperation decreases, the probability of interaction increases. The particles come closer together until they reach a region of seperation where the two particles become bound; their bonding potential energy decreases from zero to negative quantity. While the particles are bound, the distance between their centers continue to decrease until the particles reach an equilibrium, specified by the seperation distance at which the minimum potential energy is reached.

If the two bound particles are further pressed together, past their equilibrium distance, repulsion begins to occur; the particles are so close together that their electrons are forced to occupy each other's orbitals. Repulsion occurs as each particle attempts to retain the space in their respective orbitals. Despite the repulsive force between both particles, their bonding potential energy increases rapidly as the distance of seperation decreases.

Question

Calculate the intermolecular potential between two Argon (Ar) atoms seperated by a distance of 4.0. Angstroms (use = 0.997 kJ/mol and $\sigma = 3.40$ Angstroms).

Solution

To solve for the intermolecular potential between the two Argon atoms, we use equation where V is the intermolecular potential between two non-bonding particles.

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

The data given are ε = **0.997 kJ/mol,**

σ = 3.40 Angstroms, and the distance of seperation, r = 40 Angstroms. We plug these values into equation 2.1 and solve as follows :

$$V = 4\left(0.997\frac{kJ}{mole}\right)\left[(3.40/4.0)^{12} - (3.40/4.0)^{6}\right]$$

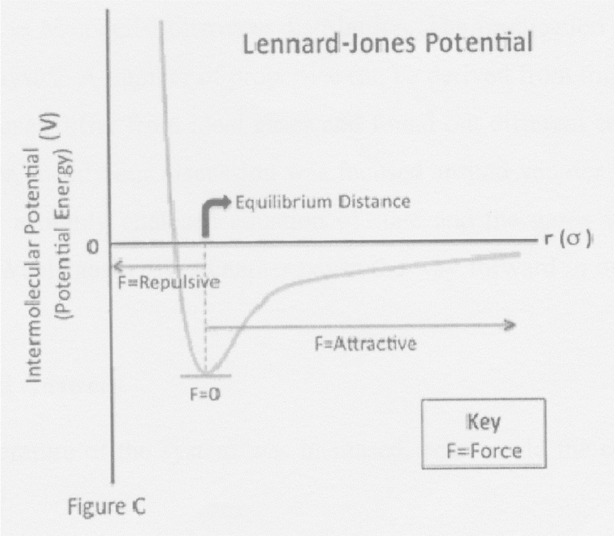
V = 3.988 (0.14-0,38)

V = 3.998 (-0.24)

V = - 0.96 kj/mol

Stability and Force of Interactions

Like the bonding potential energy, the stability of an arrangement of atoms is a function of the Lennard-Jones seperation distance. As the seperation distance decreases below equilibrium, the potential energy becomes increasingly positive (indicating a repulsive force). Such a large potential energy is energetically unfavourable, as it indicates an overlapping of atomic orbitals. However, at long seperation distances, the potential energy is negative and approaches zero as the seperation distance increases to infinity (indicating an attractive force). This indicates that at long-range distances, the pair of atoms or molecules experiences a small stabilizing force. Lastly, as the seperation between the two particles reaches a distance slightly greater than σ, the potential energy reaches a minimum value (indicating zero force). At this point, the pair of particles is most stable and will remain in that orientation until an external force is exerted upon it.



Question

Two molecules, seperated by a distance of 3.0 angstroms, are found to have a σ value of 4.10 angstroms. By decreasing the seperation distance between both molecules to 2.0 angstroms, the intermolecular potential between the molecules becomes more negative. Do these molecules follow the Lennard-Jones potential? Why or why not?

Solution

Recall that σ is the distance at which the bonding potential between two particles in zero. On a graph of the Lennard-Jones potential, then, this value gives the x-intersection of the graph. According to the Lennard-Jones petential, and value of r greater than σ should yield a negative bonding potential and any value of r smaller than σ should yield a positive bonding potential. In this scenario, as the seperation between the two molecules decreases from 3.0 angstroms to 2.0 angstroms, the bonding potential is becomes more negative. In essence however, because the starting seperation (3.0 angstroms) is already less than σ (4.0 angstroms), decreasing the seperation even further (2.0 angstroms) should result in a more positive bonding potential. Therefore, these molecules do not follow the Lennard-Jones potential.

1.19 Summary

In this unit, we learned the origin of gaseous properties from molecular motions of gas molecules. We also learned that the speed and kinetic energy of gaseous molecules follow a distribution known as Maxwell-Boltzmann distribution. The implication of this idea is huge in chemistry and physics. A number of properties can be derived from this statical concept. We saw that real gases differ from ideal gases and found out different equation of states for real gases. However, mostly our discussion was focused around van der Walls equation and its derivation. It is a highly analysed equation of state and the gases which follow it, are known as van der Waals gases. This chapter paves the way forward in our study of physical chemistry.

1.20 Questions And Answers

1. If the temparature of the system was increased, how would the collisional frequency be affected?
2. If the masses of both the reactants were increased, how would the collisional frequency be affected?
3. 0.4 moles of N_2 gas (molecular diameter $= 3.8 \times 10^{10}$ m and mass = 28g/mol) occupies a 1-liter ($0.001 m^3$) container at 1 atm of pressure and at room temparature (298K) a) alculate the number of collisions a single molecule makes in one second. (hint use Z_1) b) Calculate the binary collision frequency (hint use Z_{11})
4. What does rms velocity indicate?
5. Draw a velocity space and estimate the number of molecules in one dimension for the range of velocity v_x and $v_x + dv_x$.
6. Write down the Maxwell-Boltzmann velocity distribution function.
7. How does the Maxwell-Boltzmann velocity distribution depend on the temparature of the gas?
8. Find the dimension for A that appears in Maxwell's speed distribution $f(c) = Ac^2 e^{-mc^2}/2k_BT$

   What is the SI unit? Dimension of $A = [L^{-3} T^3]$ SI unit of A is $m^{-3}S^3$.
9. Deduce an expression for average speed of gas molecules from Maxwell's speed distribution equation.
10. At what temparature Maxwell's speed distribution plot of Cl_2 will be identical to that of N_2 at 27°C?

11. The Critical temparature of N_2 is 126 K and He is 5.3 K. Which of the gases will liquify first?

1.21 Reference

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Unit 2 ❑ Chemical Thermodynamics-I

Structure

2.1 Objectives

After completion of the study of this unit, the learner will be able to—

(i) identify the unique vocabulary associated with thermodynamics through the precise definition of basic concepts to form a sound foundation for the development of the principles of thermodynamics.

(ii) explain the basic concepts of thermodynamics such as system, state, postulate, equilibrium, process cycle etc.

(iii) recognise work and heat absorbed or released in a process.

(iv) compute the amount of work done in a thermodynamic process.

(v) distinguish between isochoric, isothermal isobaric, and adiabatic thermodynamic processes.

(vi) define and apply zeroth and first law of thermodynamics.

(vii) calculate the energy changes during chemical reactions.

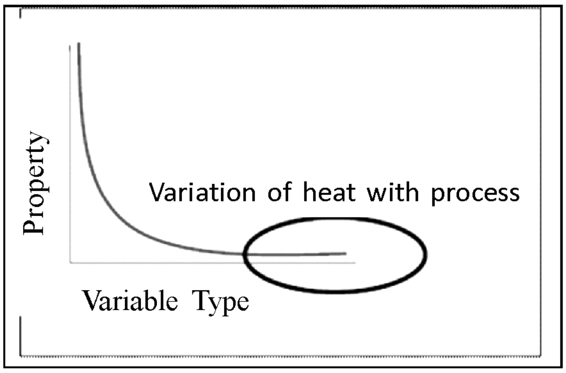
(viii) understand the concept of enthalpy for different thermodymanic processes.

2.2 Introduction

Thermodynamics is the science of the relations between heat,work and the properties of the systems due to interaction of matter and energy. In matter, energy is hidden and energy is manifested more profoundly through matter. Energy is continuous but matter is finite. To illustrate we conceive or imagine space in a room, we can identify the space at looking around the room. This can be addressed as **THERE IS SPACE IN THIS ROOM.** However it can also be perceived likewise as **THE ROOM IS IN THE SPACE.** The second statement directs our understanding towards continuity analogous to energy. If we pull down the partitions of rooms and the immediate buildings around, we will find continuous space. Energy is likewise continuous flow like space and matter is likewise the partitions whose structure holds the energy. The matter holds energy as rooms encapsulating space.

Energy changes from one form of matter to another form, either by work (order) or heat (disorder) . Thermodynamics is the branch of science that deals with **energy changes** (ΔE) accompanying all types of Physical and chemical processes/ transformations. Thermodynamics is concerned with the study of the transformations of energy and in particular the transformation of heat into work and vice versa leading to equilibrium. Somewhere natural tendency is to neutralize any differences. Albert Einstein therefore reflected, ***Thermodynamics is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown.***

A simple day to day experience of our region can be used as an illustrative example.In hot summer when temperature is around say 45°C or more, an individual whose normal body temperature say 36° C i.e. system, is often asked to take precaution otherwise the temperature difference will result in transfer of energy in the form of heat which may lead to sun stroke. The **difference** in temperature is the **cause**. The **effect** is heat transfer from surrounding to the body i.e. feeling warmer. Too much difference leads to sunstroke, so intake of water is significant. Watch the movie The Martian, **Director:** Ridley Scott. How surroundings affect the system. For system to combat surroundings it need to design otherwise system will equilibrate with surrounding.



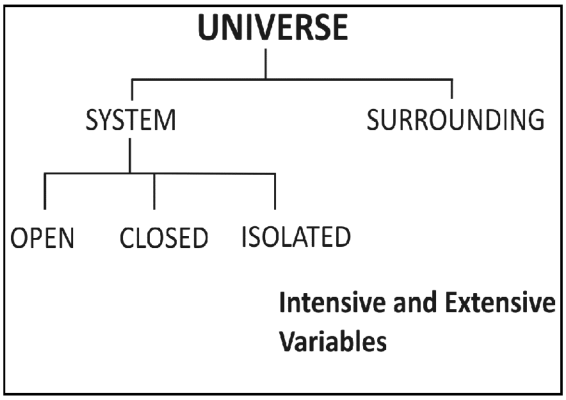
Plot of Property vs variable (time).

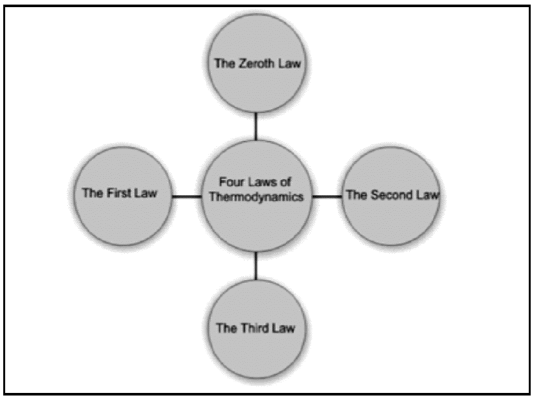
The equilibrium thermodynamics is the domain of interest. It is independent of atomic and molecular theory. Equilibrium state of a chemical system is understood by thermodynamics.

Thermodynamics, like classical Mechanics and classical Electromagnetism, is an exact mathematical science. To illustrate, water kept in kettle does not heat the water. When the kettle is heated, say by electric heater, paddling or heating on oven, the heat energy from kettle is absorbed by water getting hot. An analogy is the Area of a circle πr^2, Area = f(r). Area can be increased by increase of radius or vice versa.

The temperature of water is small if small amount of heat is transferred and more if more heat is transferred. Relationship exists between heat input and temperature. Mathematically Energy= f (T), where T is Temperature and “f” is function of “T”. Likewise Thermodynamics is the study of “physicochemical relationships” between the variables. The concept of variables will later lead us to **intensive** and **extensive** variables.

In thermodynamics attention is directed to interior of a system. A macroscopic view is employed to find macroscopic quantities which have a bearing on the internal state of a system. The function of experiment is to determine the **internal energy** of a system and temperature is the macroscopic quantity responsible for internal energy, ideal gas system. The purpose of thermodynamics is to find relation among the thermodynamic coordinates which are consistent with the fundamental laws of thermodynamics.





2.3 Extensive and Intensive variables/properties

At high temperature, water exists as steam which has different set of properties than water at normal temperature when it is liquid. At lower temperature water is obtained as ice, having different set of properties. So, the state of macroscopic system can be identified from the macroscopic properties such as T, P, V, n , their values determine the properties of the state.

The wide variety of macroscopic properties can be divided into two categories —**Extensive and Intensive properties.**

(i) Extensive property– this property depends upon the mass of the system and is additive.

(ii) Intensive Property– this property is independent of mass and has the same magnitude throughout the homogeneous system when the system is under equilibrium condition.

How can a property be characterized as intensive and extensive? To Characterize the property as intensive or extensive at ***first determine the magnitude of the property for the whole system and then determine the magnitude of the same property virtually imagining the half-portion of the system or for a portion of the system***. If the magnitudes ***are found to be the same, the property is intensive.*** Say volume of something is V, cut the volume of something into half then the magnitude alters to V/2. So volume is an extensive property.

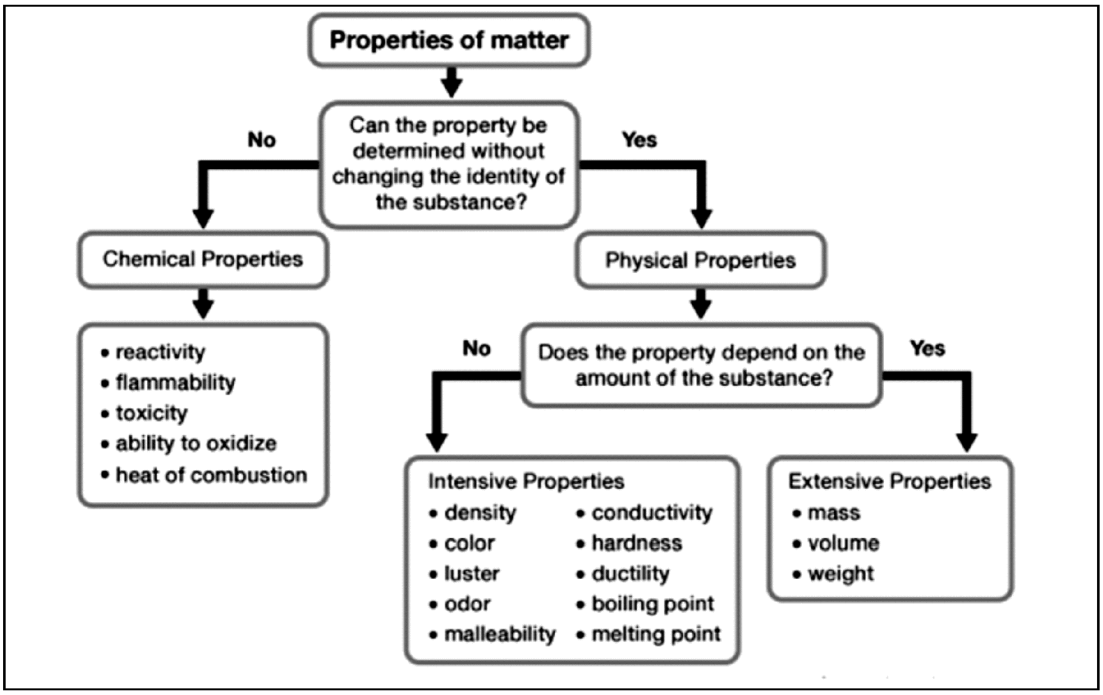
Specific molar idea when attached to heat, energy etc. the property represented are intensive.

Extensive property / Extensive property = Intensive property

Intensive property / Intensive property = Intensive property

To define the state of a pure substance values of all the intensive properties not required since all intensive properties are not independent. From P and T of a gas , ρ can be determined, $\rho = \frac{PM}{RT}$

i.e $\rho = f(P,T)$. Once ρ is known viscosity coefficient of the gas can be determined.



2.4 Definitions of thermodynamic terms

1. System

The part of the Universe which is considered for thermodynamic study is called a system.

2. Surroundings

The portion of the Universe which can interact with the system is called the surrounding.

3. Boundaries

The surfaces which separates the system from the surroundings are called the boundaries.

Two types of exchange can occur between the system and its surroundings:

a) Energy exchange (heat or work) and b) exchange of matter (movement of molecules across the boundary of the system and surroundings).

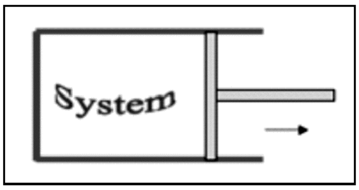
Based on the types of exchange, one can define

If the boundary does not allow heat (energy) exchange to take place it is called **adiabatic boundary** otherwise it is diathermal boundary.

Classification of different types of system

SYSTEM	Matter exchange	Energy exchange
ISOLATED [no exchange of matter and energy with surrounding]	×	×
CLOSED [no exchange of matter but some exchange of energy with surrounding]	×	√
OPEN [exchange of both matter and energy with surrounding]	√	√

We will deal with system of ideal gas, PV = nRT, in cylinder and moveable piston. [CLOSED SYSTEM]



2.5 Zeroth and first law of thermodynamics

Classical thermodynamics is that branch of science which deals with the macroscopic properties of matter. Thermodynamics is exact mathematical science that describes the relationships of heat and mechanical energy. This classical thermodynamics is based upon three general laws.

The **first law** of the conservation of energy which represents the connection between heat and mechanical work. $\mathbf{dU = dq + dw}$

The **second law** deals with the entropy change in the system and the manner in which energy change takes place divided by the absolute temperature T.

$$\mathbf{ds = \frac{dq_{rev}}{T}}$$

The **third law** deals with the absolute value of entropy. The entropy at absolute zero (0 K) is zero for any pure crystalline substance. $\mathbf{S^\circ = (0\ K) = 0}$

2.5.1 Zeroth Law of Thermodynamics

Although zeroth law of thermodynamics was formulated after first law of thermodynamics but was of primary importance and thus called Zeroth law.

This law states that—

if two systems are in thermal equilibrium with a third system then they are in thermal equilibrium with each other

i.e. if body A is in equilibrium with body C and body B is also in equilibrium with body C, then both the bodies are in equilibrium with each other. In other words if systems A and B are placed in contact with each other, then no exchange of heat will take place.

The use of **thermometer** is based on this principle. The thermometer behaves as the body C in above statement. Thus, in comparing the temperature of two systems A and B thermometer is allowed to come in equilibrium with the body A and then in equilibrium with body B by placing in contact with each other. Thus the readings of thermometer give comparative ideas of degree of hotness of the two bodies A and B. Because of small size of thermometer, an insignificant amount of energy exchange takes place during measurement of the temperature.

Change in property of fluid with degree of hotness helps in the measurement of temperature by thermometer. This property in a mercury thermometer involves change in length of the mercury column and in an air thermometer it involves change in volume (v) and pressure (P) of air enclosed within.

$$A(T_A) = C(T_C) = B(T_B)$$

$$\text{If } T_A = T_C = T_B \text{ then } T_A = T_B$$

2.5.2 First Law of Thermodynamics

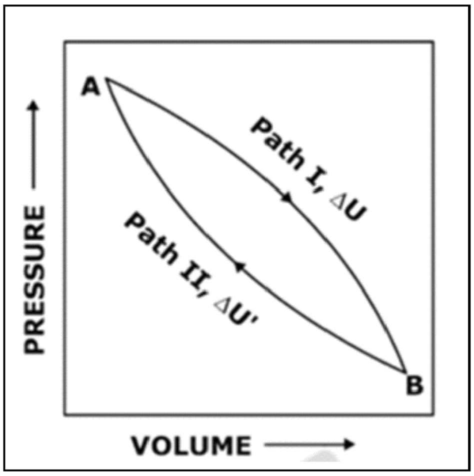
The first law of thermodynamics deals with the relation between the change in energy with work and heat. This law is also known as the law of conservation of energy. It states that energy can neither be created nor destroyed but can be transformed from one form to another. Therefore, if energy in one form disappears then equal amount of energy must appear in any other form. This law therefore states that **it is impossible to construct a perpetual motion machine i.e. machine which can produce energy without expenditure of energy**.

Internal Energy

A fundamental parameter in thermodynamics is the internal energy denoted by U. This is total amont of energy in the system , irrespective of how the energy is stored. Internal energy is sum total of kinetic and potential energy within the system. U is a state function and has a specific value at any given temperature and pressure. The value of U itself cannot be measured, however, as it involves all energy terms (potential energies associated with different internal modes of motion, electronic energy, interaction etc,) including nuclear binding energies and the mass itself. Thermodynamics considers only the macroscopic view point and hence it's change during a process depend upon the ways in which a system exchange energy with the surroundings. Internal Energy is a state function and can be represented as U = f(P,T) or U = f (V, T) or U = f (P, V) and it full fills all the criteria of a state function. It is an extensive property.

2.5.3 Internal Energy and First Law

Let us consider a system which is subjected to change of pressure and volume. Initial state can be represented by A and the final state by B (Fig. 1). U_A and U_B are respective energies associated with the system in the states A and B respectively and they are definite quantities. Then, the change in internal energy i.e. ΔU will also be definite quantity.



The change in internal energy will be given by, $\Delta U = U_B - U_A$

The change in internal energy does not depend on the path or the manner in which the change is brought about. If it is not definite quantity, it would again be possible to construct a perpetual motion machine which violates the first law of thermodynamics

For example, let the system changes from state A to state B by path I and change of energy is equal to ΔU. Now consider the same change of state which is brought by different path, say, path II, and the change of energy is $\Delta U'$. Suppose $\Delta U > \Delta U'$. Now coupling these two processes.

$A \rightarrow B$ (Path 1); $B \rightarrow A$ (Path 2)

Initial state. At this time extra energy equal to $\Delta U - \Delta U'$ would become available. Repitition of this cycle and again leads to generation of energy continuously therefore possibility of perpetual motion machine which contradicts first law. Hence $\Delta U = \Delta U'$. Thus the energy change accompanying a process is a function only of the initial and the final states of the system and does not depend on the path or the manner by which the change is brought about.

2.5.4 Energy changes in relation to work and heat changes.

Let us suppose U_A be the energy of a system in state A and U_B be the energy in state B and system is undergoing change from state A to state B. Let system absorbs heat q from the surroundings and also performs some work (mechanical or electrical) equal to w. We already know that the absorption of heat by the system raises the energy of the system while the work done by the system lowers the energy of the system as expenditure of energy is utter requirement for **performing some work**. Hence, the change of internal energy ΔU will be given by $\Delta U = U_B - U_A = q + w$.

In general, if in a given process, the quantity of heat transferred from the surroundings to the system is q and the work done in the process is w, then the change in internal energy ΔU, is given by $\Delta U = q + w$

The above equation is the mathematical statement of the First law of thermodynamics.

If work is done by the surroundings on the system (as during the compression of a gas), w is taken as positive. If however, work is done by the system on the surroundings (as during the expansion of a gas), w is taken as negative.

When the process involves infinitesimal change, then change in internal energy will be given by

$$\mathbf{dU = dq + dw}$$

dq and dw do not represent exact differentials i.e. $dq \neq q_2 - q_1$. This is due to the fact that the heat of the initial state and heat of the final state has no meaning. dq represents a small amount of heat absorbed by the system. Similarly dw is the small amount of work done on the system during the change. When only mechanical work i.e. work of expansion or compression is done then $dw = -pdV$. Therefore equation becomes $dU = dq - pdV$.

2.5.5 Work and Heat

Work in thermodynamics is defined as any quantity that flows across the boundary of a system during a change and is completely convertible into lifting of a weight in the surroundings.

Things to be noted in this definition of work are

1. Work appears only at the boundary
2. Work appears only **during** a change in state**.**
3. Work is manifested by an effect in the surroundings.
4. The quantity of work is equal to **mgh** , where m is the mass lifted, g is the acceleration due to gravity, h is the height through which the weight has been raised.
5. Work is algebraic quantity ; it is positive if the mass is lifted (h is +), in which case we say that work has been produced in the surroundings or has flowed to the surroundings: it is negative if the mass is lowered (h is -).

Heat We explain the attainment of thermal equilibrium of two systems by asserting that a quantity of heat Q has flowed from the system of higher temperature to the system of lower temperature.

In thermodynamics heat is defined as a quantity that flows across the boundary of a system during a change in its state in virtue of a difference in temperature between the system and its surroundings and flows from a point of higher to a point of lower temperature.

1. Heat appears only at the boundary of the system
2. Heat appears only during a change in state.
3. Heat is manifested by an effect in the surroundings.
4. The quantity of heat is proportional to the mass of water in the surroundings that is increased by one degree in temperature starting at a specified temperature under a specified pressure.
5. Heat is an algebraic quantity; it is positive if a mass of water in the surroundings is cooled, in which case we say that the heat has flowed from the surroundings; it is negative if a mass of water in the surroundings is warmed, in which case we say that heat has flowed to the surroundings.

WORK and HEAT flow during transformation is based on observation of effects produced in the surroundings, not upon what happens within the system.

A example to understand distinction between work and heat.

Consider a system consisting of 10g of liquid water contained in an open beaker under constant pressure of 1 atm. Initially the water is at 25°C, so that P =1 atm,T= 25°C. The system is now immersed in the 100g of water at a high temperature, 90°C. The system is kept in contact with this 100g of water until the temperature of the

100g has fallen to 89°C, whereupon the system is removed. We say that 100 units of heat has flowed from the surroundings, since the 100g of water in the surroundings dropped 1°C in temperature. The final state of the system is described by p = 1atm, T = 35°C

Now consider the same system consisting of 10g of liquid water at P = 1 atm, T= 25°C and immerse a stirring paddle driven by a falling mass. This can be adjusted in such a way that when mass m falls through height h once, the temperature of system rises to 35°C. The final state with P = 1 atm and T = 35°C. The change in state is same as in previous experiment. There was no heat flow but there was flow of work.

When we observe the system before and after the experiment, the change in state had been effected and nothing whatsoever can be said about the heat flow or work flow involved. Only conclusion that can be drawn is that the temperature of the system is higher afterward than before. This implies the energy of the system increased.

If we observe surrounding before and after, we find cooler bodies of water/or masses at lower elevations. These observations of surroundings leads in the easy deductions of the quantities heat and work.

2.5.6 State functions, exact and inexact differentials

The state function is a property of a thermodynamic system which has a definite value for a particular state of the system. It does not depend on the manner in which the state is reached. The change in the state function associated with the change in the state of the system depends only on the initial and the final states of the system and not on the path by which the change is done. Since, pressure, temperature, volume and energy depend on the initial and final states, therefore are state function While work is not a state function since the work done in a given change of state depends upon the manner in which the change is brought about. In the first law equation (ΔU, q, w) , ΔU is a definite quantity and if w is not a state function then q also is not a state function. Mathematically, we can say that while the differential of energy, dU is an *exact differential*, the differentials of heat and work, viz. dq and dw respectively, are *inexact differentials*. Exact differentials can be integrated between the appropriate limits. But this cannot be done in the case of inexact differentials. Therefore, for State Functions

$$\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P}$$

$$\frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} \text{ and } \int_{U1}^{U2} dU = U_2 - U_1 \qquad \text{Exact differential}$$

$$\text{But } \int_{w1}^{w2} dw \neq W_2 - W_1 \qquad \int_{q1}^{q2} dq \neq q_2 - q_1 \text{ Inexact differential}$$

When work done is zero and no phase transformation occurs in system then the heat transfer between the system and its surroundings results in the change in temperature of the system. This results in the change in volume and pressure of the system. The conditions can be maintained in such a way that either the volume or the pressure is kept constant. Heat exchange is also accompanied by the change in energy of the system. This change in energy will be different for the two conditions, that is when volume is kept constant and when the pressure is kept constant.

Heat Exchange at constant volume

From first law of Thermodynamics

$\Delta U = q + w$ and $dw = -PdV$

$\Delta U = q - P\Delta V$

$q = \Delta U + P\Delta V$

If volume is constant, $\Delta V = 0$ (work of expansion is zero). $P\Delta V = 0$. The heat exchanged q can be written q_v. $\Delta U = q_v$

This implies that, at constant volume, *the change in internal energy of a system becomes equal to heat exchange between the system and its surroundings.* As internal energy is a state function, therefore, heat exchange at constant volume will also be a state function.

2.5.7 The Euler Reciprocal Relation

Consider a state function z which is function of two independent variables x and y of the system i.e. $z = f(x, y)$. Since z is a state function, hence differential of z is an *exact differential*. The *exact differential*.

$$\text{Prescription } \left(\frac{\partial^2 z}{\partial y \partial x}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right) = \text{(irrespective of order)}$$

Fundamentally

$$dz = \mathbf{M(x, y)dx + N(x, y)dy} \text{ where } \mathbf{M(x, y)} = \left(\frac{\partial z}{\partial x}\right) \text{ and } \mathbf{N(x, y)} = \left(\frac{\partial z}{\partial y}\right)$$

Taking mixed second derivatives, we have

$$\left(\frac{\partial M}{\partial y}\right)=\left(\frac{\partial^2 z}{\partial y \partial x}\right) \text{ and } \left(\frac{\partial N}{\partial x}\right)=\left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

Since $\frac{\partial^2 z}{\partial y \partial x}=\frac{\partial^2 z}{\partial x \partial y}$

$\left(\frac{\partial M}{\partial y}\right)_x=\left(\frac{\partial N}{\partial x}\right)_y$ **the equation is called Euler reciprocal**

Since z is a state function, then finite change, "z when the system passes from intial state A to final state B is given by $\Delta z = z_2 - z_1$. Also $\oint dz = 0$ where cyclic integral means that the system is in the same state at the end of its path as it was in the beginning, i.e. it has traversed a closed path. Thus dz is an exact differential.

Problem

For Volume, **V, an exact differential**

$\frac{\partial^2 V}{\partial P \partial T}=\frac{\partial^2 V}{\partial T \partial P}=-\left(\frac{R}{P^2}\right)$ **(for an ideal gas)**

For work, **–pdV, not an exact differential**

$$dV = -\left(\frac{RT}{p^2}\right)dp+\left(\frac{R}{P}\right)dt$$

$$-pdV = -\left(\frac{RT}{p}\right)dp+(-R)dT$$

$$\left(\frac{\partial M}{\partial y}\right)_x=\frac{R}{P} \text{ but } \left(\frac{\partial N}{\partial x}\right)_Y=0$$

2.6 Enthalpy

When fuel burns in a cylinder with a piston , the fuel produces carbon dioxide and water vapour, which occupy more space than the original fuel and oxygen, and as a result the piston is driven out to accommodate the products. This expansion requires work. That is, when a fuel burns in a container that is free to expand, some of the energy is released in the combustion is used to do work. If the combustion is carried out in a container with rigid walls, the combustion releases the same amount of energy, but none of it is used to do work because no expansion can occur. More energy is available as heat at constant volume than at constant pressure process. To calculate the heat produced in the former case (constant pressure), we have to account for the energy that is used to make room for the carbon di oxide and water vapour and substract that from the total energy changes in energy. This is true even when there is no physical piston-reactions in test tube happen at constant pressure-the gaseous products makes room for themselves.

2.6.1 Mathematical Expression for Enthalpy

For finding an expression for enthalpy let us suppose that at constant P, when state of the system changes then the volume of system changes. Suppose the volume increases from V_A to V_B , at constant pressure P. Then, the work done (w) by the system will be $w = -P(V_B - V_A)$

Substituting $\Delta U = q + w$

$\Delta U = q - P(V_B - V_A)$

$U_B - U_A = q - P(V_B - V_A)$

In Joule Thompson Experiment where adiabatically irreversible expansion process of real gas through fine orifices takes place, $q = 0$. The above equation simplifies to

$U_B + PV_B = U_A + PV_A$.

$U_B \neq U_A$; $V_B \neq V_A$.

The quantity U + PV = H (Enthalpy) of the system. H is the Total Energy stored in the system. Since U, P and V are state functions then U + PV must also be a state function. As U and PV have dimensions of energy, then H must also have dimensions of energy. The change in enthalpy is given by dH.

The analogy for Enthalpy can be thought as a purse containing money within it. Money in the purse is used to purchase. If we lose the purse we lose money and the purse. The money is internal energy and the purse also has a price but in terms of space is the enthalpy.

$dH = d(U + PV)$

First law of Thermodynamics $dq = dU + PdV$

$dH = dU + PdV + VdP$

$dH = dq + VdP$

2.6.2. Heat exchange at constant pressure

When the pressure of the system is constant, then the change in pressure will be zero i.e. $dP = 0$

Therefore, $VdP = 0$ and $dq = dq_p$

First law gives

$$(q)_P = \Delta U + P\Delta V$$
$$= (U_2 - U_1) + P(V_2 - V_1)$$
$$= (U_2 + PV_2) - (U_1 + PV_1)$$

$H = E + PV$

$dH = dq + VdP$ if $dP = 0$ then $dH = (dq)_P$

Heat absorbed in a process at constant pressure is equal to change in enthalpy if only work done is pressure – volume work

When the change is finite, then $\Delta H = q_P$

$\Delta H = H_B - H_A$

Therefore, at constant pressure of the system, the *heat exchange* becomes equal to the change in enthalpy of the system. Whenever the system exchanges heat at constant pressure temperature of the system changes.

$(U_B - U_A) + P(V_B - V_A) = q_P$

Incorporating the above value of q in $\Delta H = q_p$ we get

$\Delta H = (U_B - U_A) + P(V_B - V_A)$ or $\Delta H = \Delta U + P\Delta V$ where ΔV is the increase in volume of the system

So, some part of heat i.e. q_P will be used to increase the internal energy and rest is used up for the change in volume. Hence, change in enthalpy results in change in internal energy as well as change in volume of the system. For solids and liquids the volume change is negligible, therefore, enthalpy and internal energy changes are practically same for them.

2.6.3. Relationship between ΔH and ΔU for an ideal gas

We know $H = U + PV$

$\Delta H = \Delta U + P\Delta V$

For an ideal gas, $PV = nRT$

$\Delta H = \Delta U + \Delta(nRT) = \Delta U + (\Delta n)RT$

Here, Δn is the change in the amount of the gas. If the temperature changes but the amount of gas is constant, then $\Delta H = \Delta U + nR\Delta T$

2.6.4. Characteristics of enthalpy

(i) When the system is kept at constant pressure, then the enthalpy change becomes equal to the *heat exchange* by the system.

(ii) It is a state function

(iii) The expression of enthalpy is $H = U + PV$

(iv) For solids and liquids, the enthalpy change (ΔH) is taken as equal to the change in the internal energy (ΔU).

(v) The unit of enthalpy is same as that of unit of energy.

(vi) When the system absorbs heat at a constant pressure, ΔH is positive and the process is known as an **endothermic process**.

(vii) When the system loses heat to the surroundings at a constant pressure, ΔH is negative and the process is known as an **exothermic process**.

2.6.5. Enthalpy of vaporization

The change in enthalpy (ΔH) when 1 mole of liquid changes into vapour phase at a given temperature and pressure per mole of the liquid is known as enthalpy of vaporization. This enthalpy has positive sign when liquid changes into vapor and negative sign when vapor changes into liquid. Thus, we can say that during evaporation, heat is absorbed, hence increase in enthalpy takes place. Similarly during condensation, heat is evolved hence decrease in enthalpy takes place.

$H_2O(l) \rightarrow H_2O\ (g)\ \Delta H^\circ\ (298\ K) = 44.0\ kJ$

2.6.6. Enthalpy of Fusion

The change in enthalpy when 1 mole of solid state changes into liquid state or liquid state freezes to solid state is known as enthalpy of fusion. In the first case, enthalpy of the system increases. In the other case, the enthalpy of the system decreases.

The enthalpy of fusion for 1 mole of water at $0^\circ C$ is 6.02 kJ. We may express this result in the following way :

$H_2O\ (s) \rightarrow\ H_2O\ (l) \qquad \Delta H_{fus} = 6.02\ kJ\ mol^{-1}$

$H_2O\ (l) \rightarrow\ H_2O\ (s) \qquad \Delta H = -6.02\ kJ\ mol^{-1}$

The heat of fusion of water is 6 kJ mol^{-1} $\Delta H\ (273K) = 6.0\ kJ$

2.7 Heat Capacity

Heat capacity of the system is defined as amount of heat required to raise the temperature of the system by 1°C.

$$C = \frac{dq}{dT}$$

So, SI unit is J K^{-1}

Heat capacity at constant volume $C_v = \left(\frac{dq}{dT}\right)_v = \frac{dq_v}{dT} = \left(\frac{dU}{dT}\right)_v$

Heat capacity at constant pressure $C_P = \left(\frac{dq}{dT}\right)_P = \frac{dq_P}{dT} = \left(\frac{dH}{dT}\right)_P$

If the amount of substrate is 1g then it is called the specific heat capacity.

2.7.1. Specific Heat Capacity

It is defined as the heat needed to cause a unit rise in the temperature of a unit mass of a substance. It is denoted by s. It SI units of J K^{-1} kg^{-1}.

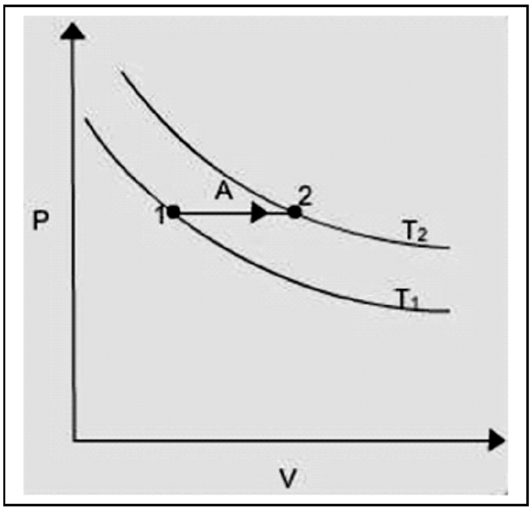
2.7.2. Molar Heat Capacity

It is defined as the heat needed to cause a unit rise in the temperature of one mole of a substance. It is denoted as $C_{m.}$ Thus, molar heat capacity of the system between temperature T_1 and T_2 will be expressed as $C = \frac{q}{T_2 - T_1}$

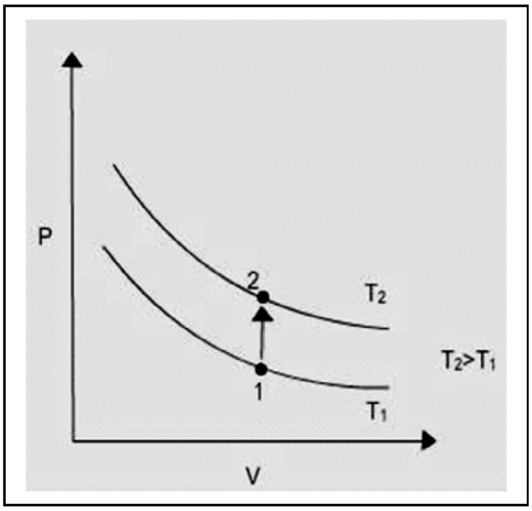
Since the heat capacity is function of temperature, hence the true molar heat capacity is defined by the differential equation

2.7.3. Relation between Cp and Cv

When a gas is heated without making change in its volume then no internal work is done by the gas. Therefore, all the heat which is supplied to the gas is used in increasing internal energy. Thus if there is rise in temperature of one of mole of gas by 1°C, the increase in its internal energy itself gives the molar heat capacity at constant volume. However when heating of gas is done under constant pressure conditions there will be increase in the volume of the gas that is the gas will expand and do some external work. Therefore, some extra heat must be supplied so that gas can perform this external work. Hence, molar heat capacity of gas at constant pressure must be greater than that at constant volume, i.e. $C_P > C_V$. The difference between these two quantities gives the work done by one mole of the gas in expansion when heated through 1°C at constant pressure. Thus, $C_P - C_V$ = work done by one mole of the gas in expansion when heated through 1C° at constant pressure.



$Q_P = \Delta H$, Isobaric path



$Q_V = \Delta U$, Isochoric Process

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

H = U + PV

$$\text{Or, } C_P - C_V = \left(\frac{\partial (U+PV)}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$\text{Or, } C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$U = f(T,V) \text{ so, } dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Differentiating w.r.t T at constant P

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Using the above equation in $C_P - C_V$

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

This expression is not very useful as $\left(\frac{\partial U}{\partial V}\right)_T$ is not measurable quantity.

The absorbed heat is utilized in two portions

(i) Absorbed heat is utilized to perform mechanical work of expansion for per degree rise in temperature, the magnitude is $P\left(\frac{\partial V}{\partial T}\right)_P$. This portion is transferred to surrounding in the form of mechanical work.

(ii) the term $\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$ is the amount of energy used up to increase the internal energy due to increase in volume per degree rise in temperature.

(iii) The other portion of supplied heat is utilized to increase the kinetic energy associated with different modes of molecular motion and hence increase kinetic energy. At constant volume the (i) mechanical work and (ii) internal work to increase intermolecular separation do not happen. The total heat is utilized to increase the temperature.

$C_P - C_V$ for different gases

(i) when system is ideal gas

The intermolecular force of attraction is absent for ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = P \times \left(\frac{nR}{P}\right) = nR$$

$$C_{P,m} - C_{V,m} = R$$

(ii) when system is defined by equation P(V – b) = RT

The correction term for attractive force is not included in the equation.

$$\left(\frac{\partial V}{\partial T}\right)_T = 0$$

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = P \times \left(\frac{nR}{P}\right) = nR$$

$$C_{P,m} - C_{V,m} = R$$

(iii) when the system is van der Waals gas in cylinder with piston,

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$, for van der Waals gas

$\left(\frac{\partial V}{\partial T}\right)_P$ for van der Waals gas need to be calculated

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

Or, $PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$ Neglecting the small term, $\frac{ab}{V^2}$

Or, $PV - Pb + \frac{a}{V} = RT$

Differentiating w.r.t T at constant P

$$P\left(\frac{\partial V}{\partial T}\right)_P - 0 - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P = R \text{ OR, } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2}}$$

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \text{ OR } C_P - C_V = \left(P + \frac{a}{V^2}\right)\frac{R}{P - \frac{a}{V^2}}$$

Mathematical tricks

$$C_P - C_V = \left(P+\frac{a}{V^2}\right)\frac{R}{P+\frac{a}{V^2}-\frac{2a}{V^2}}$$

$$\text{Or, } C_P - C_V = \left(P+\frac{a}{V^2}\right)\frac{R}{\frac{RT}{V-b}-\frac{2a}{V^2}}$$

$$\text{Or, } C_P - C_V = \left(P+\frac{a}{V^2}\right)\frac{R}{\frac{RT}{V-b}\left[1-\frac{2a}{V^2}\frac{(V-b)}{RT}\right]}$$

$$\text{Or, } C_P - C_V = \frac{\left(P+\frac{a}{V^2}\right)(V-b)}{RT}.R.\left[1-\frac{2a(V-b)}{RTV^2}\right]^{-1} = \frac{RT}{RT}.R.\left[1-\frac{2a(V-b)}{RTV^2}\right]^{-1}$$

Or, $= R[1+\frac{2a(V-b)}{RTV^2}]$ neglecting the higher terms

At ordinary pressure $(V- b) = V$ as $V >> b$

$C_P - C_V = R[1+\frac{2aV}{RTV^2}] = R+\frac{2a}{TV}$, if V is replaced by ideal gas equation as an approximation

$C_P - C_V = R + \frac{2aP}{RT^2}$, thus $(C_P - C_V) > R$ for van der Waals gas

(iv) In case of solids and liquids

Here, $\left(\frac{\partial V}{\partial T}\right)_P$ is positive but negligible, $\left(\frac{\partial U}{\partial V}\right)_T$ is also positive, C_P is slightly greater than C_V. For practical purpose $C_P = C_V$ for condensed phase.

(v) in case of water

$C_P - C_V$ for water at 4°C

The liquid water attains minimum molar volume at 4°C. So V =minimum at 4°C.

$$\left(\frac{\partial V}{\partial T}\right)_P = 0 \text{ at } 4^\circ C$$

So, $C_P - C_V = 0$

$C_P = C_V$

2.7.4. Generalised form of $C_P - C_V$

We have obtained the relation

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

Thermodynamic equation of state

$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$ [U, H are energy term equivalent PV, check dimension on LHS $\frac{PV}{V}$]

$$C_P - C_V = [P + \{-P + T\left(\frac{\partial P}{\partial T}\right)_V\}]\left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

2.7.5. $C_P - C_V$ in terms of α and β

α = thermal expansion coefficient = $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

β = co-efficient of compressibility = $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\frac{\alpha}{\beta} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T$$

Cyclic rule

For z = f (x,y)The relation is $\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1$

V = f(T,P)
cyclic rule

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T = -1 \qquad \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}$$

$\frac{\alpha}{\beta} = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V} = \left(\frac{\partial P}{\partial T}\right)_V$ and again $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \frac{\alpha^2 TV}{\beta}$$

Expression for $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for ideal gas and $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

Thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

For n moles gas, $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

Or, P = $\frac{nRT}{V - nb} - \frac{an^2}{V^2}$ or, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V - nb}$

Or, $\left(\frac{\partial U}{\partial V}\right)_T = -P + T\frac{nR}{V - nb}$

Or, $\left(\frac{\partial U}{\partial V}\right)_T = -P + \left(P + \frac{an^2}{V^2}\right) = \frac{an^2}{V^2}$ The value decreases with increase of volume.

Isothermal expansion of van der Waals gas leads to increase of U.

Q. A van der Waals gas expands isothermally and reversibly from a volume of 1 litre to 10 litre. Derive all necessary expressions to calculate the internal energychange of the gas in calories. (a = 1.4 atm lit^2 mol^{-2})

Use : $\left(\frac{\partial U}{\partial V}\right)_T = \frac{an^2}{V^2}$ and integrate to $\Delta U = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

2.8 Different type of processes

(i) Cyclic Process—After series of changes the system comes back to its initial state. All the variables take its initial value.

(ii) Isothermal Process—Temperature (T) remains constant during this process. Heat- exchange continues. Walls of the system must be perfectly conducting thermally.

(iii) Adiabatic Process—Heat exchange is not allowed with the surroundings during the process, Temperature varies.

(iv) Isobaric Process—Pressure (P) remains constant, thus volume will vary. Reactions in test-tube, atmospheric pressure is 1 atm.

(v) Isochoric Process—Volume (V) remains constant, thus volume will vary. Pressure P changes.

(vi) Polytropic process—Heat capacity remains fixed.

2.9 Isothermal and Adiabatic Expansion

An isothermal process is one which takes place at constant temperature. During expansion against external pressure, a system gets cooled, but in order for the temperature of the system may remain constant, there must be perfect thermal communication between the system to and the surroundings and heat must enter the system from the surroundings. Similarly during isothermal compression, heat should leave the system. The wall or boundary of the system that allows this kind of transference of heat is called a diathermic wall.

An adiabatic process is one that takes place without any heat transfer between the system and the surroundings. The boundary of the system in this case is called an adiabatic wall.

2.9.1. Path

It is the sequence of one step, **two step, ten, hundred** like wise may be thousand or more finite intermediate steps or stages arranged in order to follow the system from its initial to final state is. Generally this is known as irreversible path.

When **infinite steps** (sky is th limit) are considered for the change a condition gets satisfied, driving force and opposing force differ by infinitesimal amount and final state of the system can be reversed without the aid of external agency. This is known as reversible path. The amount of work obtained from reversible isothermal expansion process is always greater than irreversible process.

Illustration

Say in a classroom there happens to be a change in the arrangement of the Chair of class teacher. This change automatically inspire a few queries who and How? How can happen via a single step, may happen by two or more. For each path the value of work will be different. So, irreversible path will have many values as per number of steps involved.

2.9.2. Work done – Reversible and Irreversible processes

1. The process of transition of a system from one state to another is said to be thermodynamically reversible, if the system and the surroundings can be restored to the initial state by traversing the forward sequence of steps in the reverse order.
2. In a reversible process, the system is every time in internal equilibrium i.e., all the intermediate states can be thermodynamic variable like temperature and pressure. Also at every step, the system is in virtual equilibrium with the surroundings, because by effecting change in the opposing force over the driving force in the proper direction, the process can be reversed.
3. Since in a thermodynamically reversible process, the opposing force differs from the driving force by an infinitesimal amount, any finite process takes infinite time to go to completion i.e. the process is extremely slow (in a reversible expansion of a gas, for eg. the pressure of the gas is the driving force and the external pressure, which is smaller by an infinitesimal amount, is the opposing force).
4. Thermodynamic reversibility is a hypothetical condition and it is seldom realized in practice. But the concept is useful, since it sets the limit to quantities that may be measured in practice.

2.9.3. Magnitude of w is Path Function

Work is one way by which energy can enter or leave the system. It has direction and order so can be measured $w = \int_{\text{initial path}}^{\text{final}} -P_{opp}dV$

Nature of Work	Expression of work	Intensive Variable	Extensive Variable
Mechanical Work	$-P\ dV$	P	V
Electrical Work	$-E\ dZ$	E	Z
Extension of surface film	$-\gamma\ d\sigma$	γ	σ

Mechanical Work Turbulent motion of water → Temperature rise of water
Electric Current → Temperature rise of water
Compression of gas → Temperature rise of water
Friction of iron blocks → Temperature rise of water.

IUPAC Convention

$W > 0$, if work done on system
$W < 0$, if work done by system
$Q > 0$, for heat addition to system
$Q < 0$, for heat removal from system

Comparison of q, w, ΔU and ΔH for different Types of Isothermal Processes

Process	Expansion	Compression	Cyclic
Reversible q, (–w)	$nRT\ln\frac{V_2}{V_1}$	$nRT\ln\frac{V_1}{V_2}$	0
ΔU, ΔH	0	0	0
Free q, (–w)	0	$P_{opp}(V_1-V_2)$	$P_{opp}(V_1-V_2)<0$
ΔU, ΔH	0	0	0
Intermediate q,(–w)	$0<P_{opp}(V_2-V_1)$	$P_{opp}(V_1-V_2)$	$(P_{opp}-P_{opp})(V_2-V_1)<0$
	$<nRT\ln\frac{V_2}{V_1}$	$<nRT\ln\frac{V_1}{V_2}$	
ΔU, ΔH	0	0	0

Note : Here, V_1 is the initial volume and V_2 is the final volume of the system. The work involved during expansion is negative as V_1 is less than V_2. This negative work means that the work is done by the system on the surroundings.

A note for solving problems:

1. The formula for **irreversible** expansion work $w = -P_{opp} \times dV$
2. The formula for **reversible** isothermal expansion work for a gas $w = -nRT\ln\frac{V_2}{V_1}$
3. The mathematical form of the first law, $dU = q + w$, for expansion process, $q = dU + P_{opp}dV$
4. The definition of Enthalpy $H = U + PV$
5. The definition of molar heat capacity $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ and $C_V = \left(\frac{\partial U}{\partial T}\right)_V$
6. The change in internal energy and enthalpy of a system

   a) $dU = nC_vdT + \left(\frac{\partial U}{\partial V}\right)_T dT$ (b) $dH = nC_PdT + \left(\frac{\partial H}{\partial P}\right)_T dP$

Problem

One mole of steam is compressed reversibly to liquid water at its boiling point. The heat of vaporization of water at 100°C and 1 atm pressure is $2258.1Jg^{-1}.^{\circ}C^{-1}$ Calculate each of the thermodynamic properties (i) q, (ii) w (iii) ΔU (iv) ΔH

(i) q, heat of condensation per mole $= -18 \times 2258.1Jg^{-1} = -40.646kJmol^{-1}$

(ii) $w = P(V_l - V_g) = -PV_g = -RT = -8.31 \times 373Jmol^{-1} = -3.100kJmol^{-1}$

(iii) $\Delta U = q - w = (-40.646 + 3.100)kJ\ mol^{-1} = -37.546\ kJ\ mol^{-1}$

(iv) $\Delta H = q_P = -40.646\ kJ\ mol^{-1}$

Problem

One mole of Helium gas at 300K and 10 atm expands to 1 atm. Assuming the gas as ideal, Calculate w, q, ΔU, ΔH for (a) reversible and isothermal (b) irreversible and isothermal

(c) reversible and adiabatic (d) irreversible and adiabatic [Given, $C_v = 1.5R$]

Solution

First law, $\Delta U = q + w$ {IUPAC convention w is done on the system]

$W = \int_{\text{initial.path}}^{\text{final}} -P_{\text{opp}}dV$ and the reversible work is maximum work, it's the limit given in (a)

(a) $w_{\text{rev,iso}} = -nRT \ \ln\frac{P_1}{P_2}$ Put n = 1mol, R = 8·314 $JK^{-1}mol^{-1}$, T = 300K, P_1 = 10 atm, P_2 = 1 atm.

W = –5740J

$\Delta U = n\,C_v dT$ (T constant, isothermal process, dT = 0)= 0 and $\Delta H = nC_P dT = 0$

Here, work is done by system i.e. expansion, IUPAC convention, (–ve). First law

$\Delta U = q - 5740J$ or q = 5740 J

or, $q = \Delta U + w$ [IUPAC here w is –ve accomodated] or q = 0 + 5740 J

q = 5740 J

(b) $w_{\text{irrev.iso}} = -P_{\text{opp}}\int_{i,\text{irrev}}^{f} dV = -P_2(V_2 - V_1)$ using $V = \frac{nRT}{P}$

$$w_{\text{irrev.iso}} = -nRT(1-\frac{P_2}{P_1}) = -2244J$$

(c) $T_2 = T_1 \times \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ $\{\gamma = \frac{C_P}{C_V} = \frac{2.5R}{1.5R} = \frac{5}{3}$

T_2 = 119.4 K

First law, $\Delta U = q + w$ {IUPAC convention w is done on the system] ; Adiabatic Process q = 0

$W_{\text{rev, adiabatic}} = \Delta U = nC_V(T_f - T_i) = nC_V(T_2 - T_1) = -2251$ J

$\Delta H = nC_P(T_2 - T_1) = -3752$ J

$V_1 = \frac{nRT}{P_1}$ = 2.46 lit [T = 300K]

$V_2 \ \frac{nRT}{P_2}$ = 9.8 lit [T = 119.4K]

(d) $\Delta U = -\int P_{opp} dV = -P_{opp}(V_2 - V_1)$ Need to find T_2'

$$nC_V(T_2' - T_1) = -P_{opp}(V_2 - V_1) = -P_{opp}\left(\frac{nRT_2'}{P_2} - \frac{nRT_1}{P_1}\right) \quad [P_{opp} = P_2]$$

$$\text{or, } 1.5\ R(300K - T_2') = R\left(T_2' - 300K \times \left(\frac{1atm}{10atm}\right)\right.$$

or $T_2' = 192$ K

$W_{irrev,\ adiabatic} = \Delta U = nC_V(T_f - T_i) = nC_V[T_2'\ ;\ 192K) - T_1;\ 300K] = -1447$ J

$\Delta H = nC_P(T_2' - T_1) = -2245$ J

Process	w(J)	q (J)	ΔU (J)	ΔH (J)	T_2 (K)	V_2 lit
Isothrmal						
(a) rev	–5740	5740	0	0	300	24.6
(b) irrev	–2244	2244	0	0	300	–
Adiabatic						
(a) rev	–2251	2251	–225–	–3752	119.4	9.8
(b) irrev	–1447	1447	–1447	–2245	192.0	–

Inference

(1) Work done in reversible process W_{rev} is greater than W_{irrev}, that is in irreversible process.

(2) Work done in reversible isothermal process is greater than that in reversible adiabatic process.

(3) High Final Temperature in irreversible adiabatic expansion than in reversible adiabatic expansion (T_2)

(4) Final volume in reversible isothermal process V_2 is greater than in reversible adiabatic process (V_2') for the same change of pressure.

Adiabatic curve is steeper than isothermal curve.

Comparison of slopes of P–V adiabat and P–V isotherm in case of an ideal gas

During isothermal change, P and V related as PV = RT = K (constant)

$$\therefore \left(\frac{dP}{dV}\right)_{iso} = -\frac{k}{V^2} = -\frac{P}{V}$$

For adiabatic change, $PV^{\gamma} = k$ (constant)

$P = KV^{-\gamma}$

$$\therefore \left(\frac{dP}{dV}\right)_{adia} = -\gamma.K..V^{-\gamma-1}$$

$$= -\gamma.\frac{P}{V} (\gamma \text{ is always greater than } 1)$$

Hence the adiabatic process involving Pressure Volume changes is steeper or rapid than the isothermal process.

Question : One mole of an ideal gas expands reversibly from a volume V_1 to V_2 obeying the relation PV^{γ} = constant. If T_1 = 300K & T_2 = 200K, Calculate w.

Given $C_V = \frac{5R}{2}$. Calculate Q, ΔU, ΔH.

Adiabatic process hence q = 0, ΔU = –500 cal, ΔH = –700 cal.

Question : An ideal gas undergoes a reversible polytropic expansion according to the relation $PV^n = c$, c and n are constants, n > 1.

Calculate W for such an expansion if one mole of the gas expands from a volume V_1 to V_2 and if T_1 = 300K & T_2 = 200K, n = 2.

$$\text{Solution : } |W| = \int_1^2 PdV = c\int_1^2 \frac{dV}{V^n} = c\left[\frac{V^{-n+1}}{-n+1}\right]_{V_1}^{V_2} = \frac{c}{-n+1}(V_2^{-n+1} - V_1^{-n+1})$$

Replace $c = PV^n$

$$= -\frac{1}{n-1}(P_2V_2 - P_1V_1) = \frac{1}{n-1}(P_1V_1 - P_2V_2) = \frac{1}{n-1}(RT_1 - RT_2) = \frac{R}{n-1}(T_1 - T_2)$$

$$W = \frac{2}{2-1}(300 - 200)\text{cal} = 200\text{ cal}$$

Problem

For a constant pressure process $\Delta H = q_P$. Justify or criticize q_p is not a state function.

Ans. q_p is not a state function, $q_P = \Delta H = H_2 - H_1$.

H_2 is a function of the final state and H_1 is a functrion of the initial state, $H_2 - H_1$ is neither the function of the final state nor the function of the initial state. Thus q_P is not a state function.

2.10 Joule's experiment and its consequence

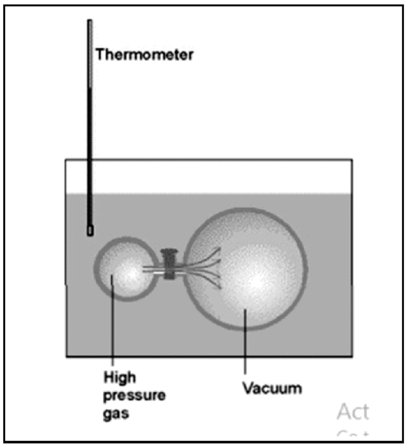
Heat, temperature and energy belong to different scales, such as the motion of microscopic particles and the thermal state of a certain body. When the gas expands the molecules are slowed since they overcome attraction. Kinetic energy gets converted into potential energy, very similar to two magnets when they are separated attraction is reduced and the same is stored as potential energy in the magnet. Allowing molecule to be apart from each other, cools the gas which results by increasing volume without allowing any heat to enter from outside.

A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally (gas expands into a vacuum). The heat absorbed by the gas is proportional to the change in temperature of the bath.

Before expansion, the entire gas is present in the small vessel. Opening the stop cock, the gas freely expands against a zero pressure. Work involved in free expansion

dw = 0. Now dU = dq + dw,

we have dU = dq



Since there is no change in temperature of the bath, the amount of heat involved, dq, is also zero.

We know U = f (T,V)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Since dT = 0 and dU = 0, $\left(\frac{\partial U}{\partial V}\right)_T$ dV = 0; dV ≠ 0

$\left(\frac{\partial U}{\partial V}\right)_T = 0$ known as Joule's law

Energy of the gas is function of Temperature only.

Joule Coefficient, $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U$

The results of Joule experiment involving any gas (real or ideal) can be expressed in terms of μ_J

- The Joule coefficient in terms of μ_J.
- The Joule coefficient μ_J can be expressed in terms of the equation of state of the gas

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\mu_J = -\frac{1}{C_V}\{T\left(\frac{\partial P}{\partial T}\right)_V - P\}$$

- Joule Coefficient for **ideal gas** is 0 (zero)
- μ_J depends on the relative magnitudes of P and $-\left(\frac{\partial P}{\partial T}\right)_V$ for **Real gas**

(i) $P > T\left(\frac{\partial P}{\partial T}\right)_V$ Then μ_J is positive dV is always positive in Joule experiment,

$\left(\frac{\partial T}{\partial V}\right)_U \cdot (dT)_U$ is positive, there is increase in temperature

(ii) $P < T\left(\frac{\partial P}{\partial T}\right)_V$ Then μ_J is negative (–ve).. Hence $(\partial T)_U$ is negative, that is,

there occurs a decrease in temperature of the gas. Here $\left(\frac{\partial U}{\partial V}\right)_T = +ve.$

Note. $\left(\frac{\partial U}{\partial V}\right)_T = -\text{ve}$ at very high pressures and is positive at ordinary pressures may be explained on the basis that the energy U consists of two types of energies, kinetic and potential energy. When the volume is increased at constant temperature, the kinetic energy remains constant but potential energy varies.

At ordinary pressures where the attractive molecular forces predominate, the potential energy increases on expansion and hence $\left(\frac{\partial U}{\partial V}\right)_T = +\text{ve}$.

At very high pressures where the excluded volume plays the dominating role, the potential energy decreases on expansion and hence $\left(\frac{\partial U}{\partial V}\right)_T = -\text{ve}$

2.11 Calorimetry and Thermochemistry— Heats of Reaction i.e. Enthalpy changes in Physical and Chemical Processes

1. An exothermic reaction is one in which heat is evolved. Here the energy content of the products is less than that of the reactants. For a reaction occurring at constant pressure, ΔH for an exothermic reaction is negative.

$N_2 + 3H_2 \rightarrow 2NH_3 + \text{heat}$.

2. An endothermic reaction is one in which heat is absorbed. The energy content of the product is more than that of the reactants. ΔH is positive

$PCl_5 + \text{heat} \rightarrow PCl_3 + Cl_2$.

3. Taking ΔE and ΔH as the energy change for a reaction at constant volume and pressure respectively, the relation between these two (called "heats" of reaction) is

$\Delta H = \Delta E + P.\,\Delta V = \Delta E + \Delta n.RT$, where Δn = no. of moles of gaseous products minus the no. of moles of gaseous reactants appearing in that stoichiometric equation representing the reaction.

4. Heat or Δ enthalpy of formation (ΔH_f)

The enthalpy of formation of a compound is the enthalpy change accompanying the formation of one mole of the compound from the elements. If the compound and its elements are in the standard state, the heat of the above reaction is referred to as standard enthalpy of formation (ΔH°_f). Eg. Formation of sucrose

$$12C(s)+11H_2(g)+\frac{11}{2}O_2(g)\rightarrow lC_{12}H_{22}O_{11}(s)+\text{heat}$$

The enthalpy change for this reaction is the enthalpy of formation of sucrose. For H_2 and O_2 the gaseous state with a pressure of 1 atm (gases being assumed to be ideal) is the standard state. For carbon, graphite is taken as the standard state. It should be noted that the above reaction is a hypothetical one and does not actually take place.

5. **Enthalpy of combustion** is the enthalpy change accompanying the complete combustion of 1 mole of the substance. e.g. Combustion of benzoic acid

$$C_6H_5COOH\,(s)+\frac{15}{2}O_2(g)\rightarrow 7\,CO_2(g)+3\,H_2O(l)+\text{heat}$$

ΔH for this reaction is the enthalpy of combustion of benzoic acid.

6. **Enthalpy of phase change** (fusion of vaporization or sublimation or transition from one allotropic state to another) is the enthalpy change accompanying the required phase transition of 1mole of the substance at a fixed temperature. Under this head, we have enthalpies of fusion, vaporization, sublimation and allotropic transition.

7. **Enthalpy of neutralization** is the enthalpy change accompanying the neutralization of one gram equivalent of an acid by one gram equivalent of a base, both in dilute solution. The enthalpy of neutralization of a strong acid (HCl, H_2SO_4, HNO_3) by a strong base (NaOH, KOH, etc.) is a constant, whatever be the acid or the base and it is –13.7kCals or –57.5kJ. This constancy is ascribed to the complete ionization of the strong acid and base and also the salt, the overall reaction being the formation of H_2O from H^+ and OH^-. If in the neutralization, either the acid or the base or both are weak, $|\Delta H|$ of neutralization will be less, since dissociation of weak acid or base during neutralization requires energy. E.g. ΔH of neutralization of acetic acid by NaOH is –55.2 kJ so that the difference, 57.5 –55.2 = 2.3 kJ, represents the energy required for ionizing 1 gm equivalent of the weak acid.

Enthalpy of solution (or heat of solution) is the enthalpy change accompanying the dissolution of 1 mole of the solute in a suitable amount of the pure solvent to give a solution of the desired concentration. It is also referred to as the integral heat of solution.

e.g. integral heat of solution of KCl in 200 moles of water is represented as:

$$KCl(s)+200\,H_2O(l)\rightarrow KCl\,(\text{solution})\Delta H\approx 18.6\text{kJ}$$

A positive value of ΔH means absorption of heat during dissolution and there is cooling. The above equation should be distinguished from the following:

KCl (s) + aq → KCl (aq). In this case 1 mole of KCl is dissolved in an excess of water. By "excess" we mean that the water taken is in such large quantity that further addition of water to the solution will not produce any thermal change.

There is another heat of solution, known as the differential heat of solution, defined by the expression, $\left[\frac{\partial(\Delta H)}{\partial n_2}\right]_{T,P,n_1}$. This is obtained by dissolving varying amounts of solute (n_2 moles) in a fixed amount of solvent (conventionally 1000gms). The slope of the plot of ΔH versus n_2 at any desired concentration (molality) gives the differential heat of solution. It is also defined as the enthalpy change when 1 mole of solute is added to a large volume of solution at a specified concentration, temperature and pressure.

9. Enthalpy of dilution or the integral heat of dilution is the enthalpy change, when a solution containing 1 mole of the

2.11.1. Laws of Thermochemistry

1st Law : Law of Lavoisier and Laplace (1780)

"The enthalpy change of a chemical reaction in one direction is equal in magnitude but opposite in sign to that accompanying the same reaction in the reverse direction."

Illustration $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l); \Delta H^0_{298K} = -68.3\text{kcal}$

So, $H_2O(l) = H_2(g) + \frac{1}{2}O_2(g); \Delta H^0_{298K} = +68.3\text{kcal}$

Consequence of the 1st Law of Thermodynamics

The law is a consequence of 1st law of thermodynamics. H is a state function, so it depends on the states of the reacting system. Let us suppose, the reactants A and B first change into products C and D with enthalpy of reaction. ΔH_1 and then C and D give reactants A and B back, the enthalpy of reaction is ΔH_2. Thus, for the whole cycle $\Delta H = \Delta H_1 + \Delta H_2$

Consequence of the 1st Law

If the initial state and final state of a system due to a process are fixed, enthalpy change or internal energy change will also be fixed, independent of the intermediate steps that occur during the process. This is due to the fact that H and U are the state functions.

2nd Law : Hess's Law of Constant Heat Summation (1840)

Statement : "For a chemical reaction, the net heat change (ΔH, ΔU) will be the same whether the process occur in one step or in several steps."

Illustration : A chemical reaction happening in one step, $A \rightarrow C : \Delta H = \Delta H_1$

But when the same reaction occurs in two steps, $A \rightarrow B : \Delta H = \Delta H_2$ & $B \rightarrow C : \Delta H = \Delta H_3$

Then, according to the law, $\Delta H_1 = \Delta H_2 + \Delta H_3$

2.11.2. Application of the Law

This law is sometimes used to calculate the enthalpy of a reaction which is difficult to determine by experiments.

For example, $C(s) + \frac{1}{2}O_2(g) = CO(g)$, ΔH of the reaction is not easy to determine experimentally as some amount of CO_2 always forms in association with CO. The value of ΔH for the reaction can be calculated as follows.

$C(s) + O_2(g) = CO_2(g) : \Delta H^{\circ}_{298K} = -94.05$ kcal, when it occurs in a single step.

The same reaction can also occur in two steps.

$C(s) + \frac{1}{2}O_2(g) = CO\,(g) : \Delta H^{\circ}_{298K} = Q$ (say)

$CO(g) + \frac{1}{2}O_2(g) = CO_2\,(g) : \Delta H^{\circ}_{298K} = -67.63$ kcal

So, according to the law, (–94.05kcal) = Q + (–67.63kcal) or Q = –26.42 kcal

Thus, $C(s) + \frac{1}{2}O_2(g) = CO(g) : \Delta H^{\circ}_{298K} = -26.42$ kcal

2.11.3. Extension of Hess's Law

The changes in entropy and in Gibbs free energy can also be calculated by applying the concepts of Hess's law. The Bordwell thermodynamic cycle is an example of such an extension which takes advantage of easily measured equilibria and redox potentials to determine experimentally inaccessible Gibbs free energy values.

Thus change in free energy $\Delta G^0_{react} = \sum \Delta G^0_{f(pdts)} - \sum \Delta G^0_{f(reat)}$

But entropy can be measured as an absolute value thus entropy of formation is not required, simply absolute values of entropy are used.

$$\Delta S^0_{react} = \sum \Delta S^0_{f(pdts)} - \sum \Delta S^0_{f(reat)}$$

2.11.4. Applications of Hess's Law

Hess's law of constant heat summation is useful in the determination of enthalpies of the following:

- Calculation of enthalpies of reactions
- Determination of enthalpy changes of slow reactions
- Calculation of enthalpies of formation
- Enthalpy of formation of reactive intermediates
- It helps in determining the lattice energies of ionic substances by building Born-Haber cycles if the electron affinity to form the anion is known

Exercise

The heat of dissociation per mole of a gaseous water at 18°C and 1 atm is 241750 J, calculate its value at 68°C. Data given are C_P (H_2O)= 33.56 ; $C_P(H_2)$ = 28.83 ; $C_P(O_2)$ = 29.12 JK^{-1}.

Solution

The dissociation reaction is

$$H_2O(g) \rightarrow H_2\ (g) + {}^1\!/_2\, O_2(g) \qquad \Delta H^\circ(291K) = 241750\ J$$

$$\Delta C_P = C_P(H_2) + {}^1\!/_2\, C_P(O_2) - C_P(H_2O)$$

$$= (28.83 + {}^1\!/_2 \times 29.12 - 33.56)\ JK^{-1}mol^{-1}$$

$$= 9.83\ JK^{-1}mol^{-1}$$

$$\Delta C_P \times \Delta T = 9.83\ JK^{-1}mol^{-1} \times 50\ K = 491.5 J\ mol^{-1}$$

$$\Delta H^\circ(341K) = \Delta H^\circ\ (291K) + \Delta C_P \times \Delta T = 241750 + 491.5 = 242241.5\ J\ mol^{-1}$$

2.11.5. Temperature dependence of the Heat of reaction (Kirchoff Equation)

If we know the ΔH° of a reaction at temperature, T_1, Kirchhoff's equation provides the calculation of ΔH° of the same reaction at another temperature, T_2.

Let us consider the chemical reaction,

$$v_1A_1 + v_2A_2 = v_3A_3 + v_4A_4 \ \text{ or, } 0 = -v_1A_1 - v_2A_2 + v_3A_3 + v_4A_4 \ \text{ or, } 0 = \sum_i v_1A_1$$

where v_i = stoichiometric coefficient and it is (+ve) for the products and (–ve) for the reactants. Enthalpy of the reaction, $\Delta H^\circ = (v_3 H^\circ_{3,m} + v_4 H^\circ_{4,m}) - (v_1 H^\circ_{1,m} + v_2 H^\circ_{2,m})$ $= \sum_i v_i H^0_{i,m}$

Since, P is fixed at the standard state of 1 atm, differentiating with respect to T at constant pressure, $\left[\frac{\partial(\Delta H^\circ)}{\partial T}\right]_P = \sum_0 v_i \left[\frac{\partial H^0_{i,m}}{\partial T}\right]_P = \sum_i v_i C_{P,i} = \Delta C_P$, called standard constant pressure molar heat capacity change of the process.

Integrating within limits, $= \int_{\Delta H^0_1}^{\Delta H^0_2} d(\Delta H^\circ) = \int_{T_1}^{T_2} \Delta C_P dT$

When ΔC_p is assumed to be temperature independent, $\Delta H^0_2 = \Delta H^0_1 + \Delta C_P(T_2 - T_1)$

When ΔC_p is assumed to be temperature dependent, $C_{P,i} = a_i + b_i T + c_i T^2 + ...$

and $\Delta C_P = \sum_i v_i C_{P,i} = \sum_i v_i(a_i + b_i T + c_i T^2 + ...)$

$$= \alpha + \beta T + \gamma T^2 ....$$

Where $\alpha = \sum v_i a_i, \beta = \sum v_i b_i$ and $\gamma = \sum v_i c_i$

Using this expression of ΔC_P, we get $\Delta H^0_2 = \Delta H^0_1 + \int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2 + ...)dT$

Or, $\Delta H^0_2 = \Delta H^0_1 + \alpha(T_2 - T_1) + \frac{\beta}{2}(T_2^2 - T_1^2).....$

The relation of internal energy of reaction with temperature is

$$\Delta U^0_2 = \Delta U^0_1 + \alpha'(T_2 - T_1) + \frac{\beta'}{2}(T_2^2 - T_1^2).....$$

These are the Kirchhoff's equations which relate the heat of reaction with temperature.

2.12 Bond Energy

Bond energy of a given bond is defined as the average of energy required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. The bond energy differs from dissociation energy which is defined as the energy required to dissociate a given bond of some specific compound.

Let us consider O – H bond. The heat of dissociation of the O-H bond depends on the nature of molecular species from which the H-atom is being separated from O-atom.

Examples For H_2O molecule,

H_2O molecule (g) → H(g) + OH(g) : $\Delta H^\circ_{298K} = 119.95$ kcal mol^{-1}.

But to break the O-H bond in the hydroxyl radical requires a different quantity of heat

O-H (g) → O(g) + H(g) ; $\Delta H^\circ_{298K} = 101.19$kcal mol^{-1}. The bond energy, ε_{OH} is defined as the average of these two values :

i.e. $\varepsilon_{OH} = ½(119.96+101.9) = 110.57$ kcal mol^{-1}.

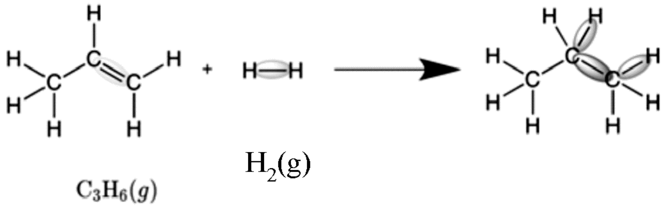
Energy in chemical bonds

Chemical bonds represent potential energy. Quantifying the energy represented by the bonds in different molecules is an important part of understanding the overall energy implications of a reaction. In this article, we'll explore two different concepts that help describe that energy: enthalpy of reaction and bond enthalpy.

Enthalpy of reaction

During chemical reactions, the bonds between atoms may break, reform or both to either absorb or release energy. The result is a change to the potential energy of the system. The heat absorbed or released from a system under constant pressure is known as *enthalpy*, and the change in enthalpy that results from a chemical reaction is the *enthalpy of reaction*. The enthalpy of reaction is often written as ΔH_{rxn}

To better understand enthalpy of reaction, let's consider the hydrogenation of propene, C_3H_6, to form propane, C_3H_8. In this reaction, propene gas reacts with hydrogen gas, $H_2(g)$, to form propane gas :



What is happening in this reaction? First we have to break the carbon C=C bond and H-H bond of the reactants. As a rule, **breaking bonds between atoms requires adding energy**. The stronger the bond, the more energy it takes to break the bond. To make the product propane, a new C-C and two new C-H. Since breaking bonds requires adding energy, the opposite process of **forming new bonds always releases energy**. The stronger the bond formed, the more energy is released during the bond formation process. In this particular reaction, because the newly formed bonds release more energy than was needed to break the original bonds, the resulting system has a lower potential energy than the reactants. This means the enthalpy of reaction is negative.

Mathematically, we can think of the enthalpy of reaction as the difference between the potential energy from the product bonds and the potential energy of the reactant bonds.

Reactions where the products have a lower potential energy than the reactants, such as the hydrogenation of propene described above, are *exothermic*. Reactions where the products have a higher potential energy than the reactants are *endothermic*.

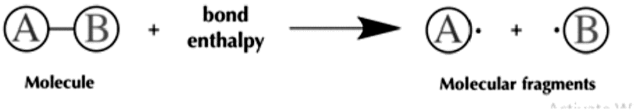
In an exothermic reaction, the released energy doesn't simply disappear. Instead it is converted to kinetic energy, which produces heat. This is observed as an increase in temperature as the reaction progresses. On the other hand, endothermic reactions often require the addition of energy to favor the formation of products. In practice, this often means running a reaction at a higher temperature with a heat source.

In order to quantify the enthalpy of reaction for a given reaction, one approach is to use the standard enthalpies of formation for all of the molecules involved. These values describe the change in enthalpy to form a compound from its constituent elements. Subtracting the standard enthalpies of formation for the reactants from the standard enthalpies of the products approximates the enthalpy of reaction for the system.

An alternative approach is to estimate the enthalpy of reaction by looking at the individual bonds involved. If we know how much energy we need to make and break each of the bonds, then we can add those values to find the enthalpy of reaction.

Bond enthalpy

Bond enthalpy (which is also known as bond-dissociation enthalpy, average bond energy, or bond strength) describes the amount of energy stored in a bond between atoms in a molecule. Specifically, it's the energy that needs to be added for the homolytic or symmetrical cleavage of a bond in the gas phase. A homolytic or symmetrical bond breaking event means that when the bond is broken, each atom that originally participated in the bond gets one electron and becomes a radical, as opposed to forming an ion.



Chemical bonds form because they're thermodynamically favorable, and breaking them inevitably requires adding energy. For this reason, bond enthalpy values are always positive, and they usually have units of kJ/mol. The higher the bond enthalpy, the more energy is needed to break the bond and the stronger the bond. To determine how much energy will be released when we form a new bond rather than break it, we simply make the bond enthalpy value negative.

Because bond enthalpy values are so useful, average bond enthalpies for common bond types are readily available in reference tables. While in reality the actual energy change when forming and breaking bonds depends on neighboring atoms in a specific molecule, the average values available in the tables can still be used as an approximation.

Tip: The bond values listed in tables in TEXT BOOKS are for a mole of reaction for a single bond. This means that if there are multiples of the same bond breaking or forming in a reaction, you will need to multiply the bond enthalpy in your calculation by how many of that type of bond you have in the reaction. This also means it's important to make sure the equation is balanced and that the coefficients are written as the smallest possible integer values so the correct number of each bond is used.

Using bond enthalpies to estimate enthalpy of reaction

We can use the following procedure:

Step 1. Identify which bonds in the reactants will break and find their bond enthalpies.

Step 2. Add up the bond enthalpy values for the broken bonds.

Step 3. Identify which new bonds form in the products and list their negative bond enthalpies. Remember we have to switch the sign for the bond enthalpy values to find the energy released when the bond forms.

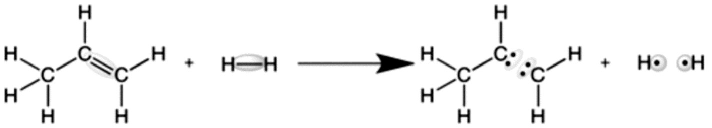
Step 4. Add up the bond enthalpy values for the formed product bonds.

Step 5. Combine the total values for breaking bonds (from **Step 2**) and forming bonds (from **Step 4**) to get the enthalpy of reaction.

Hydrogenation of propene

Step 1 : Identify bonds broken

This reaction breaks a C = C, and H – H..



Using a reference table, C = C, bond enthalpy is 610 kJ mol^{-1} and the H–H, bond enthalpy is 436kJ/mol

Step 2 : Find total energy to break bonds

Combining the values from **Step 1** gives us:

Energy added to break bonds=610 kJ/mol + 436 kJ/mol = 1046 kJ/mol as the total energy required to break the necessary bonds in propene and hydrogen gas.

Step 3 : Identify bonds formed

This reaction forms a new C – C, and two new C – H

Using a reference table (and keeping in mind that we're forming rather than breaking bonds), we find that the C – C bond enthalpy is 346 kJ/mol and the bond enthalpy for each of the C – H bonds is 413kJ/mol. To find the energy released when forming these bonds, we will multiply the bond enthalpies by –1 Also, since there are two C – H bonds, we'll need to multiply this value by 2.

Step 4: Find total energy released to form new bonds

Combining the values from **Step 3** gives us:

Energy released to make product bonds=$^{-}$346 kJ/mol + (2×$^{-}$413 kJ/mol)= $^{-}$1172kJ/mol for the total energy that will be released by forming the new bonds.

Step 5: Add up energy for bonds broken and formed

From **Step 2** and **Step 4**, we have 1046kJ of energy required to break bonds and $^{-}$1172kJ of energy released from forming bonds. Combining these values, we get for the enthalpy of reaction:

Δ Hrxn = energy added to break reactant bonds + energy released when making product bonds

= 1046kJ/mol + (–1172kJ/mol)

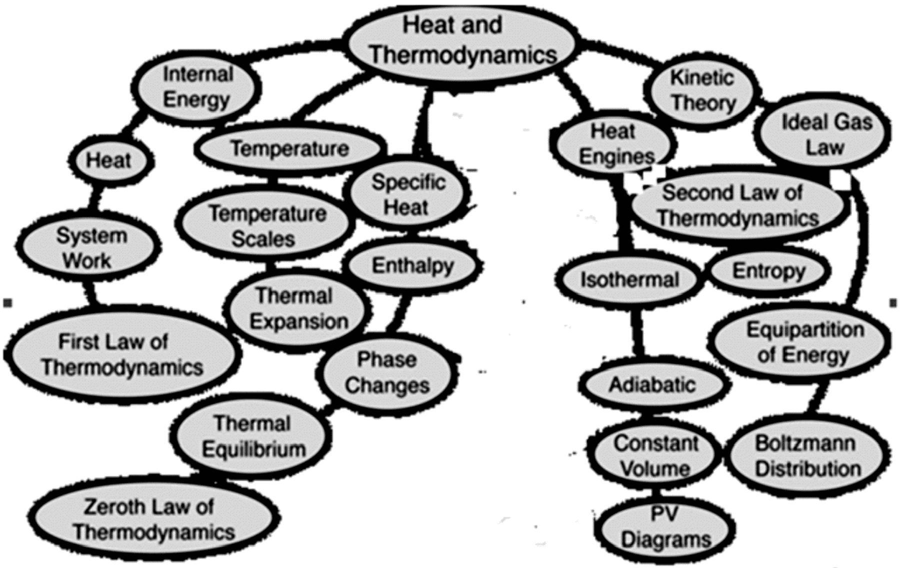
= –126 kJ/mol

Since the enthalpy of reaction for the hydrogenation of propene is negative, we know that the reaction is exothermic.

2.13 SUMMARY

1. A system is classified as open , closed, or isolated.
2. The surroundings remain at constant temperature and either constant volume or constant pressure when process occur in the system.
3. The mathematical statement of the First law of thermodynamics, $\Delta U = q + w$
4. At constant volume, the change in internal energy of a system becomes equal to heat exchange between the system and its surroundings $\Delta U = q_v$
5. An exothermic process releases energy as heat ; an endothermic process absorbs energy as heat.
6. Maximum expansion work is achieved in a reversible change.
7. The First Law of Thermodynamics states that the internal energy of an isolated system is constant.
8. Energy transferred as heat at constant volume is equal to the change in internal energy of the system.
9. Energy transferred as heat at constant pressure is equal to the change in enthalpy.
10. The heat capacity at constant volume is the slope of the internal energy with respect to temperature.
11. The heat capacity at constant pressure is the slope of the enthalpy with respect to temperature.
12. Enthalpy represents the total energy stored in the system. When the system is kept at constant pressure, then the enthalpy change becomes equal to the *heat exchange* by the system. It is expressed by $H = U + PV$.
13. The change in enthalpy (ΔH) when liquid state changes into vapor state or when vapor changes into liquid state, is known as enthalpy of vaporization
14. The change in enthalpy when solid state changes into liquid state or liquid state freezes to solid state is known as enthalpy of fusion.

15. Molar heat capacity is defined as the heat needed to cause a unit rise in the temperature of one mole of a substance.
16. The relation between Cv and C_P is, $C_P - C_v = R$
17. The branch of chemistry which deals with the energy changes involved in chemical reaction is called **thermochemistry.**
18. The relation between enthalpy at constant volume (q_v) and enthalpy at constant pressure (q_p) is given by $q_P = q_v + nRT$
19. **Hess's law** was established by the Russian chemist German H. Hess in 1840 Hess's law states that the amount of heat evolved and absorbed in a process, including a chemical change, is the same whether the process takes place in one or several steps, i.e., total change in enthalpy do not change during the course of the reaction.



2.14 Questions

1. Which of the following properties are intensive?

   (a) equilibrium constant, (b) vapor pressure, (c) free energy, (d) enthalpy of reaction.

2. Which of the following functions are perfect differential?

   (a) work, (b) adiabatic work, (c) isothermal reversible work, (d) heat of reaction at constant pressure.

3. Which of the following are correct expression(s) for mechanical work ?

   (a) $w = -\int_{V_1}^{V_2} P_{op}dV$ (b) $dw = -P_{op}dV$ (c) $dw = -\int P_{op}dV$, (d) dq + dw = dU.

4. Mechanical work will be zero when the process is / are

   (a) isochoric, (b) free expansion, (c) isothermal, (d) cyclic.

5. Expression(s) of first law of thermodynamics is / are

   (a) dq + dw = dU, (b) q + w = dU, (c) $q + w = \Delta U$, (d) dq + dw = dU.

6. We know H = U + PV, so

   (a) dH = dU + d(PV), (b) $dH \approx dU + PdV + VdP$, (c) $\Delta H = \Delta U + P\Delta V + V\Delta P$, (d) $\Delta H = \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V$.

7. Thermodynamic condition(s) for ideal gas is / are

   (a) U & H = f(T) only, (b) U & H = f(T, n) only, (c) $(\partial C_V / \partial V)_T = 0$,

   (d) $(\partial C_P / \partial P)_T = 0$.

8. For the following processes, deduce whether the quantities, q, w, ΔU, ΔH are positive, zero or negative :

   (i) Reversible melting of ice at 1 atm. & 0°C,

   (ii) Reversible isothermal expansion of a perfect gas,

   (iii) Reversible adiabatic expansion of a perfect gas,

   (iv) Adiabatic expansion of a perfect gas in vacuum,

   (v) Joule-Thomson adiabatic throttling of a perfect gas,

   (vi) Combustion of hydrogen gas in a sealed container with rigid, adiabatic walls.

   (vii) Adiabatic expansion of a non-ideal gas in vacuum,

   (viii) Combustion of hydrogen in a sealed container having rigid, thermally conducting walls immersed in a water bath at 25°C,

   (ix) Reversible heating of a perfect gas at constant pressure.

9. Define heat capacity at constant volume (c_v) and heat capacity at constant pressure (c_p). How are they are they related ? Explain the significance of ratio.

10. (a) Prove that it is impossible for two reversible adiabatic to intersect on a PV diagram.

11. (a) Derive the P – V relation or an ideal gas undergoing reversible adiabatic expansion.
12. Show that for an adiabatic reversible process, PV = Constant.
13. Starting with H = U + PV, show that, $(\partial U/\partial T)_p = C_p - P(\partial V/\partial T)_p$ and interpret the same.
14. Show that "an adiabatic expansion of a real gas" occurs with constant enthalpy, but not with constant energy
15. Define a cyclic process and differentiate a reversible cyclic process from an irreversible cyclic process.
16. (b) Justify the definition of (U+PV) as a separate thermodynamic quantity, enthalpy.
17. For a gas, obeying the equation of state $P(V - b) = RT$, find $(\partial U/\partial V)_T$ and $(\partial H/\partial P)_T$, hence, comment which one of the conditions : $(\partial U/\partial V)_T = 0$, or, $(\partial H/\partial P)_T = 0$ is a stronger criteria for an ideal gas.
18. 'In a reversible adiabatic expansion of fixed mass of an ideal gas, the work done depends, only on the temperature difference' —explain.
19. What is meant by isothermal process ?
20. What is meant by adiabatic process?

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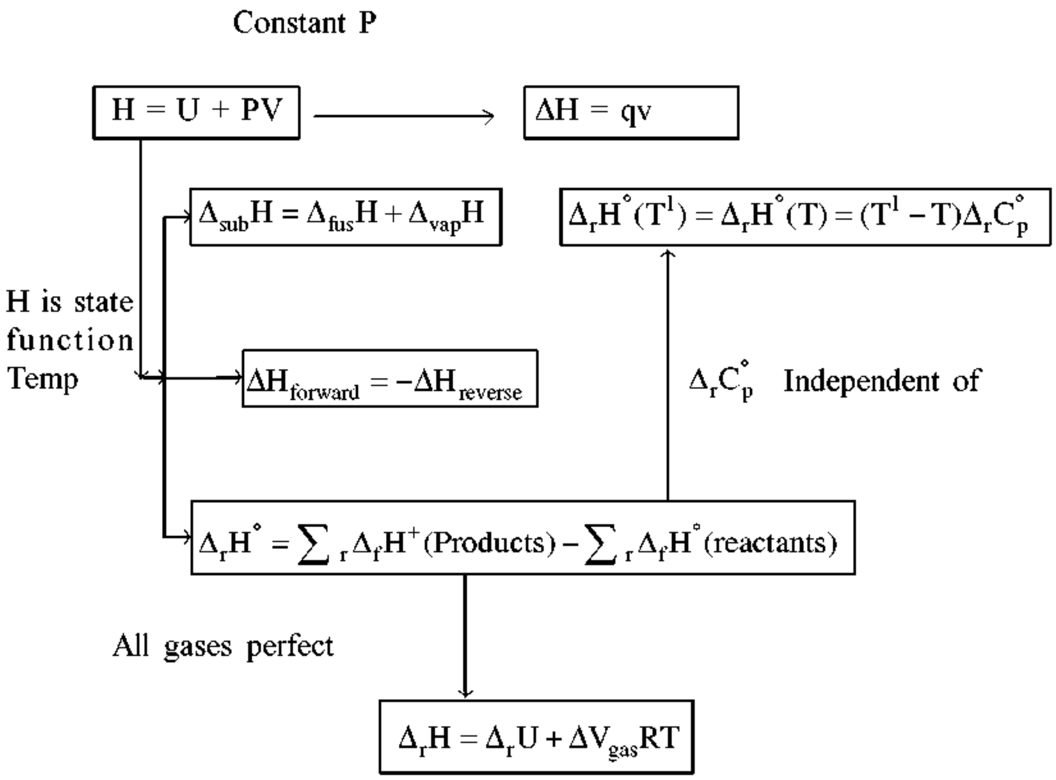
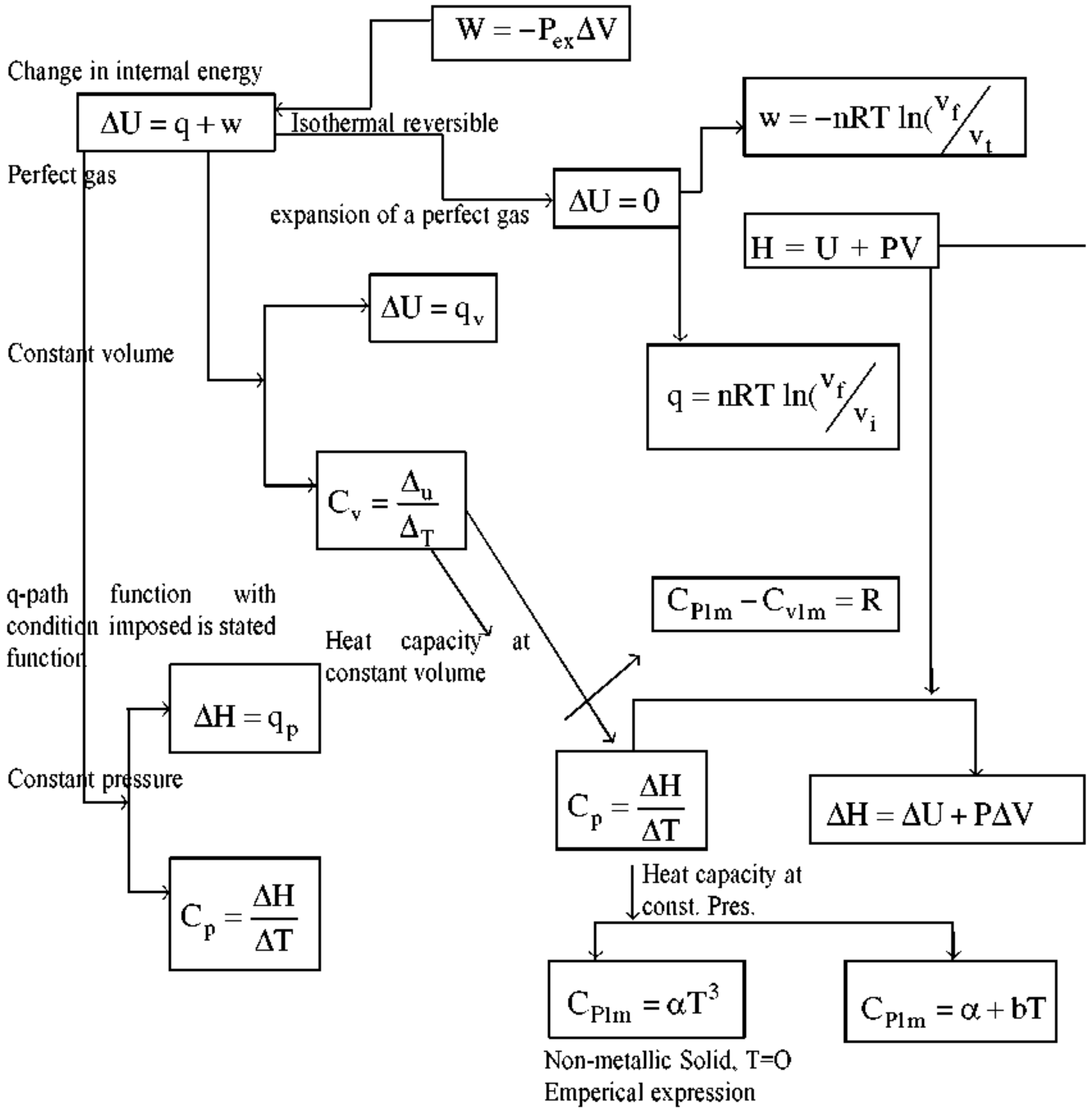
ROAD MAP OF KEY EQUATION



ROAD MAP OF KEY EQUATION

Mechanical work expansion or compression



Unit 3 ❑ Chemical Thermodynamics-II

Structure

3.1 Objectives

The objective to this unit is to—

Know the limitations of first law of thermodynamics

Learn about some thermodynamic terms required for second law of thermodynamics

Know different statements given for second law of thermodynamics by different scientists.

Learn about the concept of Entropy

Know about free energy functions i.e. Gibb's free energy and work function Joule Thomson

3.2 Introduction

Everyday experience is that whenever there exists a difference in certain properties such as pressure, temperature, electric potential etc. change is the effect that which always eliminates the difference. If difference exists between two systems and they are put together, the system as a whole is in non-equilibrium state and it will move towards equilibrium state by removing the difference in the property, either by heat flow if temperature is not uniform or otherwise. When the property has attained the uniform value, it reaches the equilibrium state. The system will continue to be in this state unless it is disturbed by an external agent.

Analogous to the mechanical system, in which the system tries to have the minimum potential energy, it was suggested that for a chemical reaction, minimization of heat content is required for the system. This means that a reaction in which heat is evolved must be spontaneous whereas in which heat is absorbed must be non-spontaneous, i.e. all exothermic reactions must be spontaneous whereas reactions in which heat is absorbed must be non spontaneous. All endothermic process reaction must be non spontaneous. But there exists a few exceptions in which ΔU is positive but the reaction is spontaneous e.g. Vaporisation of water at low pressure. Hence ΔU is not the criterion of spontaneity. Ammonium chloride added to water is endothermic and spontaneous. U and H derived from first law of thermodynamics cannot predict spontaneity.

$\Delta U = q + w$, For isothermal reversible process and for cyclic process $\Delta U = 0$, **heat is totally converted to work.** This desire to completely convert HEAT into WORK leads to aspire for process to achieve the same.

Isothermal reversible expansion only caters work by the system but to reuse one needs to return back and so cyclic idea to achieve the same required.

The reversible cycle designed by Carnot is breakthrough regarding this. The original statement of the second law of thermodynamics is much concerned with the development of the theoretical aspects of heat engines specially the Carnot cycle.

The second law of thermodynamics states that processes occur in a definite direction while the first law does not focus on the direction of the process i.e. the direction of a particular spontaneous transformation can be ascertained with the help of second law of the thermodynamics. First law indicates that in any process the total energy of the system plus the surroundings taken together is same before and after the process. As per first law it is possible to transfer heat from a body at lower temperature to body at higher temperature. In this case heat lost by cold body will be gained by hot body but this never happens. The process which satisfies the first law does not mean that it will definitely going to occur. Thus there is a need of another principle which can identify whether the process will occur or not. Before discussing about the second law of thermodynamics, the limitations of the first law will be discussed.

First law allows us to calculate the energy changes in processes. But these changes do not suggest spontaneity. Examples: ΔH, ΔU

3.3 Limitations of the First Law of Thermodynamics

1. Classical Thermodynamics can predict the **feasibility** of a physical or chemical process, under a given set of conditions, and it **does** not deal with the rate of the process.

2. The first law states that in an isolated system the energy does not change during a specified change of state. But it does not give any information about the specified change i.e. whether the change will occur spontaneously or not.
3. The methods of classical thermodynamics deal only with limiting cases. Thus it can predict the **maximum work** that can be turned out in a **physical process** and **not** the actual amount of work; it can predict **the maximum yield** in a **chemical reaction**, under a given set of conditions, but **not** the actual yield.
4. According to first law, the total energy of the system remains conserved i.e. one form of energy can be completely converted into another form of energy. But Joule's experiment has shown that the heat energy cannot be completely converted into work energy while the work energy can be completely converted into heat energy. Thus heat energy and work energy are not interchangeable form of energy. Thus there is requirement of another law, i.e. second law of thermodynamics.

Conversion of heat into work

As heat has no natural tendency to be converted into work the following conditions must be fulfilled.

(i) A mechanical device, called engine, is required to convert heat into work.

(ii) the engine must work in reversible cyclic process to produce maximum work.

(iii) There must be flow of heat from higher to lower temperature during the conversion of heat into work.

3.4 Definitions for expressing the second law of thermodynamics

3.4.1. Heat reservoir

It is a large system which is in stable equilibrium and heat can be transferred to and from it without any change in its temperature.

The heat reservoir which is at high temperature and from which the heat is transferred is known as heat source while the heat reservoir which is at low temperature and to which heat is transferred is known as heat sink.

3.4.2. Work reservoir

It is a very large system in stable equilibrium through which definite amount of work is transferred adiabatically without any change in pressure

3.4.3. Thermodynamic cycle

If the system after undergoing series of processes reaches its original state then the system is said to have completed a thermodynamic cycle. In this, the properties of the system at the beginning and at the end of the cycle are same.

Thus $P_f = P_i$ i.e. pressure of the system at initial (beginning) stage and at final (end) stage is same. Similarly, $T_f = T_i$

3.4.4. Heat engine

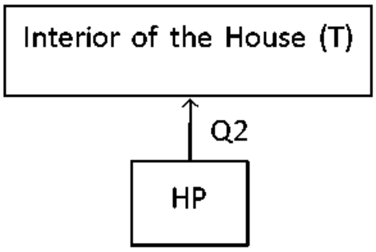
It is a thermodynamic system working in a thermodynamic cycle to which net heat is transferred and from which work is delivered.

3.4.5. Heat Pump (HP)

HP is used to warm the house in the winter by giving heat from outside, Outside the house temperature T_1 is the Low temperature reservoir.

Efficiency (ψ) = Heat pumped inside the room / work supplied

$$(\psi) = \frac{Q_2}{Q_2 - Q_1} = \frac{T_2}{T_2 - T_1}$$



3.5 Various statement of the second law of thermodynamics

The second law of thermodynamics is expressed in many ways, the most salient statements being given by Rudolf Clausius (1854), Lord Kelvin (1851), Max Planck(1926) etc. Although these statements are different but each one of them predicts the direction in which a change will take place spontaneously.

3.5.1. Kelvin statement of the second law

This statement for second law of thermodynamics was proposed by Lord Kelvin. It states that it is impossible to construct a device operating in a thermodynamic cycle to receive heat from a single heat source and produce a net amount of work. It also states that it is not possible to derive mechanical effect from any part of matter by cooling it below the temperature of the coldest of the surrounding objects.

NOTE

No Sink mentioned : $q_C = 0$ or $T_H = T_C$ Kelvin Statement

$$\frac{w}{q_H} = \frac{T_H - T_C}{T_H}$$; for $T_C = T_H$, $-w = 0$, No work

No cyclic process is possible in which heat is taken from a hot source and completely converted into work.

3.5.2. Clausius statement of the second law

The second law of thermodynamics was founded by the German scientist, Rudolf Clausius in 1850. He developed the relationship between the heat transfer and work done. His formulation of second law is also known as Clausius statement. The concept of "passage of heat" was used in Clausius statement. This statement states that it is not possible to construct a device that operates in a cycle and develops no effect other than the transfer of heat from a lower temperature (cold region) body to higher temperature (hot region) body. In other words, heat cannot transfer from cold regions to hot regions spontaneously until some external work is done on the system, for example in refrigerator.

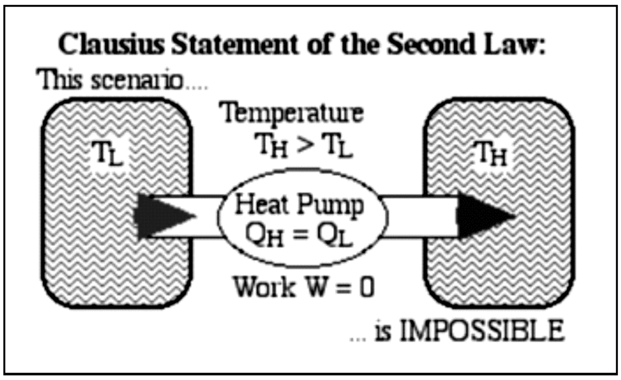
Clausius also said that "the entropy increases towards a maximum and the energy of the universe is constant"

Note

Let us keep a sink at $T_C < T_H$ but effectively $q_C = 0$

The Clausius statement "heat does not pass from a body at low temperature to one at high temperature without change elsewhere."

If the system violates Clausius statement and it will also violates Kelvin statement and vice versa. Thus both statements are equivalent.



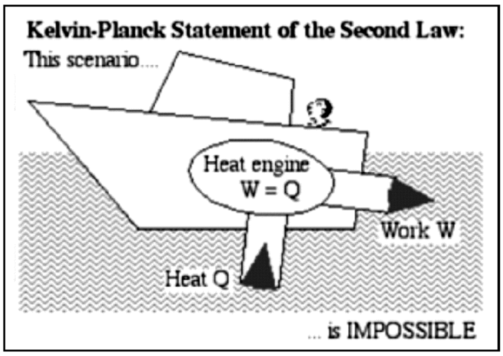
3.5.3. Planck statement for second law

Planck states that it is not possible to construct a device which will operate in a complete cyclic process and produce no effect except increasing of weight and cooling of reservoir. Or It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and cooling of a heat reservoir.

Kelvin Planck statement

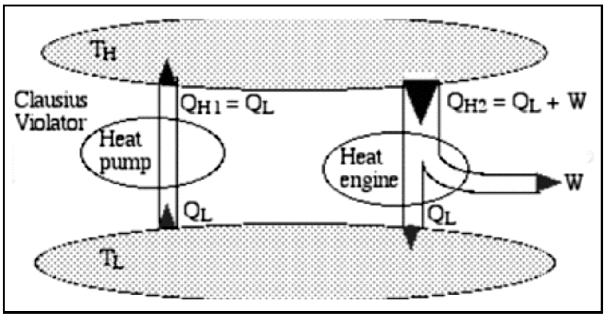
Heat cannot be completely converted into work. If it does so, the working system will suffer a permanent change. or

It is impossible for a system operating in a cycle and connected to a single reservoir (one Temperature) to produce a positive amount of work in the surrounding.

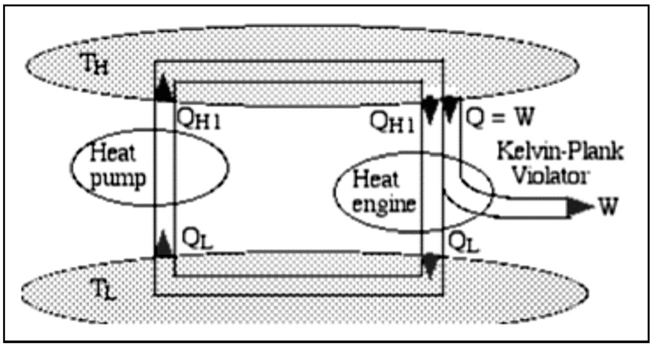


3.5.4. Equivalence of the Clausius and Kelvin-Planck Statements

It is remarkable that the two above statements of the Second Law are in fact equivalent. In order to demonstrate their equivalence consider the following diagram. On the left we see a heat pump which violates the Clausius statement by pumping heat Q_L from the low temperature reservoir to the high temperature reservoir without any work input. On the right we see a heat engine rejecting heat Q_L to the low temperature reservoir.



If we now connect the two devices as shown below such that the heat rejected by the heat engine Q_L is simply pumped back to the high temperature reservoir then there will be no need for a low temperature reservoir, resulting in a heat engine which violates the Kelvin-Planck statement by extracting heat from a single heat source and converting it directly into work.



3.5.5. Carnot's principle for second law

Carnot Principle was proposed by French engineer Nicolas Sadi Carnot

He was the first who studied the principle of second law of Thermodynamics.

The concept of cyclic operation was also introduced by him.

Carnot's principle refers to a cycle of Carnot Heat engine which is working in a quasi-static mode so that transfer of heat and work takes place between subsystems which are always in thermodynamic equilibrium.

The efficiency of reversible Carnot cycle depends on the temperature of the two reservoirs and is the same whatever be the working substance.

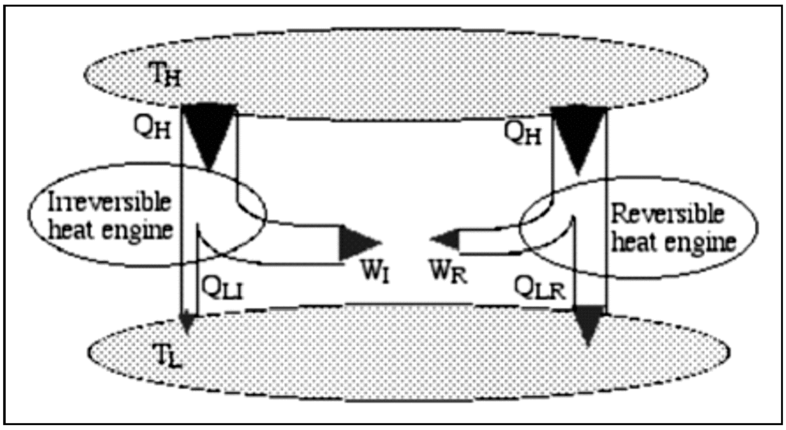
The Carnot cycle consists of four reversible processes i.e. two isothermal and two adiabatic.

3.5.6. Carnot's Theorem

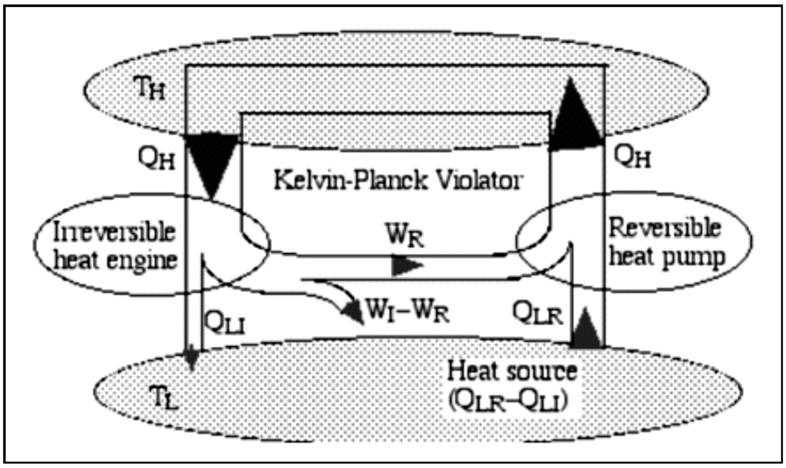
Carnot's theorem, also known as Carnot's rule, or the Carnot principle, can be stated as follows:

No heat engine operating between two heat reservoirs can be more efficient than a reversible heat engine operating between the same two reservoirs.

The simplest way to prove this theorem is to consider the scenario shown below, in which we have an irreversible engine as well as a reversible engine operating between the reservoirs T_H and T_L, however the irreversible heat engine has a higher efficiency than the reversible one. They both draw the same amount of heat Q_H from the high temperature reservoir, however the irreversible engine produces more work W_I than that of the reversible engine W_R.



Note that the reversible engine by its nature can operate in reverse, i.e. if we use some of the work output (W_R) from the irreversible engine in order to drive the reversible engine then it will operate as a heat pump, transferring heat Q_H to the high temperature reservoir, as shown in the following diagram:



Notice that the high temperature reservoir becomes redundent, and we end up drawing a net amount of heat (Q_{LR} - Q_{LI}) from the low temperature reservoir in order to produce a net amount of work (W_I - W_R) - a Kelvin-Planck violator - thus proving Carnot's Theorem.

Corollary 1 of Carnot's Theorem :

The first Corollary of Carnot's theorem can be stated as follows :

All reversible heat engines operating between the same two heat reservoirs must have the same efficiency.

Thus regardless of the type of heat engine, the working fluid, or any other factor if the heat engine is reversible, then it must have the same maximum efficiency. If this is not the case then we can drive the reversible engine with the lower efficiency as a heat pump and produce a Kelvin-Planck violater as above.

Corollary 2 of Carnot's Theorem :

The second Corollary of Carnot's theorem can be stated as follows:

The efficiency of a reversible heat engine is a function only of the respective temperatures of the hot and cold reservoirs. It can be evaluated by replacing the ratio of heat transfers Q_L and Q_H by the ratio of temperatures T_L and T_H of the respective heat reservoirs.

3.5.7. Heat engine thermal efficiency

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$$\eta_{rev} = 1 - \frac{T_L}{T_H}$$

3.5.8. Carnot cycle

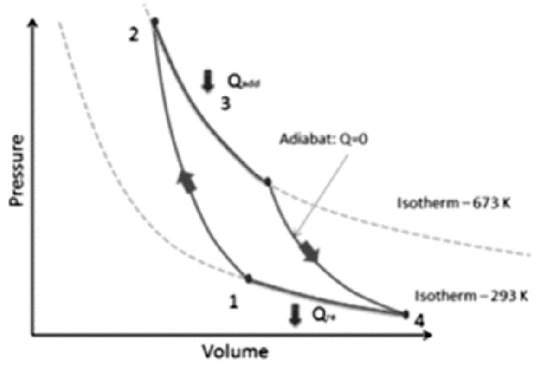
French engineer Nicolas Leonard Sadi Carnot in 1824 led to the discovery of heat engine called Carnot engine. He also showed that this engine is the most efficient engine which operates in an ideal reversible cycle called Carnot cycle. The Carnot engine establishes the maximum limit on the efficiency of all other engines. In other words, the system working through the Carnot cycle produces the maximum amount of work from given amount of energy supplied to the system.

A **reversible process** is the process by which system can be brought to its initial state along the same path, and for which every point along the path is an equilibrium state. In reversible process, the dissipative effects which convert mechanical energy to internal energy are not present.

An **irreversible process** is the process which violates the above requirement. The most natural processes are found to be irreversible in nature.

The heat engines are the device which are cyclic in nature and its working fluid returns to its initial state at the end of each cycle, and hence work is done by the working fluid during each part of the cycle. In one part of the cycle, work is done on the working fluid while in other part of the cycle, work is done by the working fluid. The difference between these two work is the net work done by the heat engine. The efficiency of heat engine cycle depends on the execution of individual processes involved in formation of the cycle. If reversible processes are used then the efficiency or net work produced by the system can be maximized. The best reversible cycle known is **Carnot cycle**. Carnot used a reversible cycle to derive the maximum convertibility of heat into work.

Carnot cycle consists of a system of one mole of ideal gas that is subjected to series of four reversible processes, commonly termed as four strokes. These are given below :



pV diagram of Carnot cycle. The area bounded by the complete cycle path represents the total work that can be done during one cycle.

Step 1 : Reversible isothermal expansion at high Temperature, T_H 2→3

Step 2 : Reversible adiabatic expansion (3→4)

Step 3 : Reversible isothermal compression, T_L (4→1)

Step 4 : Reversible adiabatic compression (1→2)

$$\eta = \frac{\text{workoutput}}{\text{heatinput}} = \frac{W_{cycle}}{Q_H} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_H}{T_L}$$

3.5.9. Discussion on the Efficiency of Carnot Engine

We have $\eta = 1 - \frac{T_1}{T_2}$ or, $\frac{w}{Q} = \frac{T_2 - T_1}{T_2}$ or, $w = Q \times \left(1 - \frac{T_1}{T_2}\right)$

1. Perpetual motion of the first kind

   If no heat is supplied to the engine Q = 0, $w = Q \times \left(1 - \frac{T_1}{T_2}\right)$, i.e. w = 0, no engine will work if heat is not added to it. This explains the impossibility of perpetual motion of the 1st kind
2. Perpetual motion of the second kind

   If $T_2 = T_1$, then also w = 0 i.e., no engine can produce any positive work if it is connected to single reservoir and extracts heat from it.
3. Incompleteness of conversion of heat into work $\eta = 1 - \frac{T_1}{T_2}$, can be unity when T_1 = 0K or $T = \infty$. Both the condition are never realized in practice so

   $\eta < 1$, i.e. $\frac{w}{Q}, < 1$

   W < Q. Heat is incompletely converted into work by an engine.
4. Unattainability of absolute zero temperature

   Second Law of thermodynamics states that η < 1 (Planck-Kelvin statement).

   $\left(1 - \frac{T_1}{T_2}\right) < 1$ or $- \frac{T_1}{T_2} < 0$, or $T_1 > 0$ so T_1 can never be equal to zero. O Kelvin temperature can never be equal to zero.
5. Comparison of efficiency

   The efficiency of the engine, $\eta < 1 - \frac{T_1}{T_2}$. So, η can be increased by lowering T_1 or increasing T_2 or by both. If the efficiency of the engine is compared by decreasing the temperature of the sink (Low Temperature Reservoir, LTR) or increasing temperature of the source (High Temperature Reservoir, HTR) to the same extent, η is higher where the sink temperature is reduced.

When T_1 is decrease by dT_1 keeping T_2 fixed, $d\eta_1 = 0 - \frac{dT_1}{T_2}$

When T_2 is increased by dT keeping T_1 fixed, $d\eta_2 = 0 + \frac{T_1}{T_2^2} dT_2$

But if $dT_1 = dT_2$

So $\frac{d\eta_1}{d\eta_2} = \frac{T_2}{T_1} > 1$

Decreasing temperature of the LTR leads to more efficiency than increasing temperature of the source keeping the same sink temperature or LTR, temperature.

6. We have $w = Q.\frac{T_2 - T_1}{T_2} = Q\frac{dT}{T_2}$. The engine converts fraction of heat supplied (Q) into work.
7. The efficiency (η) depends on temperature difference of source and sink, and temperature of the source. It does not depend on the nature of the working substance used in the engine. Thus instead of using ideal gas, if van der Waals gas is used, the efficiency would be the same. The efficiency is also independent of the kind of work and it holds also for non mechanical work.

3.5.10 Refrigerator (R)

A refrigerator is a device that extracts heat from cold reservoir (LTR) and rejects to hot reservoir (HTR). The process of extraction of heat is called refrigeration.

A Carnot refrigerator acts in the same fashion as that of Carnot engine but in reverse direction. It takes away heat (Q_1) from LTR, work (w) is supplied to it and finally it rejects heat (Q_2) to HTR. The refrigerator starts from D of ABCD Carnot Cycle. The sequence of steps

Step 1 : Reversible isothermal expansion at T_1, low temperature (D → C) Heat is taken from LTR = $Q_1 = w_1 = RT_1 \ln \frac{V_3}{V_4}$

Step 2 : Reversible adiabatic compression (C → B). Temperature increases from T_1 to T_2.

Work done $w_2 = C_V(T_2 - T_1)$

Step 3 : Reversible isothermal compression at T_2, (B → A) Heat rejected to HTR = $Q_2 = w_3 = RT_2 \ln V_1/V_2$.

Step 4 : Reversible adiabatic compression (A → D). Temperature decreases from T_2 to T_1.

Work done $w_2 = C_V(T_1 - T_2)$

Adding, $w = w_1 + w_2 + w_3 + w_4 = w_1 + w_3$

$$W = RT_1 \ln\frac{V_3}{V_4} + RT_2 \ln\frac{V_1}{V_2} = RT_1 \ln\frac{V_3}{V_4} - RT_2 \ln\frac{V_2}{V_1}, \text{ but } \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$= R(T_1 - T_2)\ln\frac{V_3}{V_4}$$

The efficiency of a refrigerator = Q_1 (heat extracted) / (–)w (work supplied)

$$\psi = (RT_1 \ln\frac{V_3}{V_4}) / -R(T_1 - T_2)\ln\frac{V_3}{V_4} = \frac{T_1}{T_2 - T_1}$$

The efficiency of refrigeration is also reported as the "coefficient of performance" of the arrangement. This quantity is defined as the ratio of heat removed from a cool object to the work that must be done in order to achieve that transfer. The higher the coefficient of performance the less work have to be done to achieve a given transfer. The best coefficient of performance that can be achieved by any arrangement when the object (the food) to be cooled is at a temperature T_{cold} and the surroundings (the kitchen) is at $T_{surrounding}$ is

$$\text{Coefficient of performance} = \frac{1}{\frac{T_{surrounding}}{T_{cold}} - 1}$$

For instance,if the cold object is cold water at 0°C (273 K) and the refrigerator is in room at 20°C(293K), then the coefficient of performance is 14, and to remove 10kJ of energy from the freezing water, which is enough thfreeze about 30 g of the water to ice. Under ideal conditions we need to do about 0.71kJof work. Actual refrigerators are much less efficient than this thermodynamic limit, heat leaks in from outside and not all the energy supplied to do the work joins the energy stream.

When a refrigerator is working, the energy released into the surrounding is the sum of that extracted from the cooled object and that used to run the apparatus. This remark is the basis of the operation of **Heat Pump**, a device for heating a region (such as interior of house) by pumping heat from outside into the interior. A heat pump is essentially a refrigerator, with the cooled object the outside world and heat transfer arranged to be in the region to be heated. That is, our interst is in the back of the refrigerator, not its interior. The coefficient of performance of a heat pump is defined as the ration of the total energy released as heat into the region to be heated (at a temperature $T_{interior}$), to the work done in order to achieve that release. By the same type of calculation as already done for the Carnot efficiency

$$\text{Coefficient of performance (heat pump)} = \frac{1}{\dfrac{T_{surrounding}}{T_{cold}} - 1}$$

Therfore the region to be heated is at 20°C (293K) and the surroundings are at 0°C (273K), the coefficient of performance is 15. Thus to release 1000J (1 kJ) into the interior, we need to do only 67J of work, In other words, a heat pump rated at 1kW behaves like 15kW heater.

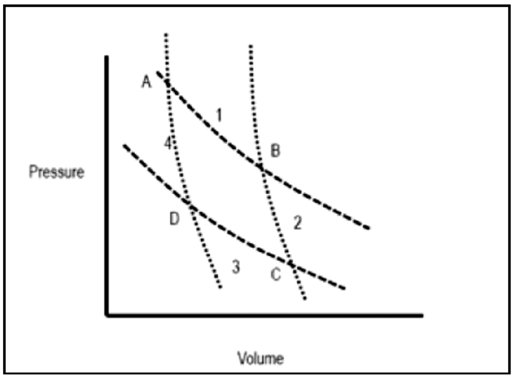
3.6 Entropy

3.6.1. Theory

The concept of entropy is vital for thermodynamics. The concept of temperature was used in zeroth law of thermodynamics while the concept of internal energy was used in first law of thermodynamics. These are state variables which define the state of the system. The state variable which is related to second law of thermodynamics is **entropy (S).** The concept of entropy was introduced by Clausius in 1865. It is considered as degree of randomness or disorderness in a molecular system. More the randomness, larger is the value of entropy. The word entropy has been made from energy (en) and trope (tropy) which is for chaos.

According to one of the statements of second law of thermodynamics, heat cannot be completely converted into work. This has been attributed to entropy. In thermodynamics, entropy is referred as the measure of the number of definite realizations or microstates that may realize a thermodynamic system, in a specified state defined by macroscopic variables. More precisely, the entropy is considered as a measure of molecular disorder within a macroscopic system. The second law of thermodynamics states that entropy of an isolated system never decreases. This kind of system spontaneously moves towards state with maximum entropy, i.e., at thermodynamic equilibrium. The system which is not isolated may lose entropy only when the entropy of environment is increased by same amount. As entropy is a state function, therefore the change in entropy of the system will remain same for any process with known initial and final states. The change in entropy does not depend upon the nature of the process, i.e., whether the process is reversible or irreversible. But the irreversible processes raise the combined entropy of the system and its surroundings. As on increasing the temperature of the system, kinetic energy of the molecules increases; therefore the degree of randomness increases thereby increasing the entropy of the system.

3.6.2. Entropy from Carnot Cycle



In the Carnot Cycle ABCD the state of the system can be changed from A to C either along The path ABC or along the path ADC, as all steps are reversible.

For the paths ABC

$$\left(\frac{dq_{rev}}{T}\right)_{ABC} = \left(\frac{dq}{T}\right)_{AB} + \left(\frac{dq}{T}\right)_{BC}$$

High Temperature if T_1 and heat absorbed reversibly q_1

$$\left(\frac{dq_{rev}}{T}\right)_{abc} = \frac{dq_1}{T_1} + 0 = \frac{dq_1}{T_1}$$

Along the path ADC, along DC , dq_{2-} quantity of heat is absorbed reversibly as in the Carnot cycle dq_2 quantity of heat is released during isothermal compression CD.

Again for the Carnot cycle

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_1} \text{or} \frac{dq_2}{T_2} = \frac{dq_1}{T_1}$$

$$\text{Or} \left(\frac{dq_{rev}}{T}\right)_{ABC} = \left(\frac{dq_{rev}}{T}\right)_{ADC}$$

i.e $\left(\frac{dq_{rev}}{T}\right)_{ABC} = \left(\frac{dq_{rev}}{T}\right)_{ADC}$ is an exact differential for the given change of state of the system.

So it expresses the difference in magnitude of some state property of a system, which is termed entropy.

3.6.3. Units of entropy

Since change in entropy is given by $dS = dq_{rev}/T$, i.e., heat term divided by the absolute temperature. Thus SI unit of entropy is given by Joules per degree Kelvin ($J\ K^{-1}$). For molar entropy, the unit is $J\ K^{-1}mol^{-1}$.

Entropy of Reversible cyclic process

$\Delta U = 0$, For isothermal reversible expansion of ideal gas and for cyclic process

$\oint \frac{dq_{rev}}{T} = \frac{q_h}{T_h} + \frac{q_c}{T_c}$ As only two steps have non-zero entropy $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$

So, $\oint \frac{dq_{rev}}{T} = 0$

Entropy is measure of the "quality" of the stored energy. When matter and energy are distributed in disorder way, as in gas, then entropy is high. when matter and energy stored in ordered manner, as in crystal, entropy is low.

Change in entropy is inversely proportional to first power of Temperature. Analogy drawn by Clausius, the change in entropy of a system at low temperature is similar to sneezing in a quiet library. A sudden sneeze is highly disruptive in a quite library. In a busy noisy street which is a metaphor for high temperature where the same sneeze will introduce relatively little additional disorder i.e. only a small increase in entropy.

3.6.4. Characteristics of entropy

1. Entropy is referred as degree of randomness. As the degree of randomness increases, the entropy of the system increases.
2. Entropy can also be related to unavailable energy.
3. For a given substance, the vapour phase has maximum randomness and solid phase has least randomness. Therefore, $S_{\text{vapour}} > S_{\text{liquid}} > S_{\text{solid}}$
4. Entropy is a state function. Therefore, $S = S_{\text{final}} - S_{\text{initial}} = S_2 - S_1$
5. It depends upon temperature, pressure, volume and amount of substance
6. Entropy is an extensive property.
7. $dS \neq dq_{irr} / T$
8. Entropy increases with increase in temperature.
9. The entropy increases as the volume of the system increases.

3.7 Entropy Change

3.7.1. Change in entropy in an isothermal expansion of an ideal gas

When an ideal gas is expanded isothermally and reversibly, then the internal energy does not changes i.e. $\Delta U = 0$ thus from first law of Thermodynamics (viz. $\Delta U = q + w$), we get

$$q_{rev} = -w = PdV = nRT\frac{dV}{V}$$

Thus change in entropy will be given by

$$\Delta S = \int_{V_1}^{V_2} \frac{q_{rev}}{T} \quad \Delta S = \int_{V_1}^{V_2} nR\frac{dV}{V}$$

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

3.7.2. Entropy change in reversible and irreversible processes

Suppose an ideal gas is expanded isothermally in vacuum keeping temperature constant. This process will proceed irreversibly. As no opposing force is applied, therefore the work done (w) by the system will be zero. As temperature is kept constant, thus change in internal energy will also be zero. According to first law equation then $q = 0$, i.e., no heat is exchanged between the system and surroundings during the process. Thus, the entropy of the surroundings does not change. The entropy of the system is defined by the state of the system, i.e., temperature and pressure (or volume). During this process let the volume changes from V_1 to V_2.

Therefore, the increase in entropy is given by (for one mole of $\Delta S = R \ln \left(\frac{V_2}{V_1}\right)$

$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$ (for n moles of ideal gas).

Thus total increase in entropy of the system and its surroundings during isothermal expansion

$R \ln (V_2 / V_1) + 0 = R \ln V_2 / V_1$

As $V_2 > V_1$ thus we can say that there is increase in entropy of the system and the surroundings during the irreversible isothermal expansion. Now considering the reversible isothermal expansion of an ideal gas at the temperature T. Suppose the volume changes from V_1 to V_2 during infinitesimally slow expansion. Expansion is done such that the pressure on the frictionless piston remains always less than that of the gas by an infinitesimally small amount. Therefore some work is done by the system, i.e., $w = -P\Delta V$ Thus at this temperature T, equivalent amount of heat is absorbed by the system. Accordingly the increase in entropy is given by $\frac{q_{rev}}{T}$. Similarly entropy of the surroundings decrease by $\frac{q_{rev}}{T}$. Conventionally applying the negative sign for decrease of entropy and positive for increase of entropy, thus the net entropy change of the system and the surroundings is given by

$$\frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0$$

Thus total entropy change during isothermal expansion for a gas is zero

Note :

During an **irreversible isothermal expansion** there is always increase in an entropy of the system and surroundings taken together while during **reversible isothermal expansion** the entropy of the system and surroundings remains same. This can be written as

$(\Delta S_{sys} + \Delta S_{surr}) = 0$ (for reversible process)

$(\Delta S_{sys} + \Delta S_{surr}) > 0$ (for irreversible process)

Combination of the above two $(\Delta S_{sys} + \Delta S_{surr}) \geq 0$

in which equal to sign stands for the reversible process and 'greater than' sign stands for irreversible process. Thus, the above equation helps in determining whether the process occurs spontaneously or not.

Since all the naturally occurring processes are spontaneous in nature thus we can say that the entropy of the universe increases continuously. This statement is also regarded as another statement of the second law.

3.7.3. Entropy change of an ideal gas due to variation in P, V and T

Entropy of the system depends upon the state of the system, i.e., on T, P and V. For a pure gaseous substance the value of entropy is dependent only on two of the three variables P, V and T. Generally T is taken as one of the variable therefore two variables to be considered are either T and V or T and P.

Case 1 : When the two variables are T and V

$dS = dq_{rev}/T$, where dq_{rev} is the infinitesimal amount of heat absorbed by the system at temperature T. According to first law of thermodynamics $\Delta U = q + w$, we get $dq_{rev} = dU - dw$

If work is done due to expansion of the gas , then infinitesimal change in volume will be given by : $-dw = PdV$.

Also $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ so, $dU = C_v dT$ and substituting

$dq_{rev} = dU - dw$; get $dq_{rev} = C_v dT + PdV$

Assuming the gas to be ideal, thus applying ideal gas equation in equation we get, (for one mole of gas) $P = RT/V$

$$dq_{rev} = C_v dT + RT\frac{dv}{V}$$

Considering and rearranging $dq_{rev} = dS/T = \frac{C_v dT}{T} + R\frac{dV}{V}$ and the above equation on integration between initial state 1 and final state 2. And C_v is assumed to be constant within the temperature range T_1 and T_2.

Therefore, the entropy change for finite change of state of the system is given by :

$$\Delta S = S_2 - S_1 = nC_v \ln\frac{T_1}{T_2} + nR\ln\frac{V_2}{V_1}$$

If we use the second basic equation dH = TdS + VdP and insert dH = nC_PdT

$\Delta S = S_2 - S_1 = nC_P\ln\frac{T_2}{T_1} - nR\ln\frac{P_2}{P_1}$ (ideal gas reversible process for the change of state $(T_1,P_1 - T_2,P_2)$

3.7.4. Change in entropy of an ideal gas in different processes

For isothermal Process, $T_1 = T_2$ $\Delta S = nR\ln\frac{P_1}{P_2}$ and $\Delta S = nR\ln\frac{V_2}{V_1}$

For isochoric Process, $V_1 = V_2$ $\Delta S = nC_v\ln\frac{T_2}{T_1}$

For isobaric Process, $P_1=P_2$ $\Delta S = nC_P\ln\frac{T_2}{T_1}$

ΔS of a system in a reversible adiabatic process, Since in adiabatic process q = O, therefore $\Delta S_{surrounding}$ = O. A reversible adiabatic process is isoentropic i.e. ΔS_{system} = O. Thus a change of state from T_1, V_1 to T_2 , V_2 of a system containing n moles ideal gas in reversible adiabatic process

$$\Delta S = nC_v\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} \text{ or, } C_v\ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

This leads to entropy change due to volume change compensates that due to temperature change in the reversible adiabatic process of an ideal gas. Again this relation shows that for reversible adiabatic compression $V_2 > V_1$, temperature of the system fall $T_2 < T_1$. i.e. increase in temperature.

ΔS for reversible phase change of a pure substance

Change of a pure substance from one phase to another at constant temperature and pressure occurs reversibly. e.g. Ice to liquid water at 0°C and 1 atm pressure. Heat change in the process at constant pressure is the enthalpy change for this type of phase transformation and $\Delta S = \frac{\Delta H_1}{T_1}$ where ΔH_1 is the enthalpy change at the transition temperature.

3.7.5. Entropy of mixing

Calculation of ΔS for the Mixing of Ideal gases at constant T and P

Consider the process where n_A moles of ideal gas A are confined in a bulb of volume V_A at a pressure P and temperature T. This bulb is separated by a valve from bulb B of volume V_B that contains n_B moles of ideal gas B at the same (T,P). When the stop cock is opened, the gas molecules mix spontaneously and irreversibly and an increase in entropy $\Delta_{mix}S$ is then simply the sum of ΔS_A, the entropy change for the expansion of gas A from V_A to $(V_A + V_B)$ and ΔS_B, the entropy change for the expansion of gas B from V_B to $(V_A + V_B)$ / That is

$$\Delta_{mix}S = \Delta S_A + \Delta S_B$$

$$\Delta S_A = n_A \ R \ ln \ \frac{V_A + V_B}{V_A} \ \& \ \Delta S_B = n_B \ R \ ln \ \frac{V_A + V_B}{V_B}$$

$$\text{Hence } \Delta_{mix}S = R[n_A \ \ln \frac{V_A + V_B}{V_A} + n_B \ln \frac{V_A + V_B}{V_B}]$$

$$\text{Using ideal gas equation, } n_A = \frac{pV_A}{RT} \ n_B = \frac{pV_B}{RT}$$

$$n_A + n_B = \frac{p(V_A + V_B)}{RT} \text{ , extensive property}$$

We know $\frac{n_A}{n_A + n_B} = \frac{V_A}{V_A + V_B} = x_A$ likewise x_B are the mole fractions of A and B in the mixture.

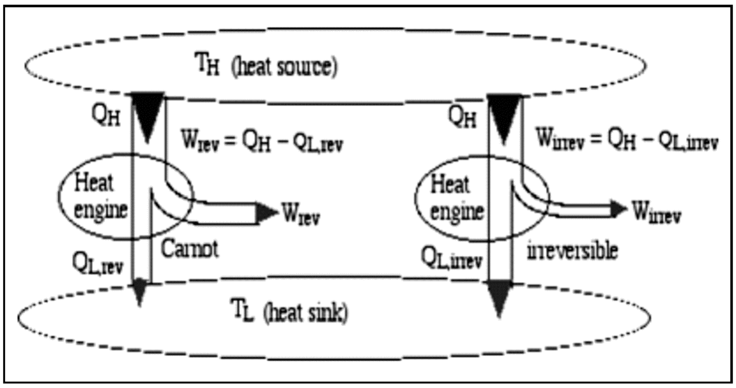
We know $\Delta_{mix}S = -R[n_A \ln x_A + n_B \ln x_B]$ {note –ve sign}

To find $\Delta_{mix}S$, the entropy of mixing for a mole of mixture, we divide the above equation by total number of moles $\boldsymbol{\Delta_{mix}S = -R[x_A \ln x_A + x_B \ln x_B]}$

3.8 Clausius Inequality

Entropy and its derivation from the second law of thermodynamics.

The first law tells about equality i.e. conservation of energy, the second law speaks about inequality. i.e. the efficiencies of any reversible engines is greater than that of an irreversible engine when both are allowed to operate separately between the same two heat reservoirs. Moreover the second law is concerned with the directional property of natural transformation.



First in the reversible (Carnot) heat Engine, the reversible heat transfer can only occur isothermally, thus the cyclic integral of the heat transfer divided by the temperature can be evaluated as follows : $\oint \frac{\partial Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{L.rev}}{T_L}$ = For reversible machines, $\oint \frac{\partial Q}{T} = 0$

Or, $0 = \frac{Q_H}{T_H} - \frac{Q_{L,trv}}{T_L}$ Or, $= \frac{Q_H}{T_H} - \frac{Q_{L,rev}}{T_L}$

Notice from the above diagram showing the two heat engines that for an irreversible engine having the same value of heat transfer from the thermal source Q_H as the reversible engine, the heat transfer to the thermal sink $Q_{L,irrev} > Q_{L,rev}$.

Let $Q_{diff} = (Q_{L,irrev} - Q_{L,rev})$, then the cyclic integral for an irreversible heat engine becomes :

$$\oint \frac{\partial Q}{T} = \left(\frac{Q_H}{T_H} - \frac{Q_{diff}}{T_L} \right) < 0$$

for any reversible or irreversible heat engine we obtain the Clausius Inequality: $\oint \frac{\partial Q}{T} \le 0$

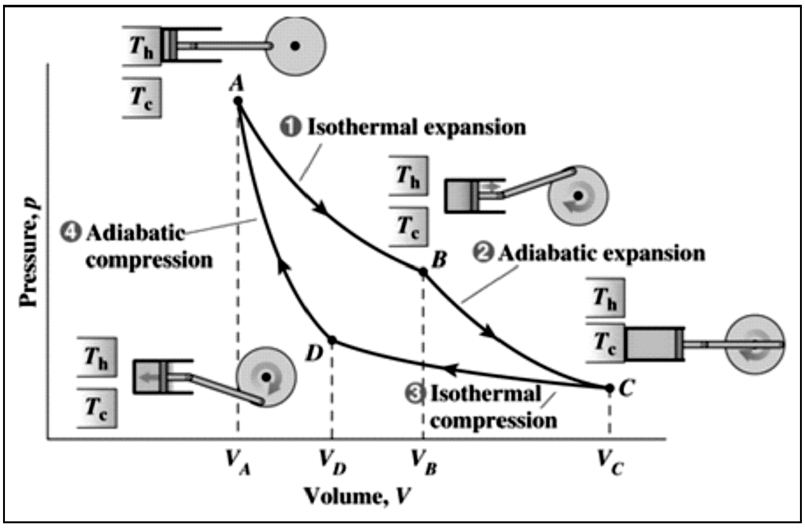
All properties (such as pressure P, volume V, etc) have a cyclic integral equal to zero.

For reversible machines, since $\oint \frac{\partial Q}{T} = 0$. This must be a property.

$dS \Rightarrow \frac{\partial q}{T}$ for reversible process (Entropy).

In case of an isothermal process at temperature T_0 we obtain : $\Delta S = \frac{q}{T_0}$

Clausius Inequility from Carnot Cycle



The heat taken from hot reservoir is q_1

Let us consider a carnot cycle **ABCD** and an irreversible cycle **abcd** between the same two heat reservoirs. The irreversible cycle is a Carnot cycle with the first step (a→b) occurring irreversibly. All other steps in the irreversible cycle occur reversibly.

For the reversible cycle

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_1}$$

$$\text{Or, } \frac{dq_2}{T_2} = \frac{dq_1}{T_1} = \frac{dq_1}{T_1} + \left(-\frac{dq_2}{T_2}\right) = 0$$

$$\oint \frac{\partial Q}{T} = 0$$

For the irreversible cycle

$$\eta_{irr} = \frac{dq_1 - dq_2}{dq_1} \text{ and } \eta_{irr} < \frac{T_1 - T_2}{T_1}$$

As $\eta_{irr} < \eta_{rev}$ in the same temperature range ;

$$\therefore 1-\frac{dq_2}{dq_1}<1-\frac{T_2}{T_1} \text{ Or, } \frac{dq_2}{dq_1}>\frac{T_2}{T_1} \text{ or } \frac{dq_2}{T_2}>\frac{dq_1}{T_1}$$

Or, $\frac{dq_1}{dq_1}+\left(-\frac{dq_2}{T_2}\right)<0$ or $\oint\frac{\partial Q}{T}<0$ (sign is included within the term dq)

So for all the process $\oint\frac{\partial Q}{T}\le 0$. The equality sign is valid for reversible process

The Laws of Thermodynamics and Cyclic Engines

[J.Bevan Ott and Julian Boreio-Goates Chemical Thermodynamics]

First Law "You can't get something for nothing"

Second Law "You not only can't get something for nothing, you can't even break even"

The Universe, the cyclic engine plus the two heat reservoirs for which $\sum\Delta U=0$

Since the process is reversible, for the universe $\sum\Delta S=0$

Since the engine is cyclic, no net change occurs in it so that for the universe

$$\sum\Delta U=q_1+q_2+w=0$$

The reservoirs are at constant temperature in which case

$$\Delta S_1=\int\frac{\partial q_1}{T_1}=\frac{q_1}{T_1};\ \Delta S_2=\int\frac{\partial q_2}{T_2}=\frac{q_2}{T_2}$$

Adding ΔS_1 and ΔS_2 ; $\Delta S = \frac{q_1}{T_1}+\frac{q_2}{T_2}=0$

Combining the two equations :

$q_1 + q_2 + w = 0$

$-w = q_1 + q_2$

$$\frac{-w}{q_1}=\frac{q_1+q_2}{q_1}=1+\frac{q_2}{q_1}$$

Using, $\Delta S = \frac{q_1}{T_1}+\frac{q_2}{T_2}=0$ or $\frac{q_1}{T_1}=-\frac{q_2}{T_2}$ or $\frac{q_2}{q_1}=-\frac{T_2}{T_1}$

$$\frac{-w}{q_1} = \eta = 1 - \frac{T_2}{T_1}$$

Another statement of the second law is the Clausius Inequality which states that $\oint \frac{\partial q}{\partial T} \leq 0$

For any cyclic process, where the equality applies to the reversible process and the inequality to the natural process. The efficiency $\eta \leq \frac{T_1 - T_2}{T_1}$

$\Delta S > 0$, provides a criterion to predict the natural direction of change in an isolated system. This result can be obtained without considering a specific process in which only P–V work is possible.

$dU = dq - P_{opp}dV$ is valid for reversible and irreversible processes. If the process is reversible, the equation can be written as

$dU = dq_{reversible} - PdV = TdS - PdV$

Because U is a State function. dU is independent of the path, holds for both reversible and irreversible processes, as there are no phase transitions or chemical reactions, and only P – V work occurs.

To derive the Clausius Inequality

$dq_{rev} - dq = (P - P_{external})\, dV$. If $(P - P_{external}) > 0$, the system will spontaneously expand, and $dV > 0$. If $(P - P_{external})dV > 0$. Therefore we conclude that

$dq_{rev} - dq = TdS - dq \geq 0$ or $TdS \geq dq$.

The equality holds only for reversible process. We write Clausius inequality as $dS > \frac{dq}{T}$.

However for an irreversible process in an isolated system, $dq = 0$. Therefore, for any irreversible process in an isolated system, $\Delta S > 0$

Use of Clausius Inequality

The Clausius Inequality is used to generate two new functions, the Gibbs Energy and the Helmhlotz energy. These functions allow predictions to be made about the direction of change in processes for which the system interacts with its environment.

The Change of Entropy in the Surroundings and $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$

The entropy of an isolated system increases in a spontaneous process. In general, a system interacts with the part of the Universe that is very close. Therefore in actual system and surroundings form interacting composites that is isolated from rest of the Universe. The part of the surroundings that is relevant for entropy calculations is a thermal reservoir at a fixed temperature, T. The mass of the reservoir is sufficiently large that its temperature is only changed by an infinitesimal amount dT when heat is transferred between the system and the surroundings. Therefore, the surroundings always remain in internal equilibrium during the heat transfer.

The entropy change (ΔS) in the surrounding which is either at constant Volume, V or constant Pressure, P. The amount of heat absorbed by the surroundings, $q_{surroundings}$ depends on the process occurring in the system. If the surroundings are at constant volume, $q_{surroundings} = \Delta U_{surroundings}$, and when the surroundings are at constant pressure P, $q_{surroundings} = \Delta H_{surroundings}$. Because H and U are state functions, the amount of heat entering in the surroundings are independent of path. In particular, the system and the surrounding need not be at the same temperature and q is the same whether the transfer occurs reversibly or irreversibly.

Therefore $dS_{surroundings} = \frac{dq_{surr}}{T_{surroundings}}$ or for a macroscopic change, $\Delta S_{surroundings}$

$$= \frac{q_{surroundings}}{T_{surroundings}}.$$

NOTE. The heat that appears in change, $\Delta S_{surroundings} = \frac{q_{surroundings}}{T_{surroundings}}$, is the actual heat transferred. The ΔS_{system} is calculated using the heat flow, $dq_{reversible}$, for a reversible process that connects the initial and final states of the system and not the actual dq for the process.

Problem

One mole of an ideal gas at 300K is reversibly and isothermally compressed from a volume of 25.0 L to a volume of 10.0 L. Because it is very large , the temperature of the water bath thermal reservoir in the surroundings remains essentially constant at 300K during the process. Calculate ΔS, $\Delta S_{surroundings}$ and $\Delta S_{total.}$

Solution

This is an isothermal process, ideal gas $\Delta U = 0$ and $q_{rev} = -w = nRT\int_{V_i}^{V_f}\frac{dV}{V} = nRT\ln\frac{V_f}{V_i}$

$q_{rev} = -2.29\times10^3$ Joule

The entropy change of the system, $\Delta S = \int\frac{dq_{reversible}}{T} = -7.62JK^{-1} = -7.62JK^{-1}$

The entropy change of the surroundings, $\Delta S_{surroundings} = \frac{q_{surroundings}}{T} = \frac{q_{system}}{T} = 7.62JK^{-1}$

The total change in entropy $\Delta S_{total} = \Delta S + \Delta S_{surroundings} = 0$

The above process is reversible, there is no direction of spontaneous change and hence $\Delta S_{total} = 0$

Problem 2

The irreversible process that goes between the same initial states of the system.

One mole of an ideal gas at 300°K is isothermally compressed by a constant external pressure equal to the final pressure in above problem. At the end of the process, $P = P_{external}$ at all but the final state, this process is irreversible. The initial volume is 25.0L and the final volume is 10.0L. The temperature of the surroundings is 300K. Calculate ΔS, $\Delta S_{surroundings}$ and ΔS_{total}.

Solution

First it is required to calculate external Pressure and initial pressure in the system.

$$P_{external} = \frac{nRT}{V} = \frac{1mol\times8.314JmolK^{-1}\times300K}{10L\times\frac{lm^3}{10^3L}} = 2.49\times10^5Pa$$

$$P_i = \frac{nRT}{V} = \frac{1mol\times8.314JmolK^{-1}\times300K}{25L\times\frac{lm^3}{10^3L}} = 9.98\times10^4\ Pa.$$

Because $P_{external} > P_i$, we expect the direction of spontaneous change will be the compression of the gas to a smaller volume. Because $\Delta U = 0$

$q = -w = P_{external} (V_f - V_i) = 2.49\times10^5 Pa \times (10\times10^{-3} m^3 - 25\times10^{-3} m^3) = 3.74\times10^3 J$

The entropy change in the surrounding is given by $\Delta S_{surrounding} = -\frac{q}{T} = \frac{3.74\times10^3 J}{300K} = 12.45\ JK^{-1}$

The entropy change of the system must be calculated on a reversible path and has the value obtained $\Delta S = \int \frac{dq_{rev}}{T} = \frac{q_{rev}}{T} = \frac{-2.29\times10^3 J}{300K} = -7.62 J\ K^{-1}$

It is seen that $\Delta S < 0$, $\Delta S_{surroundings} > 0$. The total change in entropy is given by $\Delta S_{total} = \Delta S + \Delta S_{surroundings} = -7.62 J\ K^{-1} + 12.45\ JK^{-1} = 4.83\ JK^{-1}$

3.9 The Gibbs energy and the Helmholtz energy

The direction of spontaneous change for a process is predicted by $\Delta S_{total} = \Delta S + \Delta S_{surroundings} > 0$

The spontaneity criteria can be used to derive two new state functions, the Gibbs and Helmholtz energies. These new state functions provide the basis for discussion of equilibrium.

The Clausius inequality $dS \geq \frac{dq}{T}$ Or if written in the form $TdS \geq dq$

$dq = dU - dW_T$, the equality is satisfied for reversible process

$TdS \geq dU - dW_T$, or equivalently, $-dU + dW_T + TdS \geq 0$ or $dW_T \geq dU - TdS$

For isothermal process, TdS written as d(TS), $\mathbf{dW_T \geq d(U - TS) \geq dA_T}$.

When **work is done by the system** $\mathbf{dW_T \leq dA_T}$. For reversible process maximum work done by system $dW_{T,\ max} = -dA_T$

Note. TdS represents the quantity of energy remaining associated with the change of entropy of the system and TS is called the bound energy.

A system can do different type of work on the surroundings, dW_T. It is particularly useful to distinguish between expansion work, in which the work arises from a volume change in the system, and non expansion work. $-dU - P_{external}\, dV + dw_{non\text{-}expansion} + TdS \geq 0$.

This equation expresses the condition of spontaneity for an arbitrary process in terms of the changes in the state functions U, V, S and T as well as the path-dependent functions $P_{ext}dV$ and w_{nonexp}. For an isolated system , W_T =0 and dU = 0. Therefore the equation reduces to $\mathbf{dS \geq 0}$.

Chemists are interested in systems that interact with their environment than in isolated systems. Hence defining equilibrium and spontaneity for such systems

$$\mathbf{d(U - TS) \leq dw_{expansion} + dw_{nonexpansion}}$$

$$\mathbf{dA \leq dw_{expansion} + dw_{nonexpansion}}$$

The condition that defines spontaneity and equilibrium becomes $dA_{T,V} \leq 0$. The condition for spontaneity at constant (T,V) takes simple form using Helmholtz energy, A rather than the entropy, S.

Chemical reactions are commonly studied in test tube or under atmospheric pressure than constant volume conditions. Therefore, the condition for spontaneity is considered next for an isothermal transformation that takes place at constant pressure, $\mathbf{P = P_{external}}$. At constant Pressure and Temperature, **PdV = d(PV)** and **TdS = d(TS).** The equation can be written

$\mathbf{d(U + PV - TS) = d(H - TS) \leq dw_{non\ expansion}}$. The combination of **H – TS,** which has the units of energy, defines a new state function called the Gibbs energy. Using the Gibbs energy, the conditions for spontaneity and equilibrium for an isothermal process at constant pressure becomes $\mathbf{dG_{P,T} \leq dw_{nonexpansion}}$.

For a reversible process the equality holds and the change in the Gibbs energy is a measure of the maximum non expansion work that can be produced , the condtion for spontaneity and equilibrium is $\mathbf{dG \leq 0}$

The criteria of spontaneity and equilibrium are

(i) $\mathbf{\Delta S_{univ} \geq 0}$

(ii) $\mathbf{\Delta U_{S,V} \leq 0}$

(iii) $\mathbf{\Delta H_{S,P} \leq 0}$

(iv) $\mathbf{\Delta A_{V,T} \leq 0}$

(v) $\mathbf{\Delta G_{P,T} \leq 0}$

What is the advantage of using State function G and A as criteria for spontaneity rather than entropy ?

The Clausius inequality can also be written as, $dS - \frac{dq}{T} \geq 0$

$dS_{\text{surroundings}} = -\frac{dq}{T}$, the Clausius inequality is equivalent to the spontaneity condition

$dS + dS_{\text{surrounding}} \geq 0$

G and A introduced are expressed in terms of the macroscopic state variables of the system. It is now not necessary to consider surroundings explicitly, ΔG, ΔA for the system alone is sufficient to predict the direction of natural change.

Equation $\mathbf{dG_{P,T} \leq dw_{nonexpansion}}$ allows one to calculate **the maximum nonexpansion** work that can be produced by a chemical transformation.

Use of the Equation $\mathbf{dG_{P,T} \leq dw_{nonexpansion}}$

To calculate the electrical work produced by a reaction in an electrochemical cell or fuel cell.

$$\Delta G = \Delta H - T\,\Delta S$$

Note that there are two contributions to ΔG that determine if an isothermal chemical transformation is spontaneous.

- The entropic contribution to ΔG is greater for higher temperatures.
- A chemical transformation is always spontaneous if **ΔH** < 0 (an exothermic reaction) and ΔS > **0.**
- A chemical transformation is never spontaneous if **ΔH** > 0 (an endothermic reaction) and ΔS < **0.**
- For all other cases, the relative magnitude of **ΔH, T Δ S** determine if the chemical transformation is spontaneous.

Similarly, for macroscopic changes at constant V and T in which no expansion work is possible the condition for spontaneity is ΔA < 0, where **ΔA = ΔU – T Δ S.**

3.9.1. Free energy functions

The Differential Forms of U, H, A, G

The differential forms dU, dH, dA, dG are developed. Starting from definitions

$H = U + PV$

$A = U - TS$

$G = H - TS = U + PV - TS$

The following differentials known as Gibbs equation can be formed

$\mathbf{dU = TdS - PdV}$ $U = f(S, V)$

$\mathbf{dH} = TdS - PdV + PdV + VdP = \mathbf{TdS + VdP}$ $H = f(S, P)$

dA = TdS- PdV – TdS + SdT = – **SdT – PdV** A = f (T, V)

dG = TdS + VdP – TdS – SdT = – **SdT + VdP** G = f (T, P)

3.9.2. Maxwell's Relations

The expressions or equations which relate internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy with parameters like entropy, pressure, etc., are called Maxwell's relations. Some of these are

(i) dU = TdS – PdV

(ii) dH = TdS + VdP

(iii) dA = -SdT – PdV

(iv) dG = -SdT + VdP

If volume of the system remains constant, i.e., dV = 0 then equation (i) becomes; $(\partial U / \partial S)_V = T$

If entropy of the system does not change, i.e., dS = 0, then equation (i) becomes, $(\partial U / \partial V)_S = -P$

Differentiating $\left(\frac{\partial U}{\partial S}\right)_V = T$ with respect to V keeping S constant $\left(\frac{\partial T}{\partial V}\right)_S$

Differentiating $\left(\frac{\partial U}{\partial V}\right)_S = -P$ with respect to S keeping V constant $-\left(\frac{\partial P}{\partial S}\right)_V$

Similarly following the same procedure some following relations were derived

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

The above relations are known as Maxwell's relations. Some more relations are:

$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$ from (i) and (ii) ; $\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T$ from (i) and (iii)

$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$ from (ii) and (iv) ; $\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$ from (iii) and (iv)

Free Energy Functions - Generalization

Although they are derived assuming a reversible process, as total differentials they apply to both reversible and irreversible processes. They are starting points for the derivation of general differential expressions in which we express U, H, A and G as a function of P, V, T C_p, C_v

Partial Differential Relationships

We want to express the partial derivatives

Z	$\left(\frac{\partial Z}{\partial T}\right)_V$	$\left(\frac{\partial Z}{\partial T}\right)_P$	$\left(\frac{\partial Z}{\partial V}\right)_T$	$\left(\frac{\partial Z}{\partial P}\right)_T$	$\left(\frac{\partial Z}{\partial V}\right)_P$	$\left(\frac{\partial Z}{\partial P}\right)_V$

As functions of P, V, T, C_V and C_P where Z is U, S, H, A, G

Already derived

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

The next two equations are derived and obtained as the Maxwell relationships

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Derive the equations for

(i) $\left(\frac{\partial U}{\partial T}\right)_P$ (ii) $\left(\frac{\partial U}{\partial V}\right)_T$ (iii) $\left(\frac{\partial U}{\partial P}\right)_T$

In each case we start with the first Gibbs equation
dU = TdS − pdV

(i) divide by dT to obtain $\frac{dU}{dT} = T\frac{dS}{dT} - p\frac{dV}{dT}$ **the equation is true for all condition, including constant Pressure condition**

We can substitute partial derivatives for the ratio of differentials in equation

$$\left(\frac{dU}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P$$

This can be shown as follows
U = f(P,T) so that

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

If we specify constant P, then dP = 0 so that $dU = \left(\frac{\partial U}{\partial T}\right)_P dT$

Dividing by dT indicating the condition of constant P, we write $\left(\frac{dU}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P$

Henceforth we will make substitution of the type represented by equation

$$= T\frac{dS}{dT} - P\frac{dV}{dT}$$

$$\left(\frac{\partial U}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P = T\frac{C_P}{T} - P\left(\frac{\partial V}{\partial T}\right)_P$$

The expression for is obtained by starting with the same Gibbs equation dividing by dV

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \frac{\text{related to V is P}}{\text{related to S is T}}$[cross multiply].

Substituting

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

The expression for $\left(\frac{\partial U}{\partial P}\right)_T$

dU = TdS – PdV

Dividing by dP, specifying constant T

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

Exercise 1.

The second Gibbs equation dH = TdS + VdP can be used to obtain

$$\left(\frac{\partial H}{\partial V}\right)_T, \left(\frac{\partial H}{\partial P}\right)_T$$

Exercise 2.

Derive the relationship that give the effect of P and V on A and G with T held constant

Using third Gibbs equation

dA= – SdT – pdV

3.9.3. Applications of the Differential Relationships

The relationships expanded to include differences and molar properties, serve as the starting point of many useful thermodynamic calculations.The calculation of ΔZ for a variety of processesin which P, V, T are changed. For any of the extensive variables Z = S, U, H, A or G, we can write

Z = f(V, T) (usually for S, U, A)

Integration gives $\Delta Z = \int_{V_1}^{V_2}\left(\frac{\partial Z}{\partial V}\right)_T dV + \int_{T_1}^{T_2}\left(\frac{\partial Z}{\partial T}\right)_V dT$

The three commonly encountered processes

(a) An isochoric process in which dV = 0

$$\Delta Z = \int_{T_1}^{T_2}\left(\frac{\partial Z}{\partial T}\right)_V dT \text{ (isochoric process)}$$

(b) an isobaric process in which dP =0

$$\Delta Z = \int_{T_1}^{T_2}\left(\frac{\partial Z}{\partial T}\right)_P dT \text{ (isobaric process)}$$

(c) An isothermal process where dT = 0,

$$\Delta Z = \int_{V_1}^{V_2}\left(\frac{\partial Z}{\partial V}\right)_T dV \text{ (isothermal process) or } \Delta Z = \int_{P_1}^{P_2}\left(\frac{\partial Z}{\partial P}\right)_T dP$$

Problem

Calculate ΔU, ΔS, ΔH, ΔG for the isothermal expansion of one mole of ideal gas at T= 300K, from p_1 = 0.1 MPa to p_2 = 0.200MPa

Solution

$$P = \frac{nRT}{V}$$

Calculating ΔU

$$\Delta U = \int_{V_1}^{V_2}\left(\frac{\partial U}{\partial V}\right)_T dV$$

Thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

Differentiating the ideal gas equation gives = $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$

Combining gives $\left(\frac{\partial U}{\partial V}\right)_T = T\frac{nR}{V} - p = \frac{nRT}{V} - \frac{nRT}{V} = 0$

$\Delta U = 0$

Calculating ΔS

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\Delta S = \int_{V_2}^{V_1} \left(\frac{nR}{V}\right) dV = nR \ln \frac{V_2}{V_1}$$

At constant Temp.

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

Substitution gives $\Delta S = nR \ln$ $\frac{P_1}{P_2} = -5.762 \text{ JK}^{-1}$

Calculate ΔH

$$\Delta H = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial p}\right) dP \text{ or} \left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \textbf{ we know } V = \frac{nRT}{P}$$

$$= \frac{nR}{P}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\frac{nR}{P} = V - V = 0 \text{ or } \Delta H = 0$$

Calculating ΔG

$$\Delta G = \int_{P_1}^{P_2} \left(\frac{\partial G}{\partial p}\right)_T dP \quad \partial G/\partial P = V = \frac{nRT}{P}$$

$$\Delta G = \int_{P_1}^{P_2} \left(\frac{nRT}{P}\right) dP = nRT \ln \frac{P_2}{P_1} = 1729 \text{ JK}^{-1}$$

3.9.4. The effect of temperature and pressure on Free energy

dG = VdP – SdT

The above equation gives the change in free energy on variation of temperature and pressure.

If pressure of the system kept constant then dP = 0,thus equation dG = –SdT

The temperature derivatives of G and A $\left(\frac{\partial G}{\partial T}\right)_P = -S; \left(\frac{\partial A}{\partial T}\right)_V = -S$ is thus Entropy S. We usually do not know S as a function of P, V, T these derivates have limitations. However when expressions derived for temperature derivative of G/T and A/T it do not involve S and they are used in application where the original derivative was desired.

3.9.5. Gibbs Helmholtz Equation

The variation of Gibbs free energy change with temperature is known as Gibbs Helmholtz equation. This relation is derived as follows :

G = H – TS

Dividing by T and differentiating gives $\left(\frac{\partial\left(G/T\right)}{\partial T}\right)_P = \left(\frac{\partial\left(H/T\right)}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$

Expanding $\left(\frac{\partial\left(H/T\right)}{\partial T}\right)_P = \frac{TC_P - H}{T^2} = \frac{C_P}{T} - \frac{H}{T^2}$ and $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$

$$\left(\frac{\partial\left(G/T\right)}{\partial T}\right)_P = -\frac{C_P}{T} - \frac{H}{T^2} = -\frac{C_P}{T}$$

$$= -\frac{H}{T^2}$$

Similarly $\left(\frac{\partial\left(A/T\right)}{\partial T}\right)_P = -\frac{U}{T^2}$

The Gibbs-Helmholtz equation can also be written in the form

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}\right)=\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\frac{dT}{d\left(\frac{1}{T}\right)}\right)_P=-\frac{H}{T^2}(-T^2)=H$$

The derivatives $\left(\frac{\partial Z}{\partial P}\right)_V, \left(\frac{\partial Z}{\partial V}\right)_P$, are easily obtained by making use of the properties of the exact differential = $\left(\frac{\partial Z}{\partial P}\right)_V=\left(\frac{\partial Z}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V$

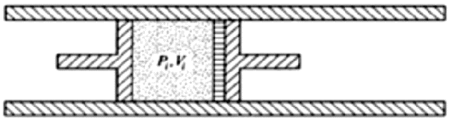
And = $\left(\frac{\partial Z}{\partial V}\right)_P=\left(\frac{\partial Z}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P$

For example = $\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P$ we know $\left(\frac{\partial S}{\partial T}\right)_P=\frac{C_P}{T}$

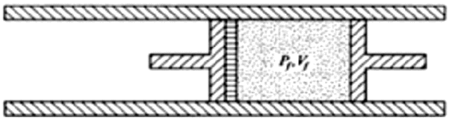
$$\left(\frac{\partial S}{\partial V}\right)_P=\frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P$$

We need to remember the equations relating $\left(\frac{\partial S}{\partial T}\right)_V, \left(\frac{\partial S}{\partial T}\right)_P, \left(\frac{\partial U}{\partial T}\right)_V, \left(\frac{\partial H}{\partial T}\right)_P$

3.10 Joule Thompson expansion



(*a*) Initial state



(*b*) Final state

The Joule-Thomson effect also known as Kelvin–Joule effect or Joule-Kelvin effect is the change in fluid's temperature as it flows from a higher pressure region to a lower pressure.

Equilibrium states, which are described by thermodynamic coordinates. From the first law,

$(U_2 - U_1) = w + q$. The throttling process occurs in an adiabatic enclosure, so $q = 0$.

The net work done by the piston on the gas causes the gas to flow across the boundary of the system enclosing the porus plug, that is

$$W = \int_{V_f}^{0} P_f dV - \int_{0}^{V_i} P_f dV$$

Since both pressures remain constant on either side of the porus plug , the net work is

$W = -(P_fV_f - P_iV_i)$ including the equation in $(U_2 - U_1) = w + q$.

$(U_2 - U_1) = -(P_fV_f - P_iV_i) + q(= 0)$., shows that the internal energy U is different for the two equilibrium end-states of the Joule-Thomson expansion. A state function can be devised for which there is no difference in the end-states $(U_2 - U_1) = -(P_fV_f - P_iV_i)$

Then $U_i + P_iV_1 = U_f + P_fV_f$ likewise the characteristic enthalpy function is introduced.

In this process $U_i \neq U_f$; $P_i \neq P_f$ and $V_i \neq V_f$ but $U_i + P_iV_I = U_f + P_fV_f$.

$H = U + PV$

In a throttling process the initial and final enthalpies are equal. One is not entitled to say that the enthalpy remains constant, since one cannot spaeak on the enthalpy of a system while it is passing through non-equilibrium states during the irreversible process. In plotting a throttling process on any diagram, the initial and final equilibrium states may be represented by points. The intermediate non equilibrium states, however cannot be plotted.

A continuous throttling process may be achieved by a pump that maintains constant high pressure on one side of a porous wall or expansion valve, and a constant lower pressure on the other side.

In order to consider other properties of enthalpy, consider the change in enthalpy that occurs when an arbitrary system undergoes any infinitesimal quasi static process from an initial equilibrium state to a final equilibrium state.

We have dH = dU + PdV +VdP

dq = dU + PdV

dH = dq + VdP

Dividing both sides by dT, $\frac{dH}{dT}=\frac{dq}{dT}+V\frac{dP}{dT}$

And at constant P,

$\left(\frac{\partial H}{\partial T}\right)_P=\left(\frac{\partial q}{\partial T}\right)_P=C_P$ The equation shows that the enthalpy is related to an experimental quantity, the isobaric heat capacity, which is also a state function.

$$H_f-H_i=\int_i^f C_P dT$$

For an ideal gas, the isobaric heat capacity is constant and $H_f - H_i = C_P(T_f - T_i)$. Enthalpy values for real vapours and gases at low pressures, with empirical temperature dependences of C_P are calculated using $H_f - H_i = \int_i^f C_P dT$

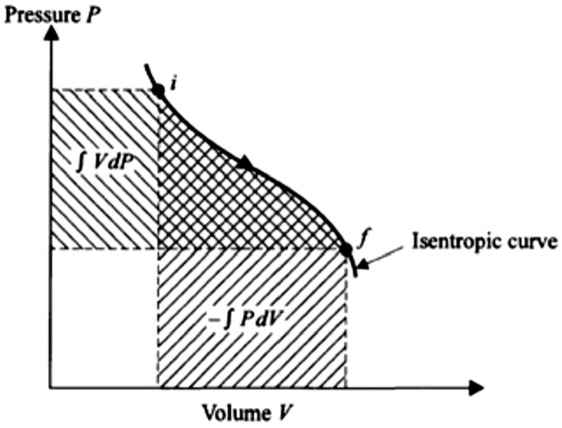
And the results are expressed as specific enthalpy or molar enthalpy as a function of temperature. Such data are extremely useful in experimental or practical work, even though , in theory, the characteristic function enthalpy H(P,S) is not expressly a function of temperature.

The enthalpy is related to heat as shown dH = dq + VdP

Thus the change in enthalpy during an isobaric process (dP = 0) is equal to the heat that is transferred between the system and the surroundings. H_f- H_i = q_P (isobaric). This very equation completes the explanation of the concept of heat began earlier with the mathematical formulation or explanation of the concept of heat in the first law . Where heat was explained as heat in transit due to a difference in temperature between the system and surroundings. For an isochoric (constant volume) process in hydrostatic system, heat is the flow of internal energy; whereas for an isobaric process in hydrostatic system, heat is the flow of enthalpy. The change of enthalpy of a system during an isobaric chemical process is commonly called the "heat of reaction", but the phase enthalpy of reaction is more informative.

If heat is added to the system during first order transition (e.g. melting, boiling or sublimation) then the change of enthalpy of the system is called "latent heat". The word "latent" acknowledges that there is no change in temperature of the system when the system during a phase transition, unlike heating without a phase transition. Again, it is more informative to use the the phrase latent enthalpy.

The change in enthalpy of a system undergoing a reversible adiabatic process has an interesting graphical interpretation. From the expression dH = dq + VdP, the change of enthalpy for an adiabatic process is $H_f - H_i = \int_i^f VdP$ (adiabatic).



PV diagram illustrating the difference between work and flow-work

The integral is represented by the area to the left of curve for an isotropic process on a PV diagram. The integral - $\int PdV$ is represented by the are under an adiabatic curve on a PV diagram. There is a thermodynamic difference between the two integrals. The integral - $\int PdV$ is adiabatic work, which changes the configuration of a system with constant mass by changing the volume. The integral $\int VdP$, known as (negative) flow-work in engineering practice, is energy that is received by a flowing gas in a region of higher pressures, perhaps from pump or piston, and then carried to a region of lower pressure, such as in the continuous Joule Thompson expansion. If a pure substance undergoes an infinitesimal reversible process, then we can write

dH = TdS + VdP, which of course, is the same as equation of enthalpy, H defined H = f(S, P) initiating from H = U + PV, since U, P and V are state function so H is also a state function in the differential form.

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

The properties of internal energy U(V,S) and enthalpy (P,S) are given in table-1 for comparison of the two function. The free expansion of gas occurs in a rigid adiabatic container, which prevents work and heat from entering or leaving the system. Consequently the internal energy U is unchanged

Joule Thompson coefficient in terms of easily determinable Derivative

Since H = f(T, P), its differential is

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Dividing by dP and introducing the condition of constant H, we get

$$0 = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H + \left(\frac{\partial H}{\partial P}\right)_T \text{ or, } \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\partial H/\partial P\right)_T}{\left(\partial H/\partial T\right)_P} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

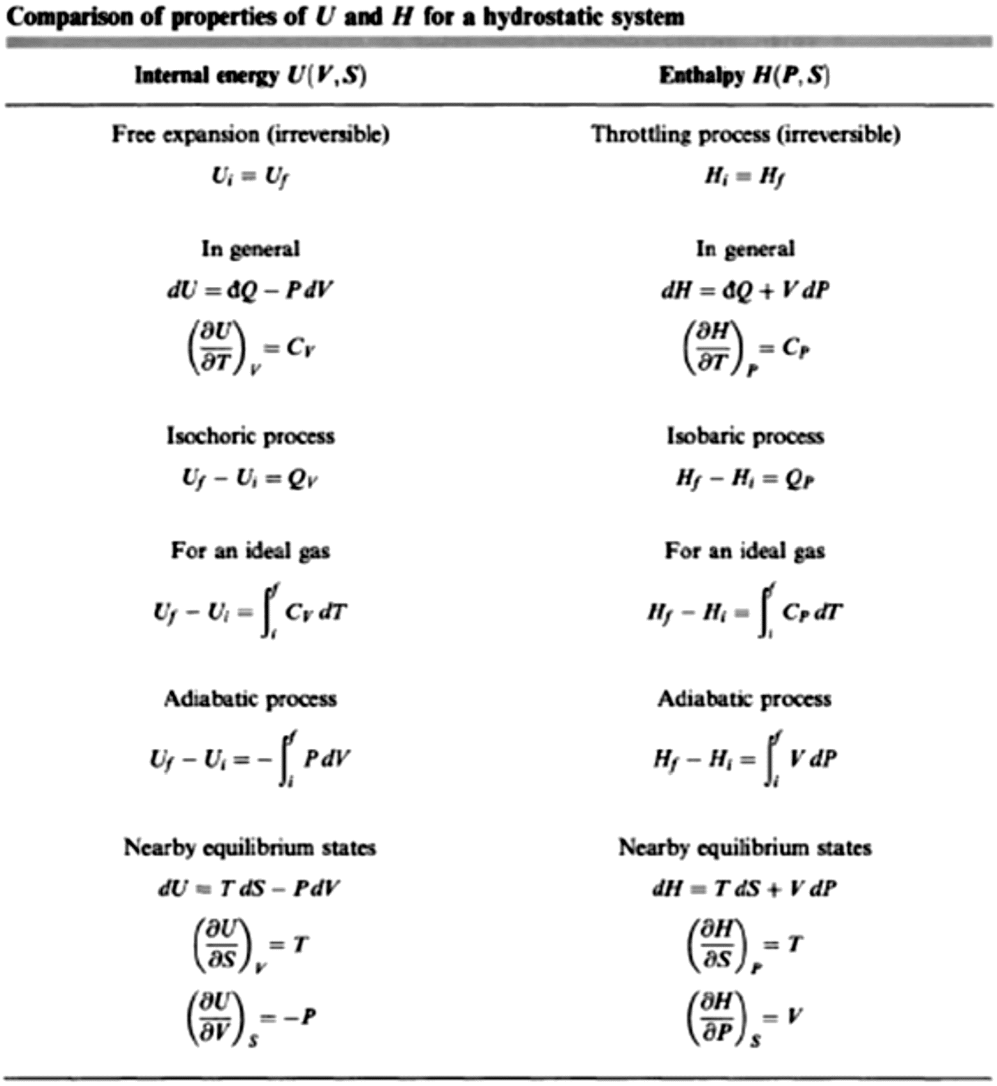
According to Thermodynamic equation of state

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P + V$$

Substituting $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T\left(\partial V/\partial T\right)_P - V}{C_P}$

Or $\mu_{JT} = \frac{V}{C_P}\left[\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P - 1\right] = \frac{V}{C_P}(T\alpha - 1)$

Table-1



Comparison of properties of U and H for a hydrostatic system

Internal energy $U(V,S)$	Enthalpy $H(P,S)$
Free expansion (irreversible)	Throttling process (irreversible)
$U_i = U_f$	$H_i = H_f$
In general	In general
$dU = \text{đ}Q - P\,dV$	$dH = \text{đ}Q + V\,dP$
$\left(\frac{\partial U}{\partial T}\right)_V = C_V$	$\left(\frac{\partial H}{\partial T}\right)_P = C_P$
Isochoric process	Isobaric process
$U_f - U_i = Q_V$	$H_f - H_i = Q_P$
For an ideal gas	For an ideal gas
$U_f - U_i = \int_i^f C_V\,dT$	$H_f - H_i = \int_i^f C_P\,dT$
Adiabatic process	Adiabatic process
$U_f - U_i = -\int_i^f P\,dV$	$H_f - H_i = \int_i^f V\,dP$
Nearby equilibrium states	Nearby equilibrium states
$dU = T\,dS - P\,dV$	$dH = T\,dS + V\,dP$
$\left(\frac{\partial U}{\partial S}\right)_V = T$	$\left(\frac{\partial H}{\partial S}\right)_P = T$
$\left(\frac{\partial U}{\partial V}\right)_S = -P$	$\left(\frac{\partial H}{\partial P}\right)_S = V$

Joule Thompson Coefficient μ_{JT}

The numerical value of the slope of the isenthalpic curve on a TP diagram, at any point is called the Joule Thompson coefficient and is denoted by μ. Thus $\mu = \left(\frac{\partial T}{\partial P}\right)_H$ **Joule Thompson coefficient** is **slope** at a point on the isenthalpic expansion curve. The locus of all points at which the Joule – Thompson coefficient is zero (the locus of the maxima of the isenthalpic curves) is known as **the inversion curve**.and is shown for Nitrogen.

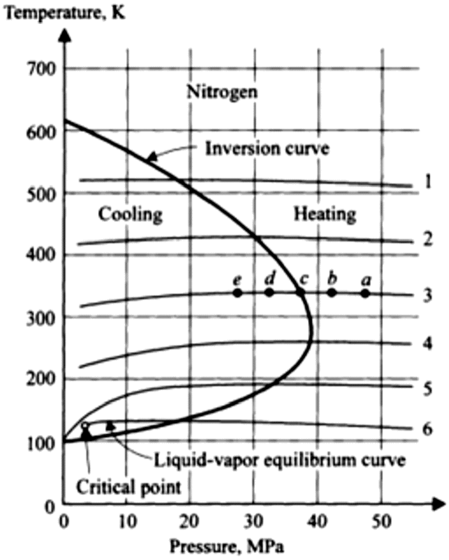


FIGURE
Isenthalpic curves, labeled 1–6, and inversion curve for nitrogen. In the region below the liquid–vapor curve, the substance is in the liquid phase.

The region inside the inversion curve is, μ, positive and is called region of cooling that is final temperature of the gas is less than the initial temperature; whereas outside the inversion curve, μ is negative is called region of heating, that is final temperature is more than the initial temperature . For example , expansion represented by movement from point (a)to either (b) or (c) raises temperature of the gas, whereas movement from (c) or (d) to (e) lowers the temperature of the gas..

Inversion Temperature

Or $\mu_{JT} = \frac{V}{C_P}2 = 0$

$T_i = \frac{1}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\alpha_1}$ where α_i is the coefficient of thermal expansion of the gas at the temperature T_i.

Joule Thompson Coefficient and van der Waals equation of state

Expression for μ_{JT} **is** $\mu_{JT} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$

The expression for = $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$

Substituting the same $\mu_{JT} = \frac{1}{C_P}\left[\frac{RT}{P - \frac{a}{V_2} + \frac{2ab}{V_3}} - V\right] = \frac{1}{C_P}\left[\frac{\left(P + \frac{a}{V^2}\right)(V-b)}{p - \frac{a}{V^2} + \frac{2ab}{V^3}} - V\right]$

$= \frac{1}{C_P}\left[\frac{\frac{2a}{V} - \frac{3ab}{V^2} - Pb}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}\right]$ Equation (i) $-\frac{a}{V^2} + \frac{2ab}{V^3}$ ignored in comparison to P (ii) PV = RT

$\mu_{JT} = \frac{1}{C_P}\left[\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b\right]$. If the temperature of the gas is not too low and pressure not too high. The equation is reduced to $\mu_{JT} = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$

OR $\left(P + \frac{a}{V^2}\right)(V - b) = PV + \frac{a}{V} - Pb - \frac{ab}{V^2}$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P \frac{\partial}{\partial V}[PV + \frac{a}{V} - Pb - \frac{ab}{V^2}] = \frac{\partial}{\partial T}(RT)$$

$\therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} = \frac{R}{P - \frac{a}{V^2}}$ neglecting $\frac{2ab}{V^3}$

$$\therefore T\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} = \frac{R}{\frac{RT}{V-b} + \frac{2a}{V^2}}$$

$$= \frac{RT}{\frac{RT}{V-b}\left[1-\frac{2a(V-b)}{RTV^2}\right]} = (V-b)\left[1-\frac{2a(V-b)}{RTV^2}\right]^{-1}$$

$$T\left(\frac{\partial v}{\partial T}\right)_P - V = (V-b)\left[1+\frac{2a(V-b)}{RTV^2}\right] - V \text{ neglecting higher terms}$$

$$= (V-b) + \frac{2a}{RT}\left(\frac{V-b}{V}\right)^2 - V = \frac{2a}{RT} - b \quad \because \frac{V-b}{V} = 1$$

$$\therefore \mu_{JT} = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right].$$

In J-T expansion cooling occurs when molecules have to do work to overcome the intermolecular attraction in order to pass through the porous plug and this occurs at low temperature where the effect of intermolecular attraction prevails. Heating occurs due to repulsive force and molecular size. In this case work is done on the molecules which are passing out through the porous plugby the molecules remaining behind the outgoing molecules within the porous plug. If the expression of $\left(\frac{\partial V}{\partial T}\right)_P, \frac{2ab}{V^3}$ is not neglected, two temperatures would be obtained.

Difference between J-T expansion and adiabatic expansion

J-T expansion :

The gas expands through porous plug under adiabatic condition. Ideal gas exhibits no change in temperature. For real gas, cooling or heating or no change of temperature depends upon , the initial temperature and pressure of the gas . $\Delta H = 0$; the process is isenthalpic. $dS_{sys} > 0$

Reversible adiabatic expansion

For any gas always cooling effect is observed and this happens whatever may be the initial pressure and temperature of the gas $\Delta H = nC_P\Delta T$ and is (–) during expansion, $dS_{sys} = 0$ if the expansion occurs reversibly and $dS_{sys} > 0$ if it occurs irreversibly. $\left(\frac{\partial T}{\partial P}\right)_H < \left(\frac{\partial T}{\partial P}\right)_S$.

3.11 Summary

In this unit we mainly learned about the second law of thermodynamics. It is one of the highly useful statement for all areas of science since it formulises spontaneous processes and gives the concept of entropy. Entropy along with enthalpy is a major contributor to the energy transfer processes including chemical transformations. combination of two laws of thermodynamics i.e. first and second law helped us in deviving principles of carnot engine. Furthermore, we learned about Gibbs and Helmholtz free energy functions and their appicability. The relationship of Gibbs and Helmholtz free energy with other thermodynamic parameters helps us in understanding and quantifying physical and chemical processes.

3.12 Questions

1. Using appropriate Carnot theorem, show that $(dq/T) < 0$ for irreversible cycle.
2. A person claims that a heat engine extracts 1000 J heat from a heat reservoir of temperature 540 K, produces 450 J of work and rest amount of heat rejects to the heat reservoir of temperature 300 K. Is his claim feasible ? Give reason(s) in support of your answer.
3. Show that $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$, using appropriate Maxwell relation. Hence find the ΔU and ΔH for isothermal expansion of n mol of a gas obeying the equation $P(V - nb) = nRT$. Comment on your findings.
4. Show that isothermal reversible expansion work is equal to decrease in work function of the system.
5. Free energy of a cup of hot tea decreases with its spontaneous decrease of temperature in open container. Justify or criticize.
6. Calculate q, w, ΔH, ΔG, ΔA and ΔS for the following change

   H_2O (v) H_2O (l) at 373 K and 1 bar.

   Given $\Delta H_{vap} = 2258 \text{ J g}^{-1}$ at 373 K.
7. (a) Prove that between two given heat reservoirs a reversible engine is always more efficient than an irreversible engine.

   (b) Prove that it is impossible for two reversible adiabatic curves on a P–V diagram to intersect.

   (c) In a Carnot Cycle, one mole of a gas ($\gamma = 1.4$) is taken as the thermodynamic substance. The initial state of the gas is 600K, 20 atm while the state of the gas at the end of second step becomes 300K and 1 atm. Calculate the work involved in the first step of the cycle and the total work per cycle.

(d) Prove that $\oint \frac{dq}{T} \leq 0$ and from this expression show that $ds \geq \frac{dq}{T}$

(e) Prove thermodynamically that $C_P > C_V$

(f) Show that for van der waals gas $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$

(g) Prove that if $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for any gas, then it does not necessarily follow that = 0 also

(h) A person claims to have devised a cyclic engine which exchanges heat with reservoirs at 300K and 540K, and which can produce 450J of work per 1000J of heat extracted from the hot reservoir. Is the claim feasible ?

8. (a) Draw T – S diagram of a Carnot cycle. Label the state and various processes involved . What does the enclosed area signify ?

(b) How much heat (in joules) is rejected to the surroundings when 10 grams of water at 0°C freezes to ice at 0°C, in a Carnot refrigerator where T_H = 298 K and T_C = 268 K ? [Latent heat of fusion of ice at 0°C = 336 $J.g^{-1}$]

(c) Show that for an isothermal expansion of an ideal gas $\Delta G = \Delta A$.

(d) 'An endothermic process with ΔS = –ve is thermodynamically impossible ' – Justify or criticize.

(e) One mole of water vapour is compressed reversibly to liquid water at 373K. Calculate w,q. ΔE, ΔH, ΔG and ΔS. Given : $\Delta H_{vap}(373K)$ = $2258.1J_g^{1}$.

9. (a) A reversible Carnot refrigerator working between 0°C 25°C is for one minute using a 0.25 horsepower electrical motor .

Find

(i) the coefficient of performance of the refrigerator.

(ii) the amount of heat (in Joules) extracted from the water kept inside at 0°C,

(iii) The mass of ice produced. [Given : 1 hp = 746 W, 1 calorie = 4.2 J, latent heat of fusion of ice = 80 cal/g.]

(a) Write expressions for the quantity q/T (with proper justifi-cation) for each of the four steps of a Carnot cycle using an ideal gas and hence for the entire cycle. Comment on the result.

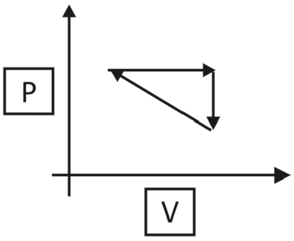
(b) Derive thermodynamically the relation.

$$C_P = -C_V = \left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)\left(\frac{dV}{dT}\right)P$$

Show that for a gas obeying the equation of state P(V – b) = nRT, C exceeds C_v by the quantity nR.

10. (a) an engine takes up 5×10^4J heat to complete the following cycle. Given $|\Delta P| = 10\text{atm}, |\Delta V| = 10$ litres, find its efficiency.

(b) Define a cyclic process, Differentiate a reversible cyclic process from an irreversible cyclic process one in terms of net work done by the system



and entropy change of the universe.

(c) One mole of an ideal gas is expanded adiabatically, but universally from V_1 to V_2 and no work is done, w = 0

(i) Does the temperature of the gas change?

(ii) What is ΔS of the gas and ΔS of the surroundings?

(d) Ten mole of an ideal gas expands isothermally and reversibly from pressure of 10 atmto 1 atm. Calculate w, q, ΔG, ΔA

(e) The molar Gibbs free energy of a certain gas is given by G = RTlnP +a + bP +cP^2, where a, b, c are numerical constants. Obtain the equation of state for the gas.

(f) Deduce Thermodynamic equation of state involving enthalpy.

Calculate $\left(\frac{\partial H}{\partial P}\right)_T$ for a gas obeying PV = RT +B(T)P

(g) Point out the characteristics of a first order phase transition. Plot G versus T and $\left(\frac{\partial G}{\partial P}\right)_P$ versus T for such a transition, with proper reasoning.

(h) Derive the following (i) $\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}[\alpha T - 1]$ (ii) $\left(\frac{\partial T}{\partial P}\right)_S = \frac{V\alpha T}{C_P}$

α, is coefficient of thermal expansion

3.13 References

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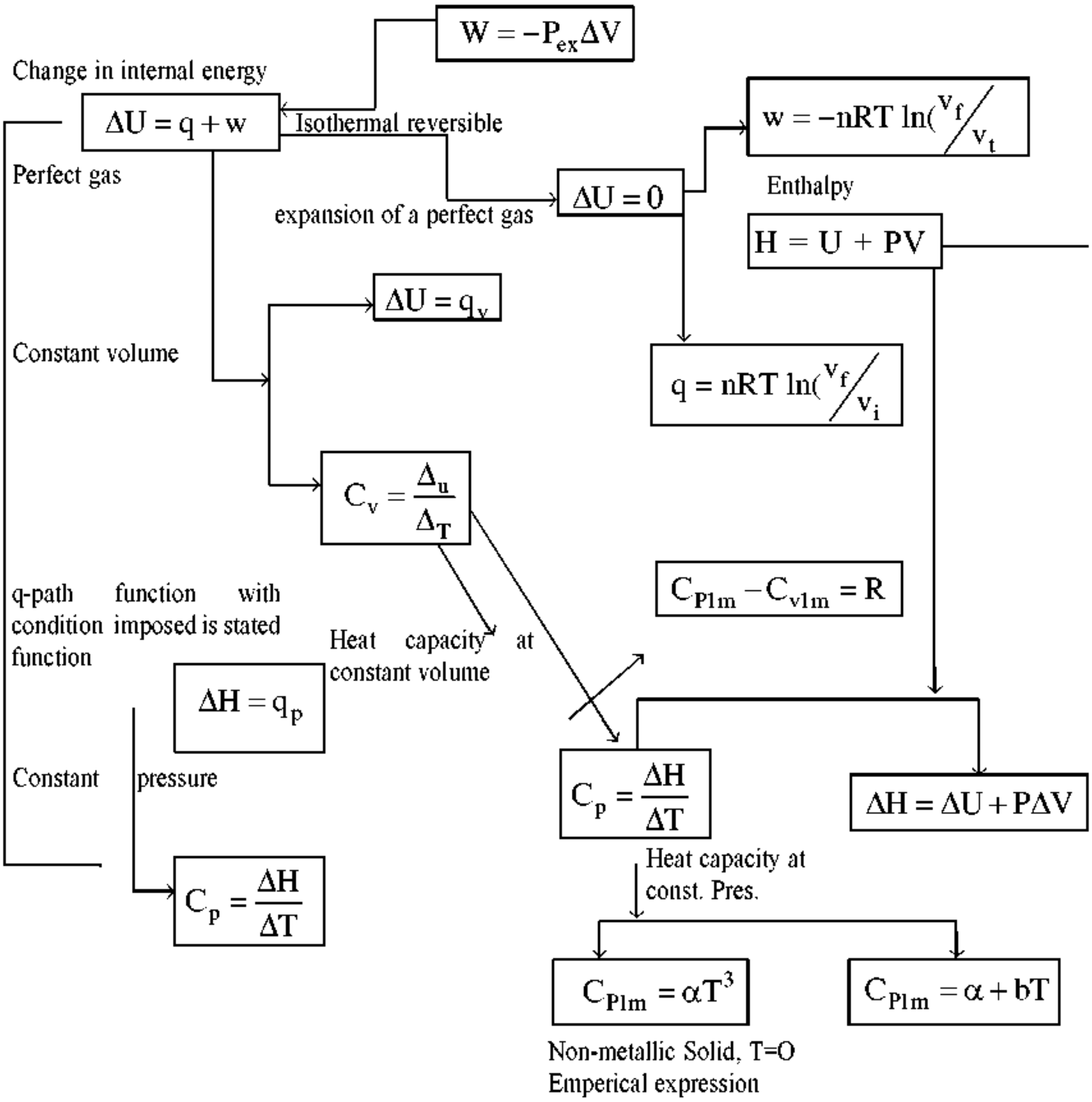
ROAD MAP OF KEY EQUATION

Mechanical work expansion or compression



Unit 4 ❑ Chemical Kinetics

Structure

4.1 Objectives

On completion of the study of this unit, the learner will be able to—

(i) determine rates of reaction.

(ii) recall the conditions which affect reaction rates.

(iii) recognize order of reaction, give rate equation, calculate rate constant.

(iv) explain collision theory and transition state theory.

(v) identify catelysts and their properties.

(vi) explain enzyme kinetics.

4.2 Introduction

In chemistry, we frequently come across two important topics viz. “Chemical Kinetics” and “Chemical Dynamics”. In fact chemical kinetics and thermodynamics are very important branches of chemistry. Thermodynamics talks about the feasibility of the reaction whereas chemical kinetics talks about the speed of the reaction. The subject is important because the designer of a chemical plant must know how the rates of reaction taking place in it are affected by changes of temperature, pressure and concentration. To be useful, the reaction must occur at a reasonable rate. Chemical kinetics is important in biology, medicine because health represents balance between large number of interdependent reactions. It provides us with plausible mechanism.

4.3 Fundamentals of Chemical Kinetics

4.3.1 Rate of the reaction

Rate of the reaction at any instant of time depends upon the concentration of reactant at that instant of time. As the reaction proceeds, the concentration of the reactants decreases with time. Thus for the following reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

$$t = 0 \quad a \quad 3a \quad 0$$

As time proceeds the concentration of reactants decrease and that of products, NH_3 increases. The rates of change of the concentration of the three species are related

$$-\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt} \text{ units mol } L^{-1} \; s^{-1}$$

Advancement of a reaction

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

If the above reaction is said to be advanced to ξ = 1mol, then, the changes in the number of moles of the reacting species are

$\Delta n_A = -\alpha\Delta\xi = -\ \alpha(1mol) = -\alpha$ mol, and similarly

$\Delta n_B = -\beta\Delta\xi = -\ \beta(1mol) = -\beta$ mol,

$\Delta n_C = \gamma\Delta\xi = \gamma\ (1mol) = \gamma$ mol,

$\Delta n_D = \delta\Delta\xi = \delta\ (1mol) = \delta$ mol,

Now during the reaction, if the reaction be advanced from ξ to $(\xi + d\xi)$ over the time period t to (t + dt) then the changes in the number of moles

$dn_A = -\alpha d\xi$; $dn_B = -\beta d\xi$; $dn_C = \gamma d\xi$; $dn_D = \delta d\xi$

The rate of change of the number of moles of the component with time

$$\frac{dn_A}{dt} = -\alpha\frac{d\xi}{dt}; \frac{dn_B}{dt} = -\beta\frac{d\xi}{dt} \qquad \frac{dn_C}{dt} = \gamma\frac{d\xi}{dt}; \frac{dn_D}{dt} = \delta\frac{d\xi}{dt}$$

$$\frac{d\xi}{dt} = -\frac{1}{\alpha}\frac{dn_A}{dt} = -\frac{1}{\beta}\frac{dn_B}{dt} = \frac{1}{\gamma}\frac{dn_C}{dt} = \frac{1}{\delta}\frac{dn_D}{dt}$$

Rate of reaction can now be defined as the rate of change of the advancement with time per unit volume of the reaction mixture. At constant volume, the rate of reaction

$$v = \frac{1}{V}\frac{d\xi}{dt} = -\frac{1}{\alpha}\frac{d[A]}{dt} = -\frac{1}{\beta}\frac{d[B]}{dt} = \frac{1}{\gamma}\frac{d[C]}{dt} = \frac{1}{\delta}\frac{d[D]}{dt}$$

Example

Note. $\frac{dn_A}{dt}$ where A is disappearing is negative quantity and it represents the rate of conversion, J, which is extensive quantity. Rate of reaction is $\frac{J}{V} = \frac{1}{V}\left(-\frac{1}{\alpha}\frac{dn_A}{dT}\right)$ is intensive.

Problem

Calculate the rate of the advancement of the reaction with time for the reaction A → P at an instant is the rate (v) at that instant is found to be 4 × 10^{-9} moldm^{-3} s^{-1}. The volume of the reaction mixture is 3L.

Solution

$$v = \frac{1}{V}\frac{d\xi}{dt}$$

$$\frac{d\xi}{dt} = v\ \ V = (4\times10^{-6}\ \text{mol dm}^{-3}\text{s}^{-1})\ (3\text{dm}^3) = 1.2\times10^{-5}\text{mol s}^{-1}$$

Q. For the reaction, $2N_2O_5 \rightarrow 2\ N_2O_4 + O_2$, the rate of the reaction at an instant is $-\frac{d[N_2O_5]}{dt}$

= x mol lit^{-1}sec^{-1} At the same instant, the rate expressed as $\frac{d[O_2]}{dt}$ is

(a) –(x/2) mol lit^{-1}sec^{-1} (b) –2x mol lit^{-1}sec^{-1} (c) 2x mol lit^{-1}sec^{-1} (d) (x/2) mol lit^{-1}sec^{-1}

Ans. d

4.3.2 Rate law and Rate Constant

Rate laws or rate equations give the relationship between the rate of a chemical reaction and the concentration of its reactants. According to rate law, the rate of the reaction is directly proportional to the product of concentration of reactants raised to the power of their numerical coefficients as determined experimentally. For the reaction

$\alpha A + \beta B \rightarrow \gamma C + \delta D$

where A and B are the reactants and C and D are products

Rate-law expression can be written as

Rate = $k[A]^m [B]^n$

where the proportionality constant k is the rate constant or is also referred to as rate coefficient and m & n refers to the order with respect to reactants A and B. The order with respect to a component is the power to which the concentration of that component is raised in the rate law

Q. Three sets of concentrations and the corresponding rates are given below for the reaction,

$A + B \rightarrow P$

[A]	[B]	rate
(mol lit^{-1})	(mol lit^{-1})	(mol lit^{-1} sec^{-1})
2×10^{-3}	3×10^{-3}	1.2×10^{-3}
2×10^{-3}	6×10^{-3}	4.8×10^{-3}
4×10^{-3}	3×10^{-3}	2.4×10^{-3}

The reaction orders with respect to A and B are respectively

(a) 0, 1 (b) 1, 0 (c) 1, 1 (d) 1, 2

Ans : d.

Characteristics of rate constant

- It is the characteristic of the reaction
- The rate constant quantifies the rate of a chemical reaction. The value of rate constant depends upon conditions like temperature, ionic strength, surface area of the absorbent etc.
- The value of rate constant is environment and reaction specific.
- It is dependent on temperature.

- For a particular reaction, the rate constant is independent of concentration.
- Rate constant for any reaction is a macroscopic quantity as it can be determined experimentally.
- Rate constants are different for different reactions.

4.3.3 Order and Molecularity

The order of a reaction with respect to a particular reactant is the power (or exponent) to which the concentration of the reactant is raised in the rate expression. (This is called partial order). The sum of the orders with respect to various reactants is called the overall order or total order of the reaction. Thus for the reaction, $xA + yB \rightarrow lL + mM$, if the rate is $\infty [A]^x [B]^y$, the total order of the reaction is $(x+y)$

Molecularity : Molecularity is defined as the minimum number of atoms / molecules / ions / radicals taking part in an elementary reaction (chemical reactions in which one or more of the chemical species react directly to form products in a single reaction step). Or simply, one can say that molecularity refers to the number of molecules consumed in a chemical reaction. Examples :

$N_2O_5 \rightarrow NO_2 + NO_3$ Molecularity = 1

$2H_2 + O_2 \rightarrow 2H_2O$ Molecularity = 2

Molecularity is defined for elementary reactions. Molecularity is a theoretical concept. Molecularity is always an integer value and can never be zero for a chemical reaction. Molecularity is invariant for a chemical equation. It provides no information about reaction mechanism.

The rate laws and the order of the reaction are determined experimentally as these cannot be predicted from the stoichiometry of the reaction. The stoichiometry of the reaction gives the relationship between the amounts of the reactants and the amounts of the products. Thus, it is important to remember that the order of a reaction need not be identical with the stoichiometric coefficient of the reactant.

Integrated, differential rate laws with Examples of zero, first and second order reactions

Order	**Reaction Type**	**Differential rate law**	**Integrated rate law**	**Straight line Plot**
0	A→P	$\frac{d[A]}{dt} = -k$	$kt = [A]_o - [A]$	[A] vs t
1	A→P	$\frac{d[A]}{dt} = -k[A]$	$[A]_t = [A]_o e^{-kt}$ or $kt = \ln \frac{[A]_0}{[A]_t}$	*l*n[A] vs t
2	A→P	$\frac{d[A]}{dt} = -k[A]^2$	$kt = \frac{1}{[A]_t} - \frac{1}{[A]_o}$	$\frac{1}{[A]}$ vs t
2	A + B→P	$\frac{d[A]}{dt} = -k$ [A] [B]	kt = $\frac{1}{([B]_o - [A]_o)} \ln \left(\frac{[A]_o [B]}{[B]_o [A]} \right)$	$\ln = \left(\frac{[B]}{[A]} \right)$vst

EXAMPLES

Order	**Reaction Type**	**Half life**	
0	**A → P**	$\frac{[A]_0}{2k}$	Several heterogeneous reactions, decomposition of HI gas on gold surface

1	**A → P**	$\ln\frac{2}{k}$	$N_2O_5 \rightleftharpoons NO_2 + NO_3$, Decomposition of H_2O_2 Decomposition of azoisopropane
2	**A → P**	$\frac{1}{k[A]_o}$	Saponification of ester $CH_3COOC_2H_5$ + NaOH → CH_3COONa + C_2H_5OH

Chemical Reactions can be classified as:

a. Fast reaction: Precipitation of AgCl

$AgNO_3 + NaCl \rightarrow AgCl$ (precipitate ↓) $+ NaNO_3$

b. Slow reaction: Rusting of iron

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$ (Rust)

c. Moderate reaction : These are those reactions that take place in few minutes or hours.

Example – Digestion of food.

Very fast and slow reactions are ruled out in laboratory exercises. Only moderate reactions are studied in laboratory. Example – Hydrolysis of methyl acetate

$CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$

Pseudo First order reaction

The reactions that appear to be second order in nature but are approximated as a first-order of reaction on close analysis. For example, a second – order of reaction is given by the equation,

A + B ——> C + D

This reaction is dependent upon the concentrations of both A and B but one of the components is present in large excess and thus its concentration hardly changes as the reaction proceeds. So, if component B is in large excess and the concentration of B is very high (minimum ten times) as compared to that of A, the reaction is considered to be pseudo-first order reaction with respect to A and if component A is in large excess and the concentration of A is very high as compared to that of B, the reaction is considered to be pseudo first order with respect to B.

e.g. $\mathbf{CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH}$

Rate = $\mathbf{k\,[CH_3COOC_2H_5]\,[H_2O]}$

In the above reaction the concentration of water is very high and thus does not change much during the course of the reaction. Thus the rate of the reaction can be said to be independent of the change in the concentration of H_2O. Putting the term for change of concentration of water in the above reaction to be zero we can write the effective rate equation as,

Rate = $\mathbf{k'\,[CH_3COOC_2H_5]}$

Here, the term k′ takes into account the value of the constant concentration of water.

4.3.4 Rate constants of Reactions

A + B → Products.

Tthe rate law of the reaction is **Rate =** $\mathbf{\mathit{k}\,[A]^m\,[B]^n}$, where the proportionality constant k is called the rate constant of the reaction or specific reaction rate. The rate constant is the rate of the reaction , when the concentration of the reacting species are each unity. The order of the overall reaction is n+m=overall order or order. Regarding the unit of the rate constant,

since rate = $k(\text{Concentration})^n$

$k = \text{rate} / (\text{Concentration})^n$

Order of reaction	**Value of n**	**Unit of rate constant**
0	0	$(\text{conc})^1\text{time}^{-1}$ i.e. mole $\text{lit}^{-1}\text{time}^{-1}$
1	1	$(\text{conc})^0\text{time}^{-1}$ i.e. time^{-1}
2	2	$(\text{conc})^{-1}\text{time}^{-1}$ i.e. lit mole^{-1} time^{-1}
3	3	$(\text{conc})^{-2}\text{time}^{-1}$ i.e. lit^2 mole^{-2} time^{-1}

Note: The Zero order rate constant has the same unit as the rate of a reaction

Determination of order of a reaction by half-life and differential method.

Half – life method

This method is used only when the rate law involved by only one concentration term. $t_{1/2} \propto a^{1-n}$

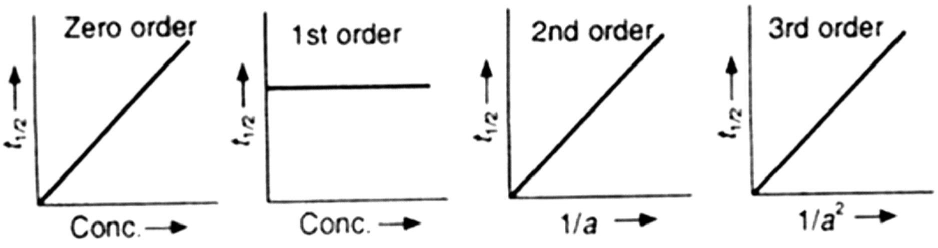
$t_{(1/2)} = k'1/a^{n-1} = \frac{\text{cons tant}}{a^{n-1}}$, **here a** is the initial concentration $\mathbf{\log t_{(1/2)} = \log k' + (1-n)a}$

Plot of log $t_{1/2}$ vs log a, gives a straight line with slope (1 – n), where ‘n’ is the order of the reaction. Determining the slope we can find the order n. If half life at different concentrations is given then.

$$t_{(1/2)} = \frac{k^1}{a^{n-1}} \qquad t_{(1/2)} = \frac{k^1}{a_1^{\,n-1}} \quad \textbf{Comparing}$$

$$\frac{t_{(t/2)}}{t_{(1/2)i}} = \left(\frac{a_1}{a_2}\right)^{n-1} \quad \text{Taking logarithm and rearranging} \quad n = 1\frac{\log(t_{1/2}) - \log(t_{1/2})_t}{\log a_1 - \log a}$$

Plots of half-lives concentration $(t_{1/2} \infty a^{1-a})$



van’t Hoff Differential Method

The rate of a reaction varies as the nth power of the concentration of the reactant where “n” is the order of the reaction. Thus for two different initial concentration C_1 and C_2.The equations can be written as

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n \log C_1 \text{ and } \log\left(-\frac{dC_2}{dt}\right) = \log k + n \log C_2$$

Substracting one from the other

$$\log\left(-\frac{dC_1}{dt}\right) - \log\left(-\frac{dC_2}{dt}\right) = n\,(\log C_1 - \log C_2)$$

$-dc_1/dt$ and $-dc_2/dt$ are determined from concentration vs. time graphs and the value of ‘n’ can be determined.

4.3.5 Complex Reactions

Opposing or Reversible Reaction

Certain reactions in which product of a chemical change react to form the original reactants are known as reversible or opposing reactions. In opposing reaction, the net rate of the reaction will be influenced by both forward and backward rates and that causes serious disturbance in the measurement of reaction

Ex : 1. Muta rotation of α D glucose into β-D glucose

2. Conversion of ammonium cyanate into urea

There are several types of opposing reaction

(1) Both forward and backward reactions are of first order

(2) First order reaction is opposed by second order

(3) Both forward and backward reactions are of second order.

Let us consider the case when the both forward and backward reactions are of first order

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

here k_1 and k_2 represents first order rate constants for the forward and backward reactions respectively. Suppose 'a' is initial concentration of A, then after time t, x mole of A decomposed to form B. Thus the concentration of A after a time t is a – x and that of B is x. Therefore, the rate of forward and backward reactions equals to k_1 (a-x) and k_2 x. Thus, the net rate of formation of B is

$\frac{dx}{dt} = k_1 (a - x) - k_2 x$, at equilibrium the net rate is zero, $\frac{dx}{dt} = 0$

$0 = k_1 (a - x_e) - k_2 x_e$ (x_e is the equilibrium concentration)

$k_2 = k_1 (a - x_e)/x_e$

Substituting the k_2 into the original equation, $\frac{dx}{dt} = k_1 (a - x) - [k_1(a - x_e)/x_e]x$

$$\frac{dx}{dt} = k_1(a - x) - k_1\left(\frac{a - x_e}{x_e}\right)x = k_1\frac{(x_e - x)a}{x_e}$$

Separating the variables, $\frac{dx}{x_e - x} = \frac{a}{x_e}k_1 dt$

Integrating, t = 0, x = 0

$$-\frac{x_e}{a}[\ln(x_e - x)] = k_1 t - \frac{x}{a}\ln x_e$$

$$k_1 t = \frac{x_e}{a}\ln\left(\frac{x_e}{x_e - x}\right)$$

$$k_1 = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right)$$, expressed in easily measureable quantities

$$k_1 + k_2 = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right) + \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right)\frac{(a - x_e)}{x_e}$$

$$k_1 + k_2 = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right)(1 + \frac{(a - x_e)}{x_e}$$

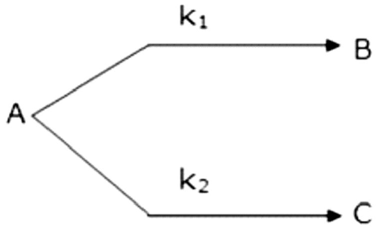
$$k_1 + k_2 = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right)\frac{a}{x_e} = \frac{1}{t}\ln\left(\frac{x_e}{x_e - x}\right)$$

$$k_1 + k_2 = \frac{1}{t}\ln\left(\frac{x_e}{x_e - x}\right)$$

knowledge of k_{1-},a and x_e The rate constant for reverse reaction can be obtained.

Parallel Reaction

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



If we assume that both of them are first order, we get

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

k_1 = fractional yield of B × k_{av}

k_2 = fractional yield of C × k_{av}

If $k_1 > k_2$ then

A → B main and

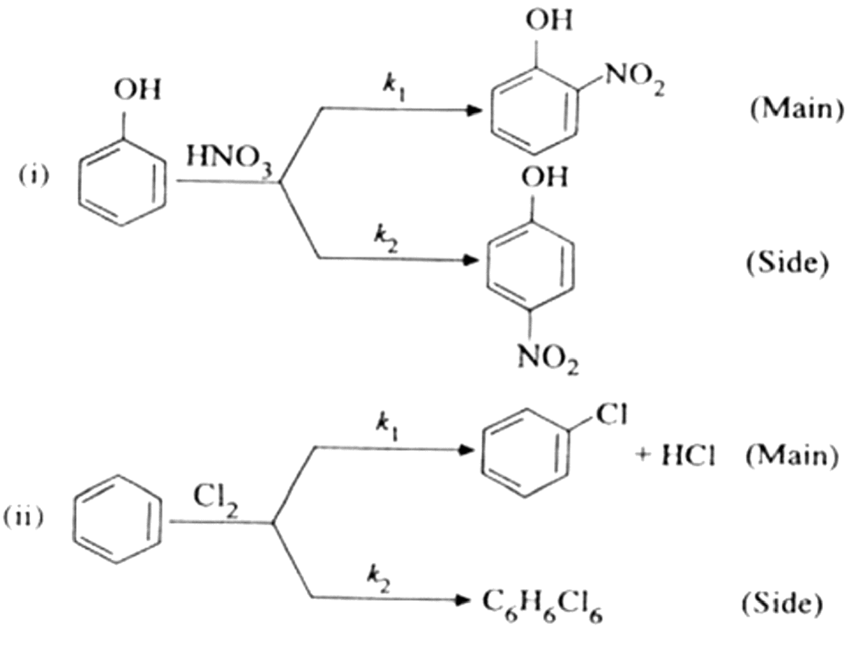
A → C is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

$$\frac{x}{y} = \frac{k_1}{k_2}$$

$$\text{i.e } \frac{\frac{d|B|}{dt}}{\frac{d|C|}{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2. Examples



Consecutive or Sequential Reactions

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successeive or consecutive steps.

A → B → C and so on

Example of Sequential Reactions

Decomposition of ethylene oxide

$$(CH_2)_2O \xrightarrow{k_1} CH_3CHO$$

$$CH_3CHO \xrightarrow{k_2} CO + CH_4$$

The pyrolysis of acetone

$$(CH_3)_2CO \xrightarrow{k_1} CH_4 + CH_2 = C = O$$

$$CH_2 = C - O \xrightarrow{k_2} C_2H_4 + CO$$

For the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

$$-\frac{d[A]}{dt} = k_1[A] ....(i) \qquad \frac{d[B]}{dt} = k_1[A] - k_2[B] ......(ii) \qquad \frac{d[C]}{dt} = k_2[B] ....(iii)$$

Integrating equation (i), we get [A] = $[A]_0e^{-kt}$. Now we shall integrate equation (ii) and find the concentration of B related to time t.

$$\frac{d[B]}{dt} = k_t[A] - k_2[B] \Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A]$$

substituting [A] as $[A]_0e^{-k_1t}$

$$\Rightarrow \frac{d[B]}{dt} + k_2[B] = k_t[A]_0e^{-k_1t}$$

Integrating of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore we multiply equation (4) by an integrating factor e^{k_2t}, on both the sides of the equation.

$$\left(\frac{d[B]}{dt} + k_2[B]\right)e^{k_2t} = k_1[A]_0e^{(k_2-k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]e^{k_2t}$

$$\frac{d}{dt}\left([B]e^{k_2t}\right) = k_t[A]_0e^{(k_2-k_1)t}$$

$$d\left([B]e^{k_2t}\right) = k_t[A]_0e^{(k_2-k_1)t}dt$$

Integrating with in the limits 0 to t

$$\left(\frac{d[B]}{dt} + k_2[B]\right)e^{k_2t} = k_t[A]_0e^{(k_2-k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]e^{k_2t}$

$$\frac{d}{dt}\left([B]e^{k_2t}\right) = k_t[A]_0e^{(t_2-t_1)t}$$

$$d\left([B]e^{k_2t}\right) = k_t[A]_0e^{(k_2-k_1)t}dt$$

4.3.6 Factors affecting the rate of the reaction

The rates at which reactants are consumed and products are formed vary from reaction to reaction. Some of the important factors that affect the rate of a reaction are:

Concentration of reactants : The rate of the reaction increases when the concentration of the reactants increases.

Nature of the reactants : The number of reacting species, their physical state, the complexity of the reaction greatly affect the rate of the reaction. Reactions that involve the breaking of chemical bonds or the rearrangement of molecules commonly are slower than the reactions that involve the simple combination of two ions of opposite charge.

Catalysts : Catalysts are the substances which affect the rate of the reaction without actually taking part in the reaction. They can increase or decrease the rate of the reaction.

The catalyst that increase the rate of the reaction are called positive catalyst. For example, the reaction between H_2 and N_2 occurs in the presence of Fe as a positive catalyst to form NH_3.

The catalyst that decreases the rate of the reaction are called negative catalyst or inhibitors. For example, Acetanilide acts as negative catalyst in decomposition of H_2O_2.

Pressure : On increasing the pressure, the reactants come closer to each other. Therefore, frequency of collisions increases thereby increasing the rate of the reaction. The effect of pressure occurs only for the gaseous molecules. The reactions involving liquids and solids are not affected by change of pressure since liquids and solids are

Intensity of radiation : In photochemical reactions, the rate of the primary step that involves light absorption depends only on the absorbed light and not on the factors like concentration and temperature.

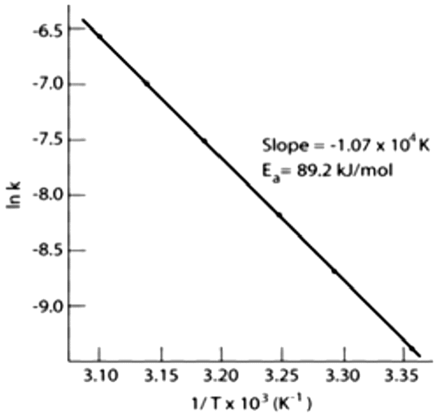
Note : The units of rate constant depend upon the order of the reaction. And the unit for Rate of reaction is always concentration/time always irrespective of order or rate constant for a particular reaction.

4.4 Arrhenius Equation

Temperature dependence of reaction rate

A- Arrhenius Parameter

It is experimentally observed that for several reactions, an increase of temperature by about 10 degrees Kelvin increases the reaction rate (or rate constant) to a large extent; usually $\frac{k_{T+10}}{k_T} = 2$. There is no rigidity about this ratio of 2; it may be less or more than 2, depending on the nature of the reaction and the temperature at which the difference of 10 K is considered.



By measuring the slope of the line, one can calculate the magnitude of activation energy.

Arrhenius observed that for a large number of reactions a plot of ln k versus $\frac{1}{T}$ is a straight line with a negative slope. The rate constant k increases exponentially with temperature : $k = A\,e^{-\frac{E_a}{RT}}$ where the proportionality constant A is called pre-exponential factor called the frequency factor. E_a is called the (experimental) energy of activation. A and E_a are known as Arrhenius parameters. From Arrhenius equation one may note that low activation energy means a fast reaction and high activation energy means a slow reaction. The rapid increase in k with increase of T is mainly due to the increase in the number of collisions between the molecules whose energy exceeded the activation energy

It is this exponential relation that explains the large change in the rate constant with temperature.

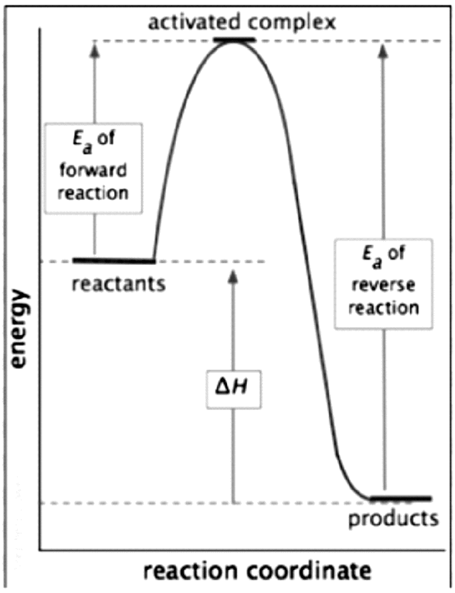
Taking logarithm, $ln\ k = ln\ A - \frac{E_a}{RT}$ i.e. $\frac{d\ln k}{dt}$ or $\frac{1}{k}\frac{dk}{dT} = \frac{E_a}{RT^2}$

In this expression, $\frac{1}{k}\frac{dk}{dT}$ or sometimes $\frac{dk}{dT}$ itself, is called the temperature coefficient of reaction rate or rate constant. The integrated form of the above expression is $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ where k_1 and k_2 are the rate constants at temperature T_1 and T_2 respectively. This expression is similar to the vant Hoff's Reaction Isochore.

4.4.1 Significance of energy of activation :

In order that molecules may react, products get formed it is necessary that they must overcome an energy barrier and for this purpose, the molecules must possess a minimum energy. When the reactant molecules come close and collide with each other at same time then during the collisions the rearrangement between the molecules takes place which leads to the formation of products. The molecular rearrangement usually involves breaking of some bonds and making others. Only when the energy of the colliding molecules is equal to or greater than the minimum energy required for the rearrangement, the molecular rearrangement takes place followed by the product formation. The difference between this minimum energy required or reacting and the average energy of the reacting molecules is known as the energy of activation (E_a). In reversible reactions, we have E_a for the forward and the reverse reactions; the difference between these two E_a values gives the heat of the reaction, as shown in the diagram.

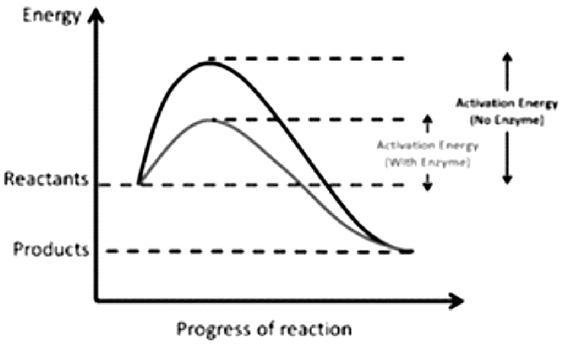
Activation energy is the energy that must be supplied to the reacting species so that an effective collision could take place whereas the minimum energy which must be possessed by the reactants to make collisions effective is referred to as Threshold energy E_o.



For elementary reactions, activation energy cannot be negative but for a complex reaction, the total activation energy can be negative.

4.4.2 The effect of catalyst on activation energy

Arrhenius equation states that the rate constant increases on increasing temperature and on decreasing activation energy. One can increase temperature easily but reducing activation energy is difficult. It can be done by addition of substance called catalyst. A catalyst accelerates or speeds up the reaction but it does not undergo any chemical change. The catalyst lowers the activation energy of the reaction by providing an alternative path that avoids slow rate determining step of un-catalyzed reaction.



Although the activation energy of a reaction can be calculated from ln k vs.1/T plot, another way of obtaining it is to calculate the rate constants at two temperatures,

Problem as illustration

The rate constants of a reaction at 25°C and 65°C are respectively 3.46×10^{-5} and 4.87×10^{-3} sec^{-1}.

Problem

Calculate the energy of activation of the reaction. Also calculate the frequency factor.

$$\ln\frac{k_2}{k_1}=\frac{E_0}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\log\frac{k_2}{k_1}=\frac{E}{2.303\times1.987}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]=\log\frac{4.087\times10^{-3}}{3.46\times10^{-3}}=\frac{E_a}{4.576}\left[\frac{40}{298\times338}\right]$$

E_a = 24750 cals

Frequency Factor A

$$k = A\,e^{\frac{E_a}{RT}}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

$A = 4.885 \times 10^{13}$

4.5 Collision Theory of bimolecular gaseous reactions

Collision Theory explains how chemical reactions occur and why reaction rates differ for different reactions. This theory is based on kinetic theory of gases and assumes that

(a) Molecules are hard spheres and are impenetrable (can at most touch each other).

(b) Reaction may occur only when molecules approach and collide with each other.

(c) Reactions occur only if molecules are energetic.

(d) Collisions should transfer certain minimum energy.

4.5.1. Principles of Collision Theory

Collision Theory predicts the rate of the reaction based on two postulates:-

(i) The product formation takes place only when the reactant molecules come close and **collide** with each other.

(ii) Only those collisions lead to the formation of products which satisfy the **criteria of energy of activation** and **specific orientation** of molecules.

Thus every collision does not lead to the product formation. Only those collisions which occur between molecules having minimum threshold energy E_A will lead to product formation and such collisions are known as **effective collisions**. If every collision leads to the formation of product, then the rate of the reaction will entirely be determined by the collision rate, i.e., frequency with which reactants collide. Thus, it gives the maximum rate that can be observed experimentally for the given reaction Now, let us consider the reaction in which the molecules are considered to be rigid, hard spheres with no forces of attraction and repulsion: **A + B → Products**

Rate of the reaction can be given by the equation: $Rate = Z_{AB}e^{-\frac{E_A}{RT}}$, where Z_{AB} refers to the number of collisions that occurs per unit volume per unit time. It is also referred to as Collision density. The number of collisions per unit volume per unit time in such reactions are given by the expression,

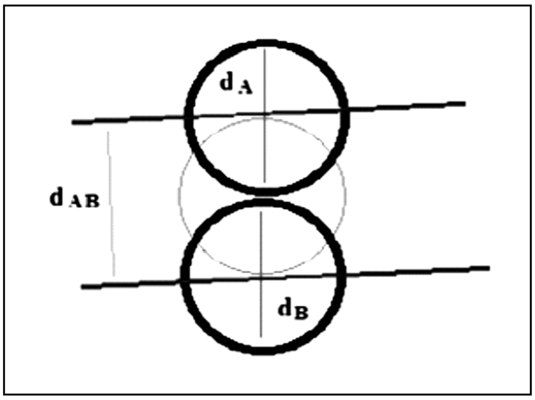
$Z_{AB} = \sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} n_A n_B$ where σ is the collision cross section and it represents the closeness of approach for molecular collisions. $\sigma = \pi d^2_{AB}$ Where $d_{AB} = \frac{d_A + d_B}{2}$

(d_A and d_B are respective diameters of reactant molecules A and B.)

The collision cross section for two molecules can be regarded as the area within which the molecule A hits molecule B for collision to occur.

The radius of the contact area of molecules A and B respectively is given by the expression: $d_{AB} = \frac{d_A + d_B}{2}$. And the area of cross section is given by the expression,

$\sigma = \pi d^2_{AB}$



Also μ is reduced mass $\frac{m_A m_B}{m_A + m_B}$, k is Boltzman constant, m_A is mass of single molecule A, m_B is mass of single molecule B, and are the respective number densities of molecules of A and B. Number density is given by relation : Number of molecules /unit volume

4.5.2 Derivation of rate constant

According to classical collision theory (hard sphere theory), rate of the reaction as given by equation (**Rate** = $Z_{AB}e^{-E_A/RT}$,) depends on collision density and exponential factor. Or one can simply say that the rate of a bimolecular gaseous reaction depends on collision frequency and its probability of success.

A + B → Products

$$\textbf{Rate} = -\frac{dn_A}{dt} = kn_A n_B$$

Molar concentration is represented as [ ]

$$[A] = \frac{n_A}{N_A},\ [B] = \frac{n_B}{N_A},\ \text{where } N_A \text{ is the Avogadro number}$$

$$-\frac{dn_A}{dt} = kn_A n_B = N_A^2 k[A]\,[B]$$

$$-\frac{d\{N_A[A]\}}{dt} = N_A^2 k[A]\,[B]$$

$$-\frac{d[A]}{dt} = N_A k[A][B]$$

Substituting the expression of collision density from equation $\mathbf{Z_{AB}} = \sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}$

into the equation **Rate** = $Z_{AB}e^{-E_A/RT}$, then the Rate = $\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_A/RT}$ including n_A and n_B also

$$\text{Rate} = \sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_A/RT}\ \mathbf{N_A^2[A]\ [B]}$$

$$\boxed{\mathbf{Rate = N_A^2\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2}[A][B]e^{-E_A/RT}}}$$

Comparing the above equation with

$$-\frac{d[A]}{dt} = \mathbf{N_A k[A][B]}$$

$$\mathbf{k} = N_A\sigma\left(\frac{8kT}{\pi\mu}\right)^{1/2} e^{-E_A/RT}$$

Factors affecting Collision frequency:

Temperature : Faster moving particles move farther each second and collide more frequently.

With increase in temperature, collision frequency increases and so the rate increases.

Concentration : Particles that are packed more tightly together collide more frequently. Gases are more concentrated at high pressure than at low pressure. With increase in pressure, the concentration increases which increases the collision frequency and so the rate increases.

Surface area : The greater the number of particles that are exposed for possible collisions. Decrease in particle size, increases the surface area which increases the collision frequency and so the rate increases.

4.5.3. Energy of activation

For the product formation to take place the molecules should possess sufficient energy required for the molecular rearrangement. This energy is not the total kinetic energy of two molecules but it is the kinetic energy corresponding to the component of the relative velocity of the two molecules along the line of their centres at the time of collision. This is the energy of the two molecules with which they must pressed together for the reaction to occur. This energy should be equal to or greater than some minimum energy$_0$. The difference between this minimum energy and the average energy of reacting molecules is known as energy of activation Ea. The fraction of collisions in which the molecules have energy greater than the minimum energy E_a is represented by Boltzmann factor $e^{-E_A/RT}$

The probability that a collision will occur successfully is incorporated by writing collision cross section as a function of kinetic energy of approach of two colliding entities and setting the kinetic energy zero below a certain threshold value.

4.5.4 Effect of orientation of molecules on the rate of the reaction

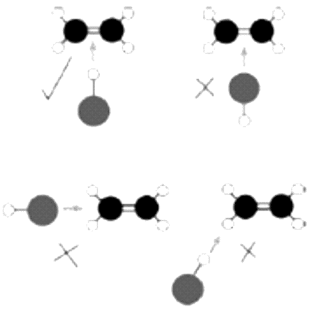
Only those collisions taking place between molecules in proper orientation and possessing certain minimum amount of energy can lead to the formation of products. Thus it is important to study the effect of orientation of molecules on the rate of the reaction.

To study the effect of orientation of molecules we will consider reaction involving a collision between two molecules – ethene, $CH_2 = CH_2$, and hydrogen chloride, HCl.

$$CH_2{=}CH_2 + HCl \rightarrow CH_3CH_2Cl \text{ (Chloroethane)}$$

As a result of the collision, the double bond between the two carbons of ethene is converted into a single bond. A hydrogen atom gets attached to one of the carbons and a chlorine atom to the other.

It is important to realize that this reaction will only occur if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. Any other collision between the two molecules will not work



Thus, we conclude that **the rate of formation of products is not only dependent on collision energy but also on the relative orientation of the molecules at the time of collision**.

This criteria of specific orientation of molecules at the time of collision is taken into account by multiplying *p* factor. The constant ***p*** **is called the steric factor** and is usually less than 1.

4.6 Lindemann's Theory of Unimolecular Reactions

The first successful explanation for unimolecular reactions was provided by Frederick Lindemann in 1921 and therefore known as Lindemann theory. This is the simplest theory of unimolecular reaction rates and was the first to successfully explain the observed first order kinetics of many unimolecular reactions.

Theory

For reactions A→P, here A acquires the necessary activation energy by colliding with another.

Lindemann hypothesized a situation where "A reactant molecule **A** becomes energetically excited by collision with another molecule of reactant **A***.

$$\mathbf{A + A \rightarrow A^* + A}$$

This step is called **energization step** in which molecule A collide with another molecule A to form energized atom A* which has acquired sufficient vibrational energy to enable it to isomerize or decompose. Where A represents inactive molecule while A* represents activated molecule. The rate for the above reaction becomes

$$\text{Rate} = \frac{d[A^*]}{dt} = k_1[A]^2$$

Now the energized molecule A* have two choices which leads to two situations.

Situation I. The Energized molecule A* might lose its energy by colliding with another molecule of A i.e. **$A + A^* \rightarrow A + A$ (de-energization step)**

This step is called **de-energization step**. In this step the excited molecule A^* is deactivated by colliding with another A molecule. Equations (1) and (3) respectively represent rapid equilibrium.

The rate for reaction becomes

$$\text{Rate} = -\frac{d[A^*]}{dt} = k_{-1}[A][A^*]$$

Situation II. The Energized molecule A* might lead to product formation i.e. unimolecular decay

$A^* \rightarrow P$. The rate for reaction becomes

$$\text{Rate} = -\frac{d[A^*]}{dt} = \frac{d[P]}{dt} = k_2[A^*]$$

If the unimolecular product formation step is slow enough to be the rate determinining step then the overall reaction will follow So, the proposed mechanism actually consists of a second order bimolecular reaction (collision activation step followed by a rate determining unimolecular step).

4.6.1 Steady State Hypothesis

If we assume that the unimolecular step is slow enough to be the rate determining then we need to know [A*] (which is not known) in terms of [A]. Thus Steady State Approximation is applied. This principle states that when a short lived reaction intermediate such as [A*] exists at low concentration in a system, the rate of formation of the intermediate can be considered to be equal to its rate of disappearance. Applying this to [A*]

$$-\frac{d[A^*]}{dt} = \frac{d[A^*]}{dt} \text{ which means } k_1[A]^2 = k_{-1}[A][A^*] + k_2[A^*]$$

Rearranging the equation

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

4.6.2 Lindemann Mechanism

Lindemann assumed that there is time lag between activation and reaction during which the activated or energized molecules may either react to give product or be de-energized (deactivated) to ordinary moelcules. Only under these conditions the behavior of unimolecular reactions can be explained on the basis of bimolecular collisions

The Lindemann mechanism includes three basic steps:

Step 1 : $A + A \rightarrow A^* + A$

Step 2 : $A + A^* \rightarrow A + A$

Step 3 : $A^* \rightarrow P$

The third step is the product formation step. If the unimolecular step is slow enough to be the rate determining step, then the overall reaction will follow first order kinetics. The rate for **Step 3** becomes

$$\text{Rate} = -\frac{d[A^*]}{dt} = \frac{d[P]}{dt} = k_2[A^*] = k_2\frac{k_1[A]^2}{k_{-1}[A]+k_2}$$

So, the above equation is the rate law expression for unimolecular reaction based on Lindemann theory. The rate law as given by equation is not first order. Equation predicts two limiting possibilities.

Case I $k_{-1}[A] >> k_2$

Rate $= \frac{d[P]}{dt} = k_2\frac{k_1[A]^2}{k_{-1}[A]} = \frac{k_2 k_1}{k_{-1}}[A] = k[A]$, the reaction is first order since $\frac{k_2 k_1}{k_{-1}}$ constant term

This case corresponds to a situation in the reaction where the [A] is high enough to produce appreciable deactivation of $[A^*]$ (as shown by situation I and situation II above)) $[A] >> \frac{k_2}{k_{-1}}$

For an ideal gas pV=nRT

$$\frac{n}{V} = \frac{P}{RT} = \text{concentration, } [A]$$

We know $[A] >> \frac{k_2}{k_{-1}}; \frac{P_A}{RT} >> \frac{k_2}{k_{-1}}$

The condition represented by equation $\frac{P_A}{RT} >> \frac{k_2}{k_{-1}}$ is possible only at very high pressures. When the pressure of the gas is very high then there will be more number of collisions between the molecules. So the energized molecule will be de-energized more by collisions rather than decomposing into products

Case II $k_{-1}[A] << k_2$

$$\text{Rate} = \frac{d[P]}{dt} = k_2\frac{k_1[A]^2}{k_2} = k_1[A]^2$$

The above equation simplifies into $k_1[A]^2$, we find that the reaction becomes second order with respect to A. This case corresponds to a situation where the energization step becomes so slow as to be rate controlling. So, the rate determining step is the bimolecular reaction

$$[A] << \frac{k_2}{k_1}\left\{\because [A] = \frac{P_A}{RT}\right\}$$

$\frac{P_A}{RT} << \frac{k_2}{k_{-1}}$ The condition represented by the equation is possible only at low pressures. When the pressure is low the molecules will be far apart and instead of getting deactivated by collision with another molecule, the energized molecule [A*] will translate into products.

So at low pressure the second order kinetics pathway is followed.

$$\text{Rate} = \frac{d[P]}{dt} = k_2\frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

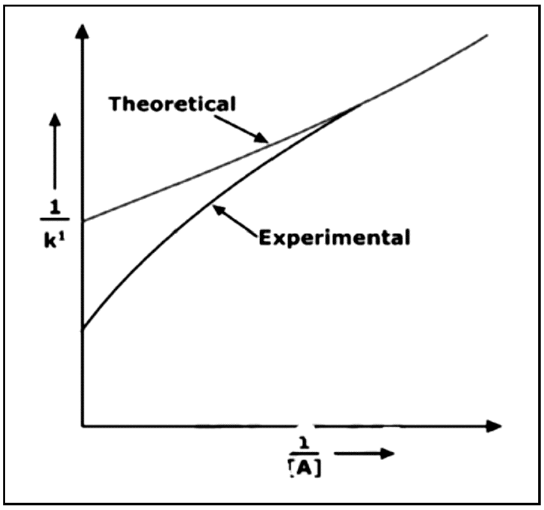
The above equation can be re-written as

$$\text{Rate} = \frac{d[P]}{dt} = k'[A] = \frac{k_2k_1[A]}{k_{-1}[A] + k_2}[A]$$

Where k' (effective rate constant) = $\frac{k_2k_1[A]}{k_{-1}[A] + k_2}$

The above equation can be rearranged in the form = $\frac{1}{k'} = \frac{k_{-1}[A] + k_2}{k_2k_1[A]}$

$$\frac{1}{k'} = \frac{k_{-1}}{k_1k_2} + \frac{1}{k_1[A]}$$



The straight line behavior is observed at low concentrations but deviations are observed at higher concentrations.

4.6.3 Lindemann approach breaks down for two reasons

The bimolecular step takes no account of the energy dependence of activation, the internal degrees of freedom of the molecule are completely ignored and the theory underestimates the rate of activation.

The unimolecular step fails to take into account that a unimolecular reaction specifically involves one particular form of molecular motion (for example rotation around a double bond).

4.7 Transition State Theory

Transition State Theory is popularly referred to as Activated Complex Theory or Theory of Absolute Reaction Rate. This theory was developed in 1935 by Henry Eyring and Michael Polanyi. Transition State Theory is an attempt to express rate constant in terms of a model of sequences or episodes that take place during the reaction. This theory is applicable essentially to gaseous reactions. The advantage of Transition State approach is that the quantity corresponding to steric factor appears automatically in the rate constant expression. The Transition State Theory depicts the formation of transition state complex (or activated complex) $X^{\ddagger}$ from the reactants A and B, as a preceding step for the formation of products.

We are using the terms Transition State and Activated Complex in this theory. It is important to distinguish the two as they have different molecular interpretation:

Activated complex refers to an aggregate of atoms formed from the reactants (assumed to be an ordinary molecule).

Transition State is the specific configuration of those atoms that lead to the formation of desired products.

Though we use these terms interchangeably for the same event but transition state is a more appropriate term in context of the theory

4.7.1 Assumptions

It is assumed that a transition state complex is in equilibrium with the reactants, and that the rate at which the transition state complex decomposes to products (slow rate determining step) depends on the rate at which it passes through the transition state.

$\mathbf{A + B \rightleftharpoons X^{\ddagger}}$ (Transition State Complex) $\rightarrow$ Products

The major assumptions of this theory are:

- Collisions are responsible for a chemical reaction.
- An equilibrium exists between the reactants and the transition state complex (this equilibrium is not conventional)
- The reaction co-ordinate describing the conversion of transition state complex to product can be mapped onto a single degree of freedom of transition state complex. If product formation involves the breaking of a bond (for a diatomic molecule), then the vibrational degree of freedom corresponding to bond stretching is taken as the reaction co-ordinate.

Let us assume bimolecular reaction of the form

$\mathbf{A + B \rightleftharpoons X^{\ddagger}}$ (Transition State Complex) $\rightarrow$ Products

The equilibrium constant of the above reaction can be expressed as $K^{\ddagger} = \dfrac{[X^{\ddagger}]}{[A][B]}$

And the rate as per transition state theory depends on two factors

(i) Concentration of the activated complex $[X^{\ddagger}]$

(ii) Frequency of decomposition of activated complex (ν)

Rate = $\nu[X^{\ddagger}]$

Rearranging $[X^{\ddagger}] = K^{\ddagger}[A][B]$

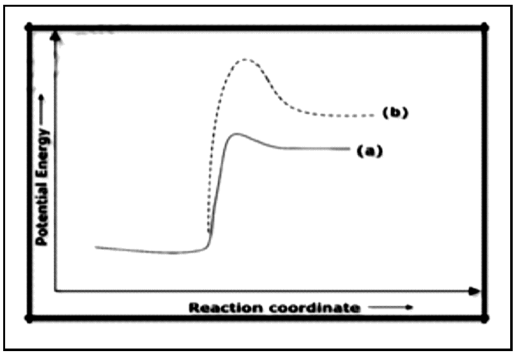
Rate equation modifies as, Rate = $\nu K^{\ddagger}[A][B]$

Rate= $r = k[A][B]$ where $k = \nu K^{\ddagger}$

4.6.2 Thermodynamic treatment of Transition State Theory

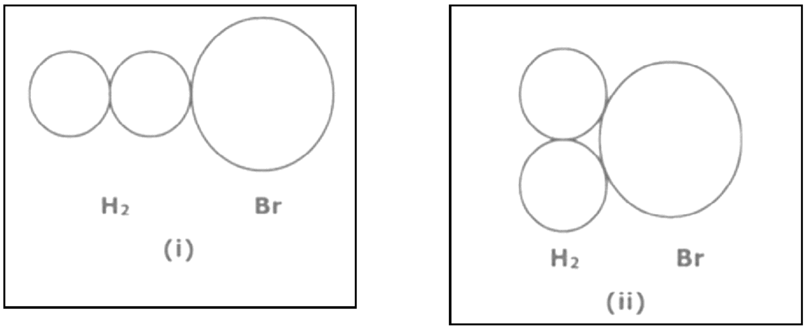
Let us consider the following reaction Br + H-H $\rightleftharpoons$ **[Br-H-H]** $\rightarrow$ **Br–H + H**

The reaction proceeds through a transition state which has energy higher than that of the reactants or products. As per the assumptions of Transition State Theory, the reaction sequence can be represented as :



Graphical Plot of Change in Potential energy as a function of reaction co-ordinate (sequence of simultaneous changes in bond distances and bond angles)

Very firstly, it is important to note that the collision between Br and H_2 can occur by two possible ways :



In the potential energy plot, curve (a) curve corresponds to the (i) way of collision and curve (b) is for (ii) way of collision.

[Br –H –H] is the transition state complex or activated complex at transition state. It is important to note that the transition state complex is not an intermediate compound. It is a molecule in the process of breaking or forming bonds. This transition state complex is not stable and is present at maximum in the potential energy curve shown above. This maximum point of the curve corresponding to the activated complex is called the **saddle point.**

The bond breaking is an energy demanding process and the bond making is an energy releasing process. The net energy requirement for the formation of transition state complex and its decomposition to products must be available through translational or vibrational energy of the reactants.

Rate constant

For the reaction $\mathbf{A + B \rightleftharpoons X^{\ddagger}}$ (Transition State Complex) → Products

Rate = $\nu K^{\ddagger}[A][B]$

Since, the transition state complex is in a process of decomposing, one of its vibrational degrees of freedom is in the process of becoming a translational degree of freedom. Let be the average vibrational energy that leads to bond rupturing.

According to Planck's equation for the quantum of energy, $E_{vib} = h\nu$

Where is ν, vibrational frequency and in activated complex theory it is taken as frequency of decomposition of activated complex and *h* is the Planck's constant.

Classical vibrational energy is given by the expression $E_{vib} = k_B T = \frac{R}{N_A} T$

$$E_{vib} = h\nu = k_B T = \frac{R}{N_A} T$$

$$\nu = \frac{k_B}{h} T = \frac{R}{hN_A} T$$

Where is the k_B Boltzmann constant, R is the gas constant and N_A is the Avogadro's number

$$\text{Rate} = \frac{R}{hN_A} T \ \mathbf{K^{\ddagger}\ [A][B]}$$

The classical rate equation is of the form for $\mathbf{A + B \rightleftharpoons X^{\ddagger}}$ (Transition State Complex) → Products

Rate = k[A][B]

On Comparing the two equations $k = \frac{R}{hN_A} T\ K^{\ddagger}$

From Classical Thermodynamics, we know that for a reaction at equilibrium change in Gibb's free energy $\Delta^{\neq}G^{o}$ (Reactants → Transition State Complex) and equilibrium constant $K^{o\neq}$ are related to each other as per the following expression,

$$\Delta^{\neq}G^{o} = -RT \ln K^{o\neq}$$

For a reaction

$$\mathbf{A + B \rightleftharpoons X^{\ddagger}}$$

$$\Delta^{\neq}G^{o} = G^{o}(X) - G^{o}(A) - G^{o}(B)$$

The equilibrium constant is given by $K^{o\neq} = e^{\frac{\Delta^{\neq}G^{o}}{RT}}$

$$\Delta^{\neq}G^{o} = \Delta^{\neq}H^{o} - T\Delta^{\neq}S^{o}$$

Where $\Delta^{\neq}H^{o}$ is the enthalpy change and $\Delta^{\neq}S^{o}$ is the entropy change under standard conditions

$$K^{o\neq} = e^{\frac{(\Delta^{\neq}H^{o} - T\Delta^{o}S^{o})}{RT}} = e^{\frac{\Delta^{\neq}H^{o}}{RT}} e^{\frac{\Delta^{\neq}S^{o}}{R}}$$

The relation between $K^{o\neq}$ and $K^{\neq}$ is

$K^{\neq} = K^{\neq} c^{o}$, where c^{o} is the unit concentration i.e. 1 Molar = 1 mol dm^{-3}

$$k = \frac{R}{hN_A} TK^{\ddagger} = \frac{R}{hN_A C^{o}} TK^{o\ddagger}$$

$$k = \frac{R}{hN_A c^{o}} T\,K^{o\ddagger} = \frac{RT}{hN_A c^{o}} e^{-\frac{\Delta^{o}H^{o}}{kT}\frac{\Delta^{\neq}S^{o}}{R}} = \frac{kT}{hc^{o}} e^{-\frac{\Delta^{\neq}H^{o}}{RT}} e^{\frac{\Delta^{\neq}S^{o}}{R}}$$

The above equation is known as **Eyring equation**. Throughout our discussion, we considered only the gas-phase reactions. The study of the reaction rates in solutions is complicated due to the role of solvent.

Problem

Calculate the entropy of activation for a reaction from the following data :

Arrhenius Energy of activation E_a =13.02kcal ; T = 298K ; rate constant at 298K = 5.7×10^{-5} litre $mole^{-1}sec^{-1}$.

Method

$\Delta H^{\neq} = E_a - RT$ for reaction in solution = 13020 – 1.987 × 298 = 12428 cal

Rate constant, $k_r = \frac{kT}{h} e^{\frac{-\Delta^{o}H}{RT}} e^{\frac{\Delta^{o}S}{R}}$

Or, $\ln k_r = \ln\frac{kT}{h} - \frac{\Delta H^{\neq}}{RT} + \frac{\Delta S^{\neq}}{R}$

Or, $\frac{\Delta S^{\neq}}{4.576} = -7.9233$

$\therefore \Delta S^{\neq} = -7.9233 \times 4.576 = -36.26 \text{ cal K}^{-1}$

Problem

How are enthalpy of activation and Arrhenius energy of activation (E_a) related

(i) a reaction in solution (ii) a gaseous reaction ?

The required relation is $\Delta H^{\neq} = E_a - RT + \Delta(PV)^{\neq}$

For a reaction in solution

Volume changes are very small at approximately constant pressure. That is $\Delta(PV)^{\neq} = 0$

$\Delta H^{\neq} = E_a - RT$

For gaseous reactions

Assuming ideal conditions, $\Delta(PV)^{\neq} = \Delta n^{\neq} RT$, where $\Delta n^{\neq}$ is the change in the number of moles on passing from the reactants to the activated complex.

$\therefore \Delta H^{\neq} = E_a - RT + \Delta n^{\neq} RT = E_a + RT(\Delta n^{\neq} - 1)$

4.8 KINETIC ISOTOPE EFFECT

Isotopes can be used as markers to keep track of positions of atoms during a chemical transformation. This strategy of determining reaction mechanisms is studied via Kinetic Isotope effect.

The alteration of reaction kinetics by the substitution of an atom by one of its isotopes is known as the kinetic isotope effect (KIE). While every isotope pair in principle can show a KIE, H/D isotope effect is the most studied one because of the large mass ratio, and the easy availability of D substituted compounds.

Different types of **kinetic Isotope effect**

(i) Primary Kinetic Isotope Effect

(ii) Alpha secondary Kinetic Isotope Effect

(iii) Beta secondary Kinetic Isotope Effect

(iv) Steric Kinetic Isotope Effect

Primary Kinetic Isotope Effect

This situation arises when the bond to the isotopic atom is broken at or before the rate determining step.

Examples are :

Mercuration of benzene (KIE 7.7)

Nitration of benzene (KIE 1)

Oxidation of isopropanol by chromium trioxide (KIE 6.5)

The origin of primary KIE can be explained based on the zero-point energy difference between the C-H and the C -D bonds. The lack of KIE in the nitration of benzene is because the formation of the sigma complex is the rate determining step.

Application: Kinetic isotope effects help us in understanding reaction mechanisms, identifying rate determining steps, etc.

4.9 Catalytic Reactions

Definition

Catalysis is the process of enhancing the rate of the reaction by means of a foreign substance which remains unchanged in mass and chemical composition.

Classification

(i) Homogeneous Catalysis

Homogeneous Catalysis is where the catalyst and the reactant constitute a single phase.

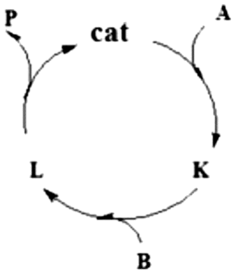
(ii) Heterogeneous Catalysis

Heterogeneous Catalysis is where the catalyst and the reactant constitute separate phase.

Homogeneous Catalysis

Homogeneous catalysis mechanism is often represented by catalytic cycles. In catalytic cycles usually catalysts are shown as member of cycle and all reactants and products are placed outside the cycle and connected to it by arrows.

For example the cycle of a catalytic reaction A+B ’→P, having intermediates K and L can be represented as



The stable metal complex added to the reaction at the beginning is called catalysts precursors or precatalysts. Turnover frequency in terms of catalytic cycle can be defined as number of times the cycles is completed in unit time.

The intermediates species can be studied using various spectroscopic studies such as FTIR, NMR, UV-Vis etc.

4.9.1. Catalysis by acids or bases

Acid –base catalysts are used in the following types of reactions:

(i) Condensation
(ii) Dehydration
(iii) Hydrolysis
(iv) Halogenations

4.9.2 Acid-base catalysis Mechanism

In acid-base catalysis both acid and bases may act as catalysts in solutions. The H^+ is used for protonating the intermediates and a base or solvent is used for removing the proton at later stage. The Rate of acid –base reactions depends on pH since the rate is a function of both H^+ and ^-OH concentrations. The proton transfer mechanism in general can be represented as

$$B^- + H - A \rightleftharpoons [B---H---A]^- \rightleftharpoons B - H + A^-$$

4.9.3 Kinetics

In acid catalysis, the proton transfer step is slower and is the rate determining step. Subsequently, the protonated substrate rapidly reacts to give the product(s) as shown below :

$$S + HA \overset{\text{slow}}{\rightleftharpoons} SH^+ + A^-$$

$$SH^+ \overset{\text{fast}}{\rightleftharpoons} \text{products}$$

Reaction rate is dependent on all acids/bases present in solution. Rate constant for reaction is function of concentrations of H^+, OH^-, HA and A^-. First order rate constant can be calculated from

$$k = k_0 + k_{H^+}C_{H^+} + k_{OH^-}C_{OH^-} + k_{HA}C_{HA} + k_{A^-}C_{A^-}$$

Where k_0 = rate constant for uncatalyzed reaction (small relative to other terms)

Activity of acid-base catalyst

Activity of an acid depends on its acid strength and molecular structure. Acids of higher strength are more catalytically active. Strength is defined in terms of equilibrium constant (KHA) for dissociation.

$$HA \rightleftharpoons H^+ + A^-$$

$$K_{HA} = \frac{a_{H^+}a_{A^-}}{a_{HA}}$$ where a_i is the respective activity

For general acid catalyst, rate constant depends on its acid strength as :

$$\log k_{HA} = \alpha \log K_{HA} + \text{constant}$$

Where,

k_{HA} = rate constant of the catalytic step

K_{HA} = dissociation constant of acid HA

α = Bronsted coefficient (normally $0 < \alpha < 1$)

α indicates the sensitivity of catalytic step for changes in acid strength of HA. Similarly Brønsted relation for general base catalysis is

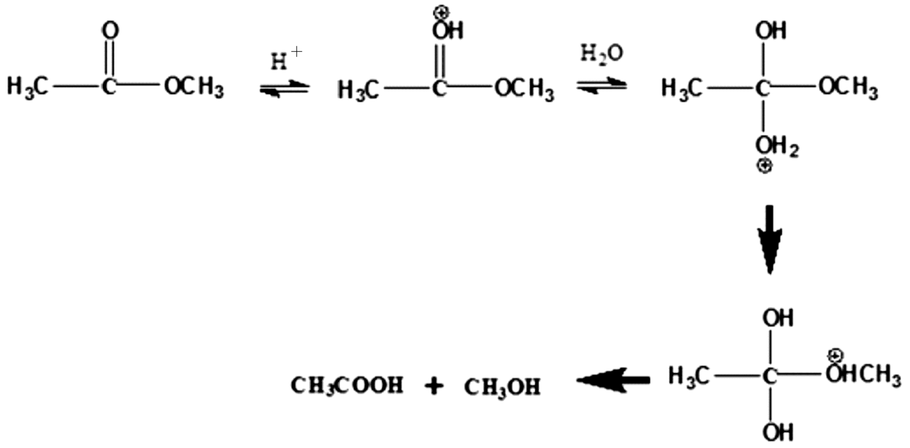
$$\log k_B = \beta \log K_{HB} + \text{constant}$$

The coefficient β has the same meaning as α for general acid catalysis.

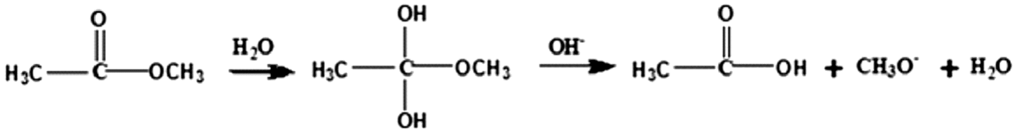
Mechanisms of few acid-base catalyzed processes are discussed below.

Ester hydrolysis : The hydrolysis of esters is catalyzed by both acid and base. H_2O act as the proton donor. The mechanism for acid and base catalyzed hydrolysis can be represented as :

Acid catalyzed hydrolysis :



Base catalyzed hydrolysis :

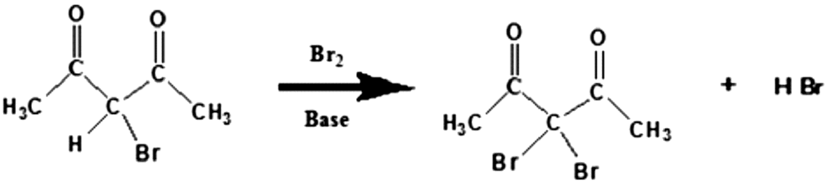


Dehydration : Acid catalyzed dehydration mechanism is illustrated by dehydration of ethyl alcohol to ethene. Alcohol is initially protonated. Then water molecules leaves forming a carbocation . Then ß-elimination occurs producing the alkene.

$$CH_3-CH_2-OH \xrightarrow{HA} CH_3-CH_2-\overset{+}{O}H_2 \longrightarrow CH_3-\overset{+}{C}H_2+H_2O \xrightarrow{A^-} CH_2=CH_2+HA$$

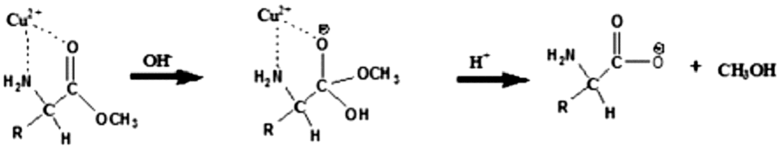
Acid or base catalyzed halogenation

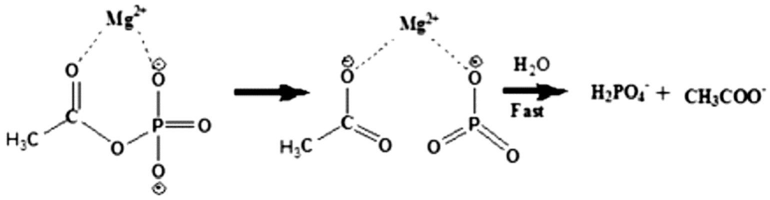
Ketones can be halogenated in the presence of acid or base and X_2 (X= Cl, Br).



Catalysis by Metal ions

The metal ions can coordinate simultaneously to electron donating atoms, such as N and/or oxygen, present in the reactant. The probable mechanism of Cu^{2+} and Mg^{2+}. ion catalyzed hydrolysis are shown below.





4.10 Enzyme Catalysis

The celebrated Michaelis–Menten expression provides a fundamental relation between the rate of enzyme catalysis and substrate concentration. The validity of this classical expression is, however, restricted to macroscopic amounts of enzymes and substrates. Enzymes are biological catalysts that accelerate chemical reactions many fold, without getting consumed in the catalytic pro-cess. Several biological processes involving the conversion of substrates to products, thus, rely crucially on the catalytic activity of enzymes. Specific enzymes control and regulate a wide range of life-sustaining processes that vary from digestion, metabolism, absorption, and blood clotting to reproduction. While specificity depends on the detailed chemical structure of enzyme proteins, the rate at which the enzymes carry out the catalytic conversion depends less on their chemical structure but more on the physical parameters, including the amounts of enzymes, substrates, temperature, pH.

4.10.1 Michaelis-Menten Kinetics

Two 20th century scientists, Leonor Michaelis and Maud Leonora Menten, proposed the model known as Michaelis-Menten Kinetics to account for enzymatic dynamics. The model serves to explain how an enzyme can cause kinetic rate enhancement of a reaction and explains how reaction rates depends on the concentration of enzyme and substrate.

Introduction

The general reaction scheme of an enzyme-catalyzed reaction is as follows:

$$E + S \rightarrow k_1[ES] \rightarrow k_2E + P \qquad (1)$$

The enzyme interacts with the substrate by binding to its active site to form the enzyme-substrate complex, ES. That reaction is followed by the decomposition of ES to regenerate the free enzyme, E, and the new product, P.

The number of moles of product (P) formed per time as *V*. The variable, *V*, is also referred to as the rate of catalysis of an enzyme. For different enzymes, *V* varies with the concentration of the substrate, S. At low S, *V* is linearly proportional to S, but when S is high relative to the amount of total enzyme, *V* is independent of S. Concentrations is important in determining the initial rate of an enzyme-catalyzed reaction.

The general enzyme reaction scheme shown below, which includes the back reactions in addition to the forward reactions :

$$\mathrm{E+S \rightarrow k_1[ES] \rightarrow k_2E+P} \qquad (2)$$

$$\mathrm{E+S \leftarrow k_3[ES] \leftarrow k_4E+P} \qquad (3)$$

The table below defines each of the rate constants in the above scheme.

k_1, The binding of the enzyme to the substrate forming the enzyme substrate complex

k_2, Catalytic rate; the catalysis reaction producing the final reaction product and regenerating the free enzyme. This is the rate limiting step

k_3, The dissociation of the enzyme-substrate complex to free enzyme and substrate

k_4, The reverse reaction of catalysis

Substrate Complex

$$E+S \xrightarrow{k_1} ES \qquad v_o = k_1[E][S]$$

$$ES \xrightarrow{k_2} \quad E+S \qquad v_o = k_2[ES]$$

$$ES \xrightarrow{k_3} \quad E+P \qquad v_o = k_3[ES]$$

$$E+P \xrightarrow{k_4} ES \qquad v_o=k_4[E][P] = 0$$

The ES complex is formed by combining enzyme E with substrate S at rate constant k_1. The ES complex can either dissociate to form E_F (free enzyme) and S, or form product P at rate constant k_2 and k_3, respectively. The velocity equation can be derived in either of the 2 methods that follow.

Method 1: The Rapid Equilibrium Approximation

E, S, and the ES complex can equilibrate very rapidly. The instantaneous velocity is the catalytic rate that is equal to the product of ES concentration and k_2 the catalytic rate constant.

$$v_o = k_2[E - S] \quad (4)$$

The total enzyme concentration (E_T) is equal to the concentration of free enzyme E (E_F) plus the concentration of the bound enzyme in ES complex :

$$[E]T = [EF] + [ES] \quad (5)$$

$$K_S = \frac{k_2}{k_1} = \frac{[E][S]}{[ES]} \quad (6)$$

$$K_S = \frac{([E_0] - [ES])[S]}{[ES]} \quad (7)$$

$$[ES] = \frac{[E_o][S]}{K_S + [S]} \quad (8)$$

$$v_o = \left(\frac{dP}{dT}\right)_o = k_3[ES] \quad (9)$$

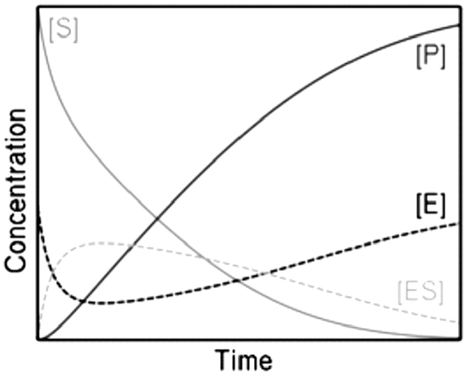
At high substrate concentrations, $[S] >> Ks$

we get :

$$v_o = \left(\frac{dP}{dT}\right)_o = k_3[Eo] = V_{max} \quad (1)$$

Method 2 : The Steady-State Approximation

The figure shows the relatively low and constant concentration of the enzyme-substrate complex due to the complex's slow formation and rapid consumption. Note the falling substrate concentration and the rising product concentration.



Change in concentrations over time for enzyme E, substrate S, complex ES and product P.

The rates of formation and breakdown of the E - S complex are given in terms of known quantities:

- The rate of formation of E – S = $k_1[E][S]$
  (with the assumption that [P] = 0)
- The rate of breakdown of E-S = $k_2[ES] + k_3[ES] = (k_2 + k_3)\ [ES]$

At steady state, $\frac{d[ES]}{dt} = k_1[E][S] + k_2[ES] + k_3[ES] = 0$ (10)

Therefore, rate of formation of E-S is equal to the rate of breakdown of E-S

So, $k_1[E][S] = (k_2 + k_3)\ [ES]$ (11)

Dividing through by k_1

$[E][S] = [E - S]$ (12)

Substituting with k_M : (Michaelis Constant)

$[E][S] = k_M[ES]$

k_M = *breakdown*$[ES]$ / *formation*$[ES]$ (13)

k_M, implies that half of the active sites on the enzymes are filled. Different enzymes have different k_M values. They typically range from 10^{-1} to 10^{-7} M. The factors that affect k_M are :

(i) pH (ii) temperature (iii) ionic strengths (iv) the nature of the substrate

Substituting $[E_F]$ with $[E_T] - [ES]$: $E_T = [ES] + [E_F]$

$$([E_T] - [ES])\ [S] = k_M\ [ES]$$

$$[E_T]\,[S] - [ES][S] = k_M\,[ES]$$

$$[E_T]\,[S] = [ES][S] + k_M\,[ES]$$

$$[E_T]\,[S] = [ES]\,([S] + k_M)$$

Solving for [ES] :

$$[ES] = ([ET][S])([S] + k_M)$$

The rate equation from the rate limiting step is :

$$V_0 = \frac{dP}{dt} = k_2[ES]$$

Multiplying both sides of the equation by k_2 :

$$k_2[ES] = k_2\frac{([E_T][S])}{(K_M + [s])} \qquad (14)$$

$$v_o = k_2\frac{([E_T][S])}{(K_M + [S])} \qquad (15)$$

When S >> K_M, v_o is approximately equal to $k_2[E_T]$. When the [S] great, most of the enzyme is found in the bound state ([ES]) and $V_o = V_{max}$

We can then substitue $k_2[E_T]$ with $V_{max}$to get the **Michaelis Menten Kinetic Equation :**

$$v_o = \frac{v_{max}[S]}{(k_m + [S])}$$

Reaction Order Note

When $[S] << K_m$

$$v = \frac{v_{max}[S]}{k_m}$$

This means that the rate and the substrate concentration are directly proportional to each other. The reaction is first-order kinetics.

When $[S] >> Km$

$$v = Vmax \qquad (16)$$

This means that the rate is equal to the maximum velocity and is independent of the substrate concentration. The reaction is zero-order kinetics.

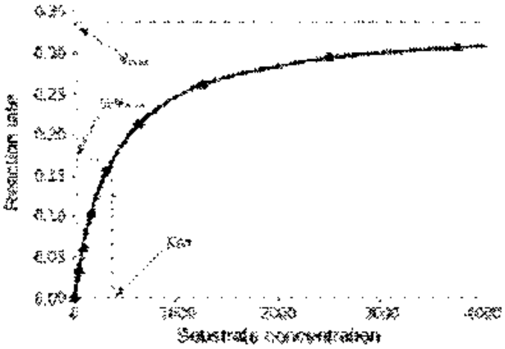


Figure 2: Diagram of reaction speed and Michaelis-Menten kinetics.

Then, at $v = \frac{V_{max}}{2}$, *Km* = [*S*]

$$v = \frac{V_{max}}{2} = \frac{V_{max}[S]}{(k_m + [S])} \tag{17}$$

Therefore, *Km* is equal to the concentration of the substrate when the rate is half of the maximum velocity. From the Michaelis Menten Kinetic equation, we have many different ways to find *Km* and *Vmax* such as the Lineweaver-Burk plot

4.10.2 Lineweaver-Burk Plot

For example, by taking the reciprocal of the Michaelis Menten Kinetics Equation, we can obtain the Lineweaver-Burk double reciprocal plot :

$$v = \frac{v_{max}[S]}{(k_m + [S])} \tag{18}$$

$$\frac{1}{v} = \frac{(k_m + [S]}{v_{max}[S]} \tag{19}$$

$$\frac{1}{v} = \frac{k_m}{v_{max}}\left(\frac{1}{[S]}\right) + \frac{1}{v_{max}} \tag{20}$$

Apply this to equation for a straight line $y=mx+b$ and we have:

$$y = \frac{1}{v} \tag{21}$$

$$x = \left(\frac{1}{[S]}\right) \tag{22}$$

$$m = slope = \frac{k_m}{v_{max}} \tag{23}$$

$$b = y - intercept = \frac{1}{v_{max}} \tag{24}$$

When we plot $y = \frac{1}{v}$ versus $x = \left(\frac{1}{[S]}\right)$, we obtain a straight line.

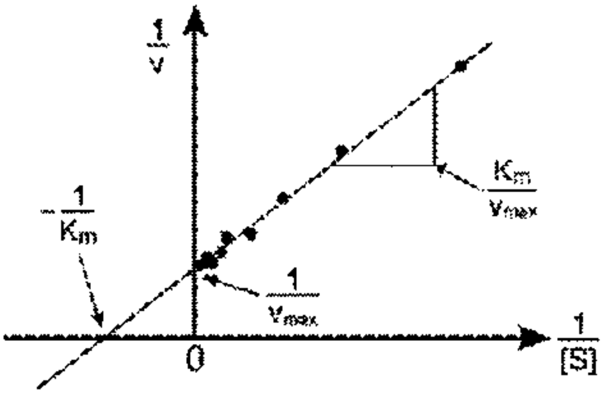


***Figure** 3. An example of a Lineweaver-Burke plot.*

4.11 Summary

In this unit we learned about rate of chemical reaction. Rate of the reaction is essential for understanding and application of chemical reactions in different conditions. We learned that chemical reactions can be classified based on their order and rate equations of different orders of reactions. Rate constants very with temperature and Arrhenius law is used to quantify that rate constants. We also understood the concept of activation energy based on collision theory as well as transition state theory. Chemical kinetic form the basis of chemical reaction dynamic and along with thermodynamics, it determines several aspects of reactions.

4.12 Questions

Essay answer type questions :

1. H^+-catalyzed inversion of sucrose is a pseudo-first-order reaction though partial order of the reaction with respect to sucrose is one. —Explain. [3]
2. Sketch and explain the variation of the logarithm of the rate constant with pH for H^+—catalyzed reaction. [3]
3. The rate of H^+-catalyzed hydrolysis of ester is almost doubled when the pH is changed from 0.8 to 0.5. Find the order of the reaction with respect to catalyst. [2]
4. Consider the following reversible reaction, first order in both directions $A \rightleftharpoons B$; forward and reverse rate constants are k_f and k_r respectively and $k_f / k_r = 2$. Plot curves that give the concentrations of A and B as functions of time. [4]
5. For a simultaneous reaction $A \rightarrow B$ (k_1, E_1) and $A \rightarrow C$ (k_2, E_2), if E_a is the observed activation energy for the disappearance of A then show that $E_a = (k_1E_1 + k_2E_2) / (k_1 + k_2)$. Respective rate constant and activation energy are in the parenthesis. [4]
6. A substance decomposes by two competeting paths with rate constants k_1 and k_2. The values of (k_1 / k_2) at 10 and 40°C are 10 and 0.1 respectively. Find the difference of activation energies for these two reactions? [4]
7. Derive the Michaelis-Menten equation for enzyme-catalysed reaction. Under what condition maximum rate will be attained ? [5]
8. Show that the ratio, $t_{1/2} : t_{3/4}$ of an 'n' order reaction is function of 'n' alone. Calculate its value for a second reaction. [3]
9. Justify or criticize the following statements with reason(s). [5×2=10]
   (a) Zero and fractional order-reactions are always multi-step.
   (b) First order reaction can not be completed in finite time interval.
   (c) 'Steady-state-approximation' is applicable for all chemical species involved in the multi-step reaction mechanism.
   (d) Rate of first order reaction decreases linearly.
   (e) The slope of '$t_{1/2}$' vs. 'C_o' for zero-order reaction is its rate constant.
9. A substance decomposes at 600 K with rate constant of $3.72 \times 10^{-5} s^{-1}$.
   (a) Calculate the half-life of the reaction.

(b) What fraction will remain undecomposed if the substance is heated at 600 K for 3.0 h? [4]

10. The rate constant for the reaction, $H^+ + OH \rightarrow H_2O$, is 1.3×10^{11} dm^3 mol^{-1} s^{-1}. Calculate the half-life for neutralization process when $[H^+]_o = [^-OH]_o = 0.1$ (M). [2]

11. For a reaction: $A + B \rightarrow Z$; let the proposed mechanism be, in terms of elementary steps: $A + B \rightarrow X$ (rate constant = k_1)

$X \rightarrow A + B$ (rate constant = k_{-1})

$X \rightarrow Z$ (rate constant = k_2)

(b) Write down the equation for the rates : $d[A]/dt$, $d[X]/dt$, & $d[B]/dt$.

Assuming that the steady-state-approximation is valid for concentration of X, find the overall rate equation for the reaction. [4]

Short answer type questions:

1. Find the time required for the decomposition of $\left(\frac{n-1}{n}\right)$ fraction of the initial amount of A undergoing a first order reaction: $2A \rightarrow$ products. 2
2. Demonstrate graphically the variation of concentration of reactant against time for zero-order and 1st-order reactions separately. 2
3. What is the lowest possible value of the activation energy for an endothermic reaction? 2
4. Find out the order of the reaction in following cases :
   (i) $t_{1/2} \times Q$ = constant (Q being the initial concentration of the reactant)
   (ii) On doubling the concentration of the reactant, the rate of the reaction is doubled.
   (iii) The reaction is complete in time $2 \times t_{1/2}$ 3
5. H_2 — I_2 reaction does not follow a chain mechanism like H_2 — Br_2 reaction. —Explain. 1
6. Assuming $k_{-1} >> k_2$, derive the rate equation for formation of C for the following reaction : 2

$$A + B \underset{k_{-1}}{\overset{k_1}{=}} AB \xrightarrow{k_2} C$$

7. Plot of concentration of product vs. time of a given reaction gives a straight line. Explain the order of the reaction. 2
8. Find an expression for the half life period of a simple nth order reaction. 2
9. How does the Arrhenius equation, $k = Ae^{-E/RT}$ look at $T \rightarrow \infty$? Mention its significance. 2
10. What are Pseudo-first order reactions? Give one example. 2
11. Consider the simple consecutive reaction involving first order steps : $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, where only A is presetn initially. If a_t, b_t, c_t are the respective concetrantions of A, B and C at time t, show schematically the variation of these quantitites with time. 2
12. The temperature variation of rate constant (k) of a reaction is given by : $k = A,\ Te^{+E/RT}$. Suggest a suitable graphical plot for the determination of E. 2
13. For a 1st order reaction after some time τ, the concentration of the reactant is 1/e times the initial concentration. Show that rate constant $k = 1/\tau$. 2
14. Justify whether the half-life period for a zero order reaction is directly proportional to the initial concentration of the reactant. 2
15. What is "bottle neck principle" in chemical kinetics ? 2
16. A second order reaction $X \rightarrow$ Products is never theoretically complete— Justify Or,
    What is the time for completion for a second order reaction ? 1
17. Define the order of a reaction.
18. 'The balanced chemical equation does not give the order of the reaction'— Elucidate. 3
19. 'A first order reaction is never theoretically complete'— explain mathematically. 2
20. On which factors the rate of a zero order reaction depends ? Explain. 2
21. Show that a zero order reaction can lead to completion. 2
22. A reaction $A \rightarrow$ Products is of zero order with respect to A. Two experiments are performed with initial concentrations $[A]_0 = 0.1(M)$ and 0.05 (M) respectively. Sketch the plots to show variation of the concentration of A with time. 2

23. 'Half decomposition period' for a zero-order reaction is independent of initial concentration of the reactant (with respect to whom the reaction is zero order) —Comment. 2

24. Find the unit of $\frac{d\ell nk}{dt}$ for a nth order reaction. 2

25. The rate constant of a reaction has unit mol $dm^{-3}s^{-1}$. What is the order of the reaction? 2

26. Cite an example of a chemical reaction which does not have an order. 2

27. Define an elementary reaction. 2

28. What is the unit of rate constant for a second order reaction? 2

29. If $\frac{d\ell nk}{dt} = \frac{\alpha}{T^2}$ find the unit of α. 2

30. Draw the rate versus time profile for (i) a zero order reaction (ii) a first order reaction. 2

Numerical problems :

1. The rate of decomposition of a gas 'A' was 7.25 in some unit when 5% had reacted and it was 5.14 in the same unit when 20% had reacted. Calculate the order of the reaction.

2. Calculate the temperature coefficient of a reaction taking place at 300K. The energy of the activation is given as 80kJ Mol-1.

3. A 1st order reaction is 20% complete in 10 minutes at 27°C and 40% complete in 12 minutes at 40°C. Calculate the energy of activation of the reaction. Find also the value of K at very high temperature.

4. A 1st order reaction is 20% complete in 15 minutes at 25°C, but for the same extent of reaction at 37°C, only 5 minutes are required. Calculate activation energy of the reaction.

5. The rate constants for the reaction $2HI \rightarrow H_2+I_2$ is determined to be 3.52×10^{-7} and 3.95×10^{-2} $M^{-1}s^{-1}$ at 556 and 781K, respectively. Calculate the activation energy and pre-exponential factor for this reaction.

6. The rate of decomposition of a gas 'A' was estimated to be 7.25 in some unit when 5% had reacted and it was 5.14 in the same unit, when 20% had reacted. Calculate the order of the reaction.

7. The first order rate constant (k) of a reaction A→products follows the equation $\log k(\text{min}^{-1}) = 33.91 - \frac{18000}{T}$ How long will it take for one mole of A to decompose 75% at 227°C ? Calculate the energy of activation.
8. What is the order of the reaction A + 2B = 2C given that

Rate	0.12	0.24	0.24
C_A	0.10	0.10	0.20
C_B	0.10	0.20	0.20

9. Calculate the percentage increase of rate constant for a 5% increase in temperature. Given E=20kJ mol^{-1} and T=300K.
10. Calculate the percent change in rate constant (k) when the energy of activation changes by 0.1 kCal/mol.
11. If a first order reaction is 25% complete in 20 minutes, how long will it take to complete 85% ?
12. Entropy of activation of two reactions differs by 2 cal mol^{-1}. Compare the rate constants (other factors are the same).
13. A gas decomposes according to second order kinetics. When the initial pressure is 500 torr, 40% decomposition occurs in 30 min. Find out the time required for 75% decomposition of the gas and the value of the rate constant.
14. Consider the parallel reaction:

$$A \xrightarrow{k_1} B \,;\, A \xrightarrow{k_2} C$$

In an experiment, it was found that 60% decomposition of A takes place in 20 minutes and analysis of products showed that B and C are in 3:1 ratio. Calculate k_1 and k_2.

4.13 Further Reading

(1) D. A. McQuarrie, J. D. Simon, Physical Chemistry: A Molecular Approach, 1st Ed, University ScienceBooks, California (1997).

(2) P. W. Atkins, J de Paula, Physical Chemistry, 8th Ed, Oxford University Press, New Delhi(2006).

(3) I. N. Levine, Physical Chemistry, 6th Ed, Mcgraw Hill Education (2011).

(4) e-Pathsala lectures on chemical kinetics

(5) nptel

Unit 5 ❑ Transport Processes

Structure

5.1 Objectives

On completion of the study of this unit, the learner will be able to—

(i) explain viscosity and equation related to viscosity.
(ii) determine viscosity in laboratory.
(iii) understand theory of electrolytes.
(iv) relate ionic conductance with resistance.
(v) explain different terms and instruments related to electrolytic conductance.
(vi) quantify conductance for strong and weak electrolytes.
(vii) apply Kohlrausch's law of independent migration of ions.
(viii) explain and use Debye-Hückel theory.

5.2 Introduction

We are familiar that a lot of chemistry happens in solution especially where the solvent is a liquid. Therefore it is essential that we understand the transport processes happening in solution. Viscosity is one of the most important properties of fluids that affects transport process. So we will learn about it in the first portion of this unit. The second portion of the unit focuses on migration of ions in solution. Electrolytes are essential part of chemistry and the study of electrolytes are very important. So, in this unit we will learn about electrolytic conductance with relation to defferent types of electrolytes. We will also focus on how we can use them for chemical applications.

5.3 Viscosity

The internal friction which opposes the relative motion of adjacent layers of a fluid is known as viscosity

Viscosity of gases

When a fluid is flowing through a cylinder tube, layers just touching the sides of the tube are stationary, and velocities of the adjacent layers increase towards the centre of the tube, the layer to the centre of the tube having the maximum velocity. There thus exist a velocity gradient.

In case of gases because of their continuous movement, there will be an interchange of molecules between two layers, with the result that a fraction of the momentum of one layer will pass over to the other layer. The net effect will be a decrease in the relative rate of movement of one layer with respect to the other. In order to maintain a uniform velocity gradient, one will have to apply a force acting along the direction of movement of layers. This applied force is the measure of internal friction of viscosity of the fluid.

Viscosity of liquids

In case of liquids the internal friction arise because of intermolecular attractions. Molecules in the slower moving layer try to decrease the velocity of the molecules in the faster moving layer and vice versa, with the result that some tangential force is required to maintain a uniform flow.

Definition of Coefficient of viscosity

The tangential force required to maintain uniform velocity will depend upon two factors

(i) Area of contact A between the two layers

(ii) Velocity gradient

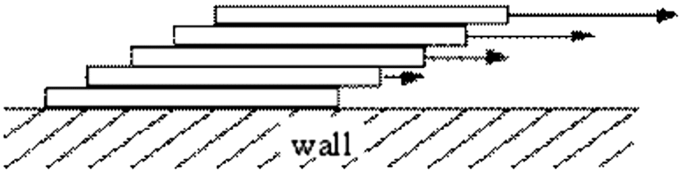
Thus, $F \propto A\frac{du}{dz}$ that is $F = \eta A\frac{du}{dz}$

Where η is known as the coefficient of viscosity. It is the tangential force that must be applied in order to maintain a velocity difference of unity between two parallel layers unit distance apart and having unit area of contact. SI unit of the coefficient of viscosity is **$Nm^{-2}s$.** In CGS units, it has the unit of **$dyn\ cm^{-2}s$** and is known as the **poise** unit.

5.3.1. General features of fluid flow

Laminar flow

In order to measure gas viscosities, **laminar flow** is assumed in the capillary. Laminar flow implies that the gas flows in "layers" such that each layer moves at a velocity infinitesimally different than the layers adjacent to it.



Since the wall is stationary, the layer along the wall has a velocity of zero. The fluid flows more quickly the further away it is from the stationary wall. Laminar flow is commonly experienced in smooth streams and rivers, where water flows slowly along the banks and rapidly in the center.

Fluid Flow is a part of fluid mechanics and deals with fluid dynamics. Fluids such as gases and liquids in motion are called as fluid flow. The motion of a fluid subjected to unbalanced forces. This motion continues as long as unbalanced forces are applied.

For example, if you are pouring water from a mug, the velocity of water is very high over the lip, moderately high approaching the lip, and very low at the bottom of the mug. The unbalanced force is gravity, and the flow continues as long as the water is available and the mug is tilted.

Types of Fluid

Following are the types of fluid:

- **Ideal fluid :** A fluid is said to be ideal when it cannot be compressed and has no internal resistance to flow (Zero viscosity). It is an imaginary fluid which doesn't exist in reality.
- **Real fluid:** All the fluids are real as all the fluid possess viscosity.
- **Newtonian fluid:** When the fluid obeys Newton's law of viscosity, it is known as a Newtonian fluid.
- **Non-Newtonian fluid:** When the fluid doesn't obey Newton's law of viscosity, it is known as Non-Newtonian fluid.

- **Ideal plastic fluid:** When the shear stress is proportional to the velocity gradient and shear stress is more than the yield value, it is known as ideal plastic fluid.
- **Incompressible fluid:** When the density of the fluid doesn't change with the application of external force is known as an incompressible fluid.
- **Compressible fluid:** When the density of the fluid changes with the application of external force is known as compressible fluid.

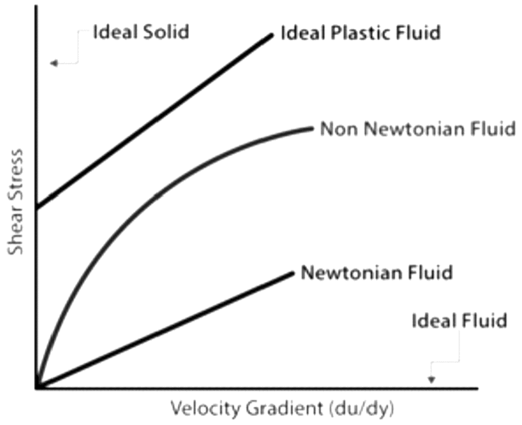
Below is the tabular representation of the fluid types :

Types of fluid	Density	Viscosity
Ideal fluid	Constant	Zero
Real fluid	Variable	Non zero
Newtonian fluid	Constant / Variable	$\iota = \mu \frac{du}{dy}$
Non-Newtonian fluid	Constant / Variable	$\iota \neq \mu \frac{du}{dy}$
Incompressible fluid	Constant	Non zero/ zero
Compressible fluid	Variable	Non zero/ zero

Classification of flows on the basis of Mach number :

- Incompressible flow has M<0.3.
- Compressible subsonic flow has M between 0.3 to 1.

Graph of types of fluid flow :



Types of Fluid Flow

Fluid flow has all kinds of aspects — steady or unsteady, compressible or incompressible, viscous or nonviscous, and rotational or irrotational, to name a few. Some of these characteristics reflect the properties of the liquid itself, and others focus on how the fluid is moving.

Steady or Unsteady Flow: Fluid flow can be steady or unsteady, depending on the fluid's velocity:

- **Steady :** In steady fluid flow, the velocity of the fluid is constant at any point.
- **Unsteady :** When the flow is unsteady, the fluid's velocity can differ between any two points.

Viscous or Nonviscous Flow: Liquid flow can be viscous or nonviscous.

Viscosity is a measure of the thickness of a fluid, and very gloppy fluids such as motor oil or shampoo are called **viscous fluids**.

Fluid Flow Equation

The volume of fluid replaced in a given interval of time is called the fluid flow equation.

Mass flow rate = ρAV

Where,

ρ = density

V = Velocity

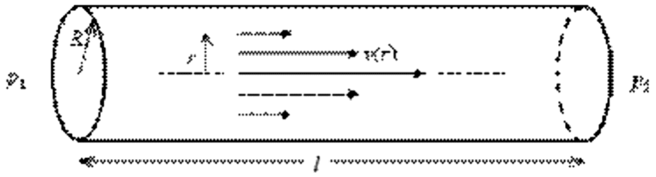
A = area

Flowrate = *Area* × *Velocity*

5.3.2. POISEUILLE'S EQUATION

Assumptions :

1. The fluid is Newtonian i.e. the tangential stress is proportional to the velocity gradient.
2. The liquid in contact with the wall of the tube is at rest
3. No acceleration acts along the axis of the tube.
4. The pressure difference is solely utilised to just balance the viscous force
5. Pressure is same at all points along the radius i.e. , there is no radial flow of the liquid
6. The motion is stream-line and parallel to the axis of the tube.



Let us consider steady flow of a liquid through a capillary of radius, r; length, l; under the pressure difference $(P_1 - P_2)$.

Considering a thin liquid cylinder of thickness dz at a distance z from the axis of the tube which flows with velocity, v.

The volume of the liquid coming out due to the flow of the thin liquid cylinder.

$= \pi\left[(z+dz)^2 - z^2\right]v = 2\pi z.dz.\,v$ (neglecting dz^2)

Therefore, the rate of the liquid through the capillary is,

$$\frac{dv}{dt} = \int_0^r 2\pi z.v.dz$$

The outer surface of the liquid cylinder of radius (z) is in contact with the slower moving layer and f_2 frictional force experienced opposite to the flow.

The inner surface is in contact with a faster moving layer feels frictional force, f_1, negative.

$f_1 = -\eta.2\pi z.1\frac{dv}{dz}$ since $\frac{dv}{dz}$ is (–ve) and $f_2 = \eta.2\pi z.1\frac{dv}{dz} + d(\eta.2\pi z.1\frac{dv}{dz})$

Total frictional force (dragging force) $f = f_1 + f_2 = d(2.\pi z.\eta.1\frac{dv}{dz})$

The driving force for the liquid in the cylinder = $\pi\left[(z+dz)^2 - z^2\right](P_1 - P_2)$

$= 2.\pi z.dz(P_1 - P_2)$

For steady flow, driving force + dragging force = 0

$$\therefore 2.\pi z.dz.(P_1 - P_2) + d(2.\pi z.\eta.1\frac{dv}{dz}) = 0.$$

Or, $d(2.\pi z.\eta.1\frac{dv}{dz}) = -2.\pi z.dz.(P_1 - P_2)$

Integrating $2.\pi z.\eta.1\frac{dv}{dz} = -\pi(P_1 - P_2)z^2 + A$

The equation is arranged

Or, $dv = \frac{(P_1 - P_2)}{2\eta\ell}z.dz + \frac{A}{2\pi\eta\ell} \times \frac{1}{z}dz$

Integrating again

Or, $v = -\frac{1}{4}\frac{(P_1 - P_2)}{\eta\ell} \times z^2 + \frac{A}{2\pi\eta\ell} \times \ln z + B$

When z = 0, v is maximum, in other words, finite. So, A must be zero otherwise v will be undefined.

$\therefore v = -\frac{P_1 - P_2}{4\eta\ell} + B$

Case 2.

When z = r and v = 0, B = $\frac{P_1 - P_2}{4\eta\ell} \times r^2$

The general expression of v becomes

$v = \frac{P_1 - P_2}{4\eta\ell} \times (r^2 - z^2)$. The plot of the equation represents parabolic for laminar flow through a capillary.

V is V_{maxm} at z = 0

$\therefore v = \frac{P_1 - P_2}{4\eta\ell} \times (r^2)$, Pressure difference $P_1 - P_2 = P$

$\therefore v = \frac{P}{4\eta\ell} \times (r^2)$

Rate of flow through the capillary is $\frac{dv}{dt} = \int_0^r 2\pi z. \times \frac{P_1 - P_2}{4\eta\ell} \times (r^2 - z^2)zdz$

$= \frac{P_1 - P_2}{2\eta\ell} \times \left(\frac{r^4}{2} - \frac{r^4}{4}\right) = \frac{P_1 - P_2}{8\eta\ell} \times r^4$

$$\therefore \eta = \frac{P_1 - P_2}{8\ell\left(\frac{dv}{dt}\right)} \times (r^4)$$

Error in the determination of η largely depends upon the error of r

From equation η is related to 4th power term r. So, a small error in the determination of r will cause four times error in the determination of η.

$$\therefore \eta = \frac{P_1 - P_2}{8\ell\left(\frac{dv}{dt}\right)} \times (r^4) \quad \text{Or } \eta = Ar^4$$

$$\frac{d\eta}{dr} = A\frac{d(r^4)}{dr} = 4Ar^3$$

Integrating $d\eta = 4Ar^3dr = 4\ \frac{\eta}{r}dr$

$$\frac{d\eta}{\eta} = \frac{4}{r}dr$$

$\ln\ \eta = 4\ln r + \ln A$

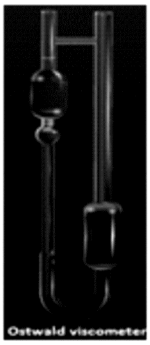
If dr is 1% of r {(0.001)r} then dη is 4% of η i.e. error in the determination of η becomes 4% when the error in the determination of r is 1%.

5.3.3 Determine the absolute viscosity of organic liquids.

The internal property of a fluid for its resistance to flow is known as viscosity. In 1844 Hagen–Poiseuille did their work concerning the interpretation that liquid flow through tubes and he proposed an equation for viscosity of liquids. This equation is called Poiseuille's equation.

$$\eta = \frac{\pi r^4 Pt}{8Vl}$$

Where η is called the viscosity coefficient, *t* is the time of flow of liquid, *V* is the volume of the liquid, *P* is the hydrostatic pressure, and *L* is the distance travelled by the liquid during time *t*. In the honour of Hagen–Poiseuille the unit of viscosity is called the Poise (P). The official SI unit for absolute viscosity is kg/m s (or Pascal-seconds, Pa s).



Viscosity can be measured using a viscometer.

The different types of viscometer are as follows:

1. Ostwald viscometer
2. Falling sphere viscometer
3. Falling piston viscometer
4. Oscillating piston viscometer
5. Vibrational viscometers
6. Rotational viscometers
7. Bubble viscometer

Ostwald viscometer is a commonly used viscometer, which consists of a U-shaped glass tube held vertically. For more accurate measurements it is held in a controlled temperature bath. It is also known as a glass capillary viscometer. A liquid is allowed to flow through its capillary tube between two etched marks and the time of flow of the liquid is measured using a stopwatch.

In an Ostwald viscometer the measured distance the liquid travels, L, will be always a constant ; the radius, r will always be a constant ; and by procedure the volume of liquid, V will also be constant. Equation (1) can then be simplified to :

$$\eta = KPt \quad \ldots \ldots (2)$$

$$K = \frac{\pi r^4}{8VL}$$

Where K is a constant and

The hydrostatic pressure is P proportional to the density of the fluid being measured. In our experiment we will be measuring the mass of equal volumes of liquid so that the viscosity will be proportional to the masses measured. Therefore we have the relation :

$$\eta \propto Kmt \qquad \ldots \quad \ldots.(3)$$

Where K and t are defined above and m is the mass of the liquid.

For finding the viscosity of liquids it is important to calibrate the viscometer using a reference liquid. Water is a commonly used reference liquid. The viscosity of water at 30.0°C is 0.8007 centipoise (cP). Knowing the values for the reference liquid and relation (3), we get :

$$\frac{\eta}{\eta_r} = \frac{mt}{m_r t_r} \qquad \ldots. \quad \ldots.(4)$$

Where : η_r is viscosity coefficient of the reference sample (water), m_r is the mass of the reference sample, and t_r is the time flow of the reference sample. Note that K cancels out. The other variables are the viscosity coefficient, mass, and time flow of the sample respectively.

With an Ostwald viscometer we can measure the time flow of a liquid (mass can be measured using standard laboratory procedures, e.g. a relative density bottle and a scale) and determine its viscosity by solving equation (4) for η.

$$\eta = mt\left(\frac{\eta_r}{m_r t_r}\right) \qquad \ldots \quad \ldots (5)$$

5.3.4 Temperature Dependence of Viscosity

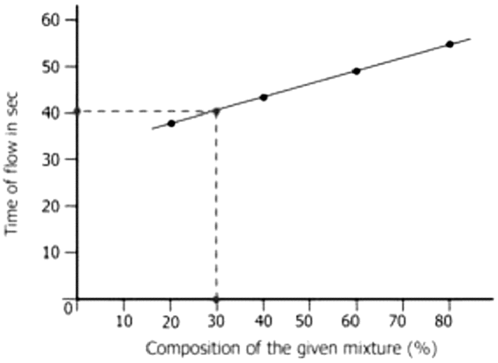
In 1889 Arrhenius expressed an equation for temperature dependent chemical reaction rates. Since then, many temperature dependent chemical and physical processes have been found to behave in accordance with Arrhenius-like equations. For the viscosity of many liquids, the viscosity decreases as the temperature increases in accordance with the following equation :

$$\eta = Ae^{(E_\eta/RT)} \qquad \ldots \quad \ldots(6)$$

Where A is a constant known as the Arrhenius constant, E_η is the activation energy for flow, R is the ideal gas constant, and T is the temperature of the liquid using an absolute scale (almost always K — the units of E_η and R and T should be chosen so that the ratio is dimensionless, A will have the same dimensions as η, in our case cP). A plot of η vs. 1/T should be linear and have a slope equal to E_η /R if the liquid's viscosity exhibits Arrhenius-like behaviour.

Determination of unknown composition

Using an Ostwald viscometer, we can also calculate the unknown composition of a mixture. The viscosities of mixtures of different known compositions are measured and a graph is plotted with viscosity against the compositions of the different mixtures. From the graph, the composition of the unknown mixture corresponding to the viscosity can be determined.



5.4 Conductance

Conductance is defined as a degree to which an object or a conductor can conduct the electric current through it. The conductance is a property which is labelled as G . Conductance is the reciprocal of resistance as it is calculated as a ratio of current '*I*' passing to the potential difference '*V*'. Ohms law is used to define the conductance. The unit of conductance is Siemens (S) or mho. Therefore, the conductance $G = I/V = 1/R$ mho or S. Not only in electronics but conductivity measurements are also done in ecology and environmental science to the level of nutrients in lakes and rivers.

5.4.1 Factors on which the conductance depends upon are as follows:

(1) Length of the conductor.

When the length of the conductor increases, the resistance increases. Hence the resistance is directly proportional to the length of the conductor and is inversely proportional to conductivity.

$R\ \alpha\ l$ where l is the length of the conductor

(2) Area of cross-section of the conductor.

The area of cross-section is inversely proportional to the resistance. $R\ \alpha\ 1/A$ where A is area of cross-section

Advantages :-

(a) Conductivity offers a fast, reliable, non destructive, inexpensive and durable means of measuring the ionic content of a sample. (b) Reliability and repeatability are excellent.

Disadvantages

The main drawback of conductivity is that it is a nonspecific measurement; that is, it cannot distinguish between different types of ions, thereby giving instead a reading proportional to the combined effect of all ions present. Therefore, it must be applied with some pre-knowledge of the solution composition or used in relatively pure (single solute) solutions to be successful.

5.5 Electrolytic Conductance (Conductometry)

5.5.1. Introduction

Conductometry is an electrochemical method of analysis concerned with electrical conductance through an electrolyte solution.

Electric conductivity of an electrolyte solution depends on,

1. type of ions (cations, anions, single or doubly charged) , solvation / size
2. number of ions (strong or weak electrolyte) concentration of ions (viscosity)
3. temperature,
4. mobility of ions.

5.5.2. Principle

The principle is based on the conductance of electrical current through electrolyte solutions similar to metallic conductions.

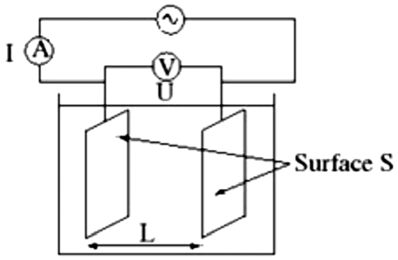
The electric conductance in accordance with Ohms law states that the strength of current (I) passing through conductor is directly proportional to potential difference and inversely to resistance.

$I = V/R$

[Electrolytic conductance is defined as the flow of electricity through an electrolytic conductor. The electrolytic conductor is a conductor through which the electricity passes in the form of ions. When a conductor is melted or the temperature is increased at one end then the dissociation of electrolyte takes place in the form positive ions and negative ions. In case of electrolytes, the conductor is an electrolytic solution and hence its ability to conduct ions through it is measured. The conductance of an electrolyte is calculated by measuring the resistance between the two nodes. When heat or electricity passes through an electrolyte, the solution dissociates into cations, that is, positive ions and anions that is negative ions. The conduction in electrolytes takes place when the electrolytes are in their liquid form.

Some factors that effect the conductance in electrolytes such as temperature, viscosity also depends upon how much concentrated the ions are.

The nature of the electrolyte also plays the important role in the conductance. The size of the ions produced and their solvation also effects the conductivity of an electrolytic solution. The number of ions in the electrolyte decides the nature of an electrolyte solution that is, if an electrolyte is a weak electrolyte it means that the number of ions in the solution are less. If the electrolyte is weak then the conduction will also be weak. Stronger the concentration, the greater will be the conductance. Similarly the temperature is an important parameter. The temperature helps to dissolve an electrolyte and hence enhances the degree of dissociation and automatically the conduction. The electrolytic conductivity also depends upon the mobility of the ions. The attraction between the ions decreases with an increase in the temperature which in turn increases the mobility and the ions in the electrolytes gain energy which increases their velocity and hence the conductivity.]



The following figure shows how the conductance of the electrolyte is obtained using the galvanic cell or by the method of electrolysis.

The two plates placed as electrodes in the solution and are connected with the help of voltmeter and the AC current is supplied so that electrolysis does not take place.

5.5.3. Resistance of a conductor

The resistance R of a conductor is proportional directly to length and inversely to cross-sectional area $G = \frac{1}{R} = \frac{1}{\rho}.\frac{A}{\ell} = \kappa.\frac{A}{\ell}$.

5.5.4. Conductance (G)

The ease with which current flows per unit area of conductor per unit potential applied and is reciprocal to resistance, is quantity, the conductance of a cubic material of edge length unity.

- The SI units is known as Siemens (S)

5.5.5. Specific Conductance (κ)

Conductance of the body of uniform length (l) and uniform area of cross-section (A) $\kappa = \frac{I}{R}\times\frac{\ell}{A} = G\times\frac{\ell}{A}$ *i.e* κ can be obtained from measured resistance. The ratio $\frac{\ell}{A}$ for the particular cell has fixed value and called cell constant. It can be obtained without knowing the actual value of l and A.

Potassium chloride is the accepted standard for accurately determining the values of cell constant, κ, at different concentrations and temperature in aqueous solutions.

SI units of κ is $\Omega^{-1}m^{-1}$ or $\Omega^{-1}cm^{-1}$

Conductance of 1 ml solution is κ (specific conductance)

5.5.6. Equivalent Conductivity (Λ_{eq})

Suppose 1 equivalent mass of an electrolyte is dissolved in volume V of the solution. Let this whole solution placed in conductivity cell. G = $\kappa\times\frac{A}{\ell}$, multiplying and dividing right side by the distance between the two electrodes, ℓ, of the cell, G = $\kappa\times\frac{A\times\ell}{\ell^2} = \kappa\times\frac{V}{\ell^2}$

$$\Lambda_{eq} = G\,\ell^2 = \kappa V.$$

The term $G\,\ell^2$ is known as equivalent conductivity.

$\Lambda_{eq} = \kappa V$, κ is specific conductance and V the volume of the solution containing 1 gm equivalent of the electrolyte.

or Equivalent conductance of an electrolyte is the conductance of 1 gm equivalent of the electrolyte placed between two parallel electrodes unit distance apart (1cm or 1metre).

or The conductance of a volume of solution containing one equivalent mass of a dissolved substance when placed between two parallel electrodes which are at a unit distance apart, and large enough to contain between them the whole solution.

Alternatively equivalent conductance, $\frac{\kappa}{c}$, where κ the specific conductance is in ohm^{-1} metre^{-1}, while c is the concentration of the electrolyte in equivalent of solute per metre^{3} of the solution. Here the unit of is ohm^{-1} metre^{2}equiv ^{1}.

The unit in CGS $\Lambda_{eq} = \kappa V, = (\Omega^{-1}cm^{-1}eq^{-1}) = \Omega^{-1}cm^{2}eq^{-1} = S\,cm^{2}eq^{-1}$

If c is the concentration of the solution then V will carry, $\frac{1000}{c}$ gmequiv

$\Lambda_{eq} = \kappa V = \kappa\frac{1000}{c}$, κ here is Ω^{-1} cm^{-1} and c here is in equivalent of solute per litre of solution).

Λ_{eq} is expressed in Ω^{-1} $cm^{2}eq^{-1}$

If κ is expressed in Ω^{-1} m^{-1}, and c in equivalent of solute per litre of solution.

$\Lambda_{eq} = \kappa\frac{1}{1000 \times c}$, expressed in Ω^{-1} $m^{2}eq^{-1}$

NOTE

Conductance of 1 cm^{3}or 1 ml solution is also known as **specific conductance**

Note

[c gm equivalent	dissolves in 1000ml
1gm equivalent dissolve in	$\frac{1000}{c}$ ml
Now, $\frac{1000}{c}$ ml or V ml contains	1gm equivalent
1 ml contains	$\frac{1000}{c}$ ml $\times \frac{1\,\text{gmequiv}}{1\text{ml}} = \frac{1000}{c}$ gmequiv

5.5.7. MOLAR CONDUCTANCE (Λ_m)

Conductance of a solution containing 1 mol of the solute in 1000 cm^{3} of the solution which placed between two parallel electrodes which are 1 cm apart

$$\Lambda_m = \kappa\frac{1000}{C}$$

5.5.8. Cell Constant

This is a constant characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrode of the cell and the area of cross-section of the electrodes. For a cell in which the electrodes are of equal area and aligned parallel,

$$\text{the cell constant} = \frac{\text{distance between electrodes}}{\text{area of cross section of each electrode}} = \frac{1}{a}$$

$$\text{Specific conductance, } \kappa = \frac{\text{cell constant}}{\text{resistance of electolyte}}$$

Note

1. **In an experimental measurement of conductance, direct current is not used : alternating current is used. This is to prevent polarisation at the electrodes and electrolysysis.**
2. **The various stages of the experiment are:**

   (a) determination of the cell constant using 0.1N or 0.01N KCl, whose specific conductance is known.

   (b) determination of the specific conductance of the given electrolyte, using the above cell constant

   (c) evaluation of equivalent conductance from specific conductance.

5.5.9. Specific Conductance and Equivalent Conductance – Their Variation with Concentration

Specific Conductance: Dilution spreads the ions of an electrolyte through a larger volume decreasing the number of ions per unit volume and hence decreasing the specific conductance. But with dilution, the degree of dissociation of the electrolyte increases tending to increase the number of ions in solution. The former effect (i.e. spreading of ions) being predominant, specific conductance decreases with dilution (i.e. κ decreases in concentration).

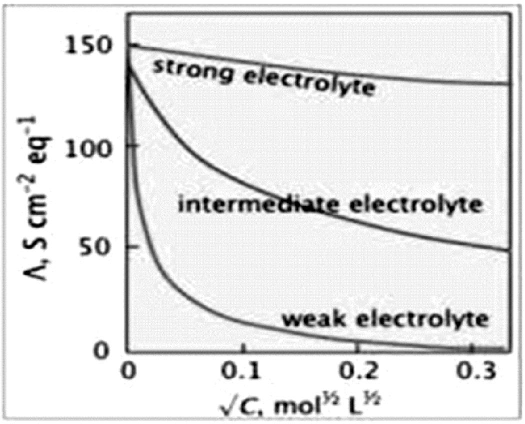
Equivalent Conductance : If there had been complete dissociation of a weak electrolyte into ions, equivalent conductance should not change with dilution (in this case specific conductance and dilution are inversely related). But due to increase in the degree of dissociation of the electrolyte with dilution, the equivalent conductance increases. This variation holds good for strong electrolytes are completely ionised at all concentrations (even in the solid state, salts like NaCl, KCl are completely ionised), their equivalent conductance increases with dilution.

5.5.10. Anomalous Behaviour of Electrolytes

For strong electrolytes, the plot of $\Lambda \text{ vs } \sqrt{c}$ is a straight line in the low concentration region. Λ attains a limiting value at very large dilution and this value is referred to as equivalent conductivity at infinite dilution Λ_∞ or Λ_0. At very large dilution, influences that tend to lower the conductivity are absent and hence limiting value of Λ at such dilutions. The variation of Λ with c is given by the Debye-Huckel-Onsager Conductance equation.

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c}$$

Λ_0 is the equivalent conductance at infinite dilution, which is a constant for the given electrolyte in a given solvent at a particular temperature. A and B are constants for the given solvent and temperature. For weak electrolytes, however, the plots of Λ vs $\sqrt{c}$ is not a straight line ; as c → 0, the curve approaches the Λ axis with a sharp rise.



5.5.10.1. Anomaly of strong electrolytes

Strong electrolytes are electrolytes which are completely ionized in solution. Typically, electrolytes like KCl and NaCl are known to be completely ionized even in the solid state (X-ray diffraction studies). Due to complete ionization of strong electrolytes, the concentration of ions, even in dilute solutions, is appreciable and hence interionic attraction i.e. attraction between oppositely charged ions is quite significant. The forces of interionic attraction are of long range character i.e. they operate over longer distances, compared to the van der Waals forces. Interionic attraction responsible for the anomalous behaviour of strong electrolytes. Two important anomalies are discussed below.

5.5.10.2. Conductivity :

It *is* well-known that the equivalent conductivity of a weak electrolyte increases with dilution and this is explained by the increased ionization of the electrolyte with dilution. But strong electrolytes are completely ionized in solution at all concentrations and hence one would not expect any variation of Λ with concentration. However it is found that for strong electrolytes too, Λ increases with dilution, but the cause is fundamentally different. Conductivity of an electrolyte depends on the speed of the ion and the concentration of the ion, besides other factors. The motion of an ionic in species an electrical field is retarded by the oppositely charged species due to interionic attraction. In a more methodical treatment, the retarding influence of the oppositely charged ionic species is described as the asymmetry or relaxation effect and the electrophoretic effect. Λ decrease in the concentration of the electrolyte decreases these retarding influences; consequently the speed of the ions increases and hence the conductivity also increases. The variation of Λ with concentration for strong electrolytes is given by the Debye-Huckel-Onsager conductance equation, which holds good for very low concentrations of the electrolyte. The conductance equation for an electrolyte, usually of 1 : 1 valence type, is

$$\Lambda = \Lambda_o - (A + B\Lambda_o)\sqrt{c}$$

where, Λ is the equivalent conductance at concentration 'c' (in equivalents of the electrolyte per litre of solution). Λ_0 is the maximum limiting value of Λ, called the equivalent conductance at infinite dilution.

The term on the right-hand side viz., $[A + B\Lambda_0]\sqrt{c}$ represents the retarding influence on equivalent conductivity. The constants A and B include two important properties of the solvent viz., dielectric constant and viscosity besides temperature.

Apart from the above retarding influence, there is another factor contributing to the lowering of conductivity. Ion, particularly of high valence type, in solvents of low dielectric constant, form what a re-called 'ion- pairs', which do not contribute to conductivity. There is a dynamic equilibrium between the ion pairs and the separated ions or free ions. With dilution, the equilibrium shifts towards the free ions resulting in an increase in equivalent conductivity.

5.5.10.3. Ostwald's dilution law :

Another notable anomalous behaviour of strong electrolytes is with respect to Ostwald's dilution law. The law holds good for weak electrolytes. Taking a weak electrolyte of 1 : 1 valence type.

$AB \rightleftharpoons A^+ + B^- : \dfrac{[A^+][B^-]}{[AB]}$ is practically a constant = K, called the dissociation constant (A true constant would, however, involve activities in the place of concentration).

Thus $\dfrac{\alpha^2 c}{1-\alpha}$ is nearly a constant; here α is determined through the equivalent conductance of the weak electrolyte at each concentration.

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Thus $\dfrac{\left(\dfrac{\Lambda}{\Lambda_0}\right)^2}{1-\left(\dfrac{\Lambda}{\Lambda_0}\right)} \approx \text{constant}$

But this ratio is not a constant for strong electrolytes, which are completely ionized. In fact a constancy is not expected, even if we consider the ion-pairs in strong electrolytes on par with the unionized molecules in weak electrolytes is obtained from the value, which is influenced not only by ion-pair formation but also by the two retarding influences, namely 'asymmetry effect' and 'electrophoretic effect'. (see next section).

Therefore $\dfrac{\Lambda}{\Lambda_0}$ in the case of strong electrolytes does not represent its degree of dissociation into free ions and hence it is given the non-commital name, 'conductance ratio'. It is worthwhile comparing Onsager conductance equation for a strong electrolyte and Ostwald's dilution law for a weak electrolyte, both of a 1 : 1 valence type.

Onsager Equation : $\Lambda = \Lambda_0 - [\text{constant}]\sqrt{c}$

Ostwald's dilution law : $\Lambda^2 c = (\text{constant})(\Lambda_0^2 - \Lambda_0\Lambda)$

The two equations above are totally of different forms.

5.6 Kohlrausch's law of independent migration of ions

Each ion of an electrolyte makes a definite contribution to the equivalent conductance of the electrolyte and at infinite dilution this contribution is independent of the presence of the other ionic species. Thus the equivalent conductance is independent of the presence of the other ionic species. Thus the equivalent conductance of an electrolyte is the sum of the equivalent conductance of the constituent ions at infinite dilution.

5.6.1. Application of Kohlraush's law

1. The Kohlraush's law is useful in evaluating Λ_0 of a weak electrolyte from the Λ_0 values of suitably chosen strong electrolytes.

(Λ_o of a weak electrolyte cannot be determined by extrapolation of the plot of Λ vs c or $\sqrt{c}$. For a strong electrolyte, however, it is possible – see above section). This can be illustrated by a numerical example.

Λ_o of CH_3COONa, HCl, NaCl at infinite dilution are respectively 91.426 and 126 $ohm^{-1}cm^2equiv^{-1}$at a certain temperature, Λ_o of the weak electrolyte viz. CH_3COOH may be evaluated thus

$$\Lambda_o(CH_3COOH) = \lambda_o(CH_3COO) + \lambda_o(Na^+) \quad \ldots\ldots..(1)$$

$$\Lambda_o(HCl) = \lambda_o(H^+) + \lambda_o(Cl^-) = 426 \quad \ldots\ldots\ldots\ldots(2)$$

$$\Lambda_o(NaCl) = \lambda_o(Na^+) + \lambda_o(Cl^-) = 126 \quad \ldots\ldots\ldots..(3)$$

$$\therefore \Lambda_o(CH_3COONa) + \Lambda_o(HCl) - \Lambda_o(NaCl) = \lambda_o(CH_3COO^-) + \lambda_o(H^+) = \Lambda_o(CH_3COOH)$$

= 91 + 426 -126 = 391

2. Equivalent conductance of an ion in an electrolyte can be determined from Λ of the electrolyte thus :

$\lambda_{iion} = t_{ion} \times \Lambda$, where t_{ion} is the transport number of the ion.

3. From λ_o(ion) it is possible to calculate the absolute speed of the ion, using the relation :

$$u_o \text{ of an ion } = \frac{\lambda_o}{F}$$

where u_o is the speed of the ion at infinite dilution at unit potential gradient (1 volt per cm) and F is the Faraday= 96,500coulombs

(If instead of equivalent conductance, molar conductance or ionic conductance is known, then u_o of the ion $uo = \frac{\text{ion conductance}}{ZF}$, where Z is the valence of the ion.

Note. There are also methods for direct determination of ionic speed.

5.7 The Debye-Huckel Theory

5.7.1 Introduction

In a non-electrolytic solution, the solute particles are uncharged, therefore long range columbic interactions are not observed in these type of solutions. The short-range interactions, arising from dipole-dipole or dispersion forces become significant only when the concentration of the solute is high. Thus, in a dilute non electrolytic solution there are no interactions between solute particles. On the other hand electrolytic solution contains strong ion-ion interactions and ion-solvent interactions. Such solutions where ion-ion interactions cannot be ignored are termed as real / non-ideal solutions.

Non–ideality in these solutions arises because, oppositely charged species attract each other due to electrostatic forces while ions of same charge repel each other.

We can appropriately say that there are no interactions between solute particles in dilute electrolytic solutions Long-range columbic interactions between ions is ignored and only ion-solvent interactions are considered.

Since in non-ideal solutions, ion-ion interactions are present, it is not just the analytical concentration of the species that can be used but its effective concentration is used. We define this effective concentration as activity (a_i) of the species.

Mathematically, it is given by : $a = \gamma m$

Where, a = activity, γ = activity coefficient (concentration dependent), m = molality (mol/kg)

Individual ionic-activity coefficients cannot be determined experimentally. This is because in an electrolytic solution, positive and negative ions cannot be treated separately, as the cations are always accompanied by anions and vice versa. Therefore, the individual contributions of the ionic species to the concentration cannot be determined. Thus, activity coefficients of individual ions, are inaccessible to experimental measurement. We can only measure the activity coefficient of the net electrolyte. Therefore we define mean ionic terms for the ions in solution of strong electrolytes.

Mathematically $A_xB_y \rightarrow xA^{y+} + yB^{x-}$ Mean Ionic Activity is given as;

$$a_\pm = a_+^x a_-^y$$

Where, y_+ = activity coefficients for cations, y_- = activity coefficients for anions, m = molality.

The mean activity of the electrolyte is defined as $a_\pm = (a_+^x . a_-^y)^{\frac{1}{x+y}}$

Similarly the mean activity coefficient of the electrolyte is $\gamma_\pm = (\gamma_+^x, \gamma_-^y)^{\frac{1}{x+y}}$

Mean molality of the solution, $m_\pm = (m_+^x . m_-^y)^{\frac{1}{x+y}}$

From the above definitions from the definitions of γ_+ and γ_- it follows that

$$a_{\pm} = m_{\pm}.y^{\pm} \quad \text{or} \quad y^{\pm} = \frac{a_{\pm}}{m_{\pm}}$$

Note : If the concentration is expressed as molar, (i.e. moles of solute per litre of solution) activity coefficient is represented by the symbol ‘f’ instead of ‘γ_+’.

Thus $$f_+ = \frac{a_+}{c_+}; \quad f_- = \frac{a_-}{c_-}; f_{\pm} = \frac{a_{\pm}}{c_{\pm}}$$

The following numerical examples would illustrate the above definitions.

Example : Relate $a_{\pm}$ to ‘a’ and $c_{\pm}$ to ‘m’ in the case of KCl and $CaCl_2$ solutions.

For KCl solution

Here x = 1 and y = 1

$\therefore a_{\pm} = (a_+^1 . a_-^1) = a^{\frac{1}{2}}$, where ‘a’ is the total activity

$m_{\pm} = (m_+^1, m_-^1)^{\frac{1}{2}}$. But $m_+ = m_- = m$, the molacity of KCl solution.

$$\therefore m_{\pm} = m. \quad \therefore \gamma_{\pm} = \frac{a_{\pm}}{m_{\pm}} = \frac{a_{\pm}}{m}$$

For $CaCl_2$ solution

Here x = 1 and y = 2

$$\therefore a_{\pm} = (a_+^1, a_-^2)^{\frac{1}{2}} \text{ or } a^{\frac{1}{2}}$$

$m_{\pm} = (m_+^1, m_-^2)^{\frac{1}{2}}$. But $m_+ = m$ and $m_- = 2m$, where ‘m’ is the molacity of $CaCl_2$ solution.

$$\therefore m_{\pm} = (m.4m^2)^{\frac{1}{2}} = 4^{\frac{1}{2}}.m \qquad \therefore \gamma_{\pm} = \frac{a_{\pm}}{m_{\pm}} = \frac{a_{\pm}}{4^{\frac{1}{2}}.m}$$

5.7.2. Ionic Strength

The interionic attraction in an electrolyte depends on the valences and concentration of the ions. These two factors are combined in a single entity, known as the ionic strength, defined as

$$I = \frac{1}{2}\Sigma m_i z_i^2,$$

where z_i is the valence of the ionic species of the i'th kind and m_i its molality. Ionic strength is an important concept used in the theory of strong electrolytes. The evaluation of ionic strength in the case of electrolytes of a few valence types is shown below :

1-1 type electrolyte : Examples NaCl, KNO_3; molality = m

$m_+ = m$, $m_- = m$, $z_+ = z_- = 1$

$$I = \frac{1}{2}(m.1^2 + m.1^2) = m$$

Thus for a 1-1 type of electrolyte, the ionic strength is the same as molality.

1-2 2-2 type electrolyte: Examples $CuSO_4$; molality = m

$m_+ = m_- = m$; $z_+ = z_- = 2$

$$I = \frac{1}{2}(m.\ 2^2 + m.\ 2^2) = 4m$$

Debye Huckel suggested a theory which relates the theoretical individual activity coefficients $(\gamma_{\pm}, \gamma_{-})$ to the experimentally accessible mean ionic-activity coefficient $(\gamma_{\pm})$.

With the help of this theory, the distribution of charges around ions in solution was clearly understood.

5.7.3. The Debye – Hückel Theory

The Debye Hückel theory for determination of mean activity coefficients $(\gamma_{\pm})$ was proposed by Peter Debye and Erich Hückel in 1923. This theory is applicable to strong electrolytes (salts). Strong electrolytes are neutral and dissocial completely. It is a theoretical explanation for deviation from ideality in solutions of strong electrolytes. This theory is an analytical approach to the factors influencing activity coefficients of ionic solutes.

Debye and Hückel developed this theory with which individual activity coefficients can be calculated, and using this mean activity coefficients is calculated which could be tested against experimental data.

5.7.4. Postulates of Debye-Hückel Theory

The basis of the Debye-Hückel Theory is laid on strong electrolytes. The electrolytic solution consists of solvated ions and water molecules. The basic representation of an idealized electrolytic solution is shown in fig.1. The ions are represented as spheres with unit electrical charge. The solvent (pale blue) is shown as a uniform medium. Each ion is surrounded more closely by ions of opposite charge than by ions of same charge. The principal assumption is that departure from ideality is due to electrostatic interactions between ions (which varies as $\frac{1}{r^2}$)

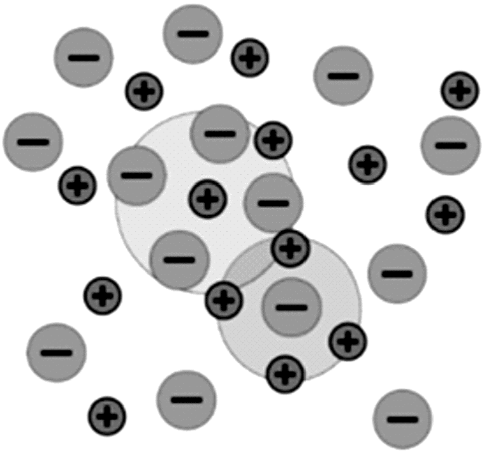


Fig. Ideal representation of a 1:1 electrolyte

The postulates of the Debye-Hückel theory are as follows:

1. The ion were treated as point charges
2. The ion-ion interactions were assumed to be long range coulombic forces (which varies as $\frac{1}{r^2}$) while short range non-couloumbic forces (dispersion forces) play a negligible role.
3. The role of solvent is to provide a medium which is a continuum of dielectric constant (ε) which is necessary for the operation of interionic forces (In the present case the water molecules are looked upon as a continuous dielectric medium)
4. The concept of charge density was introduced which measured charge density (ρ) as a function of distance (r).
5. All the ions in the electrolytic solution are free to contribute to charge density.

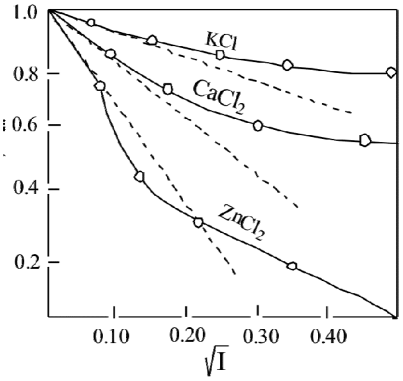
Bulk charge density was assumed to be zero, which means that the solution is overall electrically neutral.

The basic percept of this theory is that because of attraction between positive and negative ions, there are, on an average in the vicinity of a particular ion more ions of opposite sign and this will reduce the 'effective concentration of ions'. Consequently if the solution is diluted the separation of ions involves doing an additional work to overcome these interionic interactions and this represents deviation from an idealsolution. Ultimately, Debye- Hückel theory generates a relationship between mean activity ($\gamma\pm$) coefficient and strength (I).

$$\log \gamma_{\pm} = -0.509|z+z-|\sqrt{I}$$

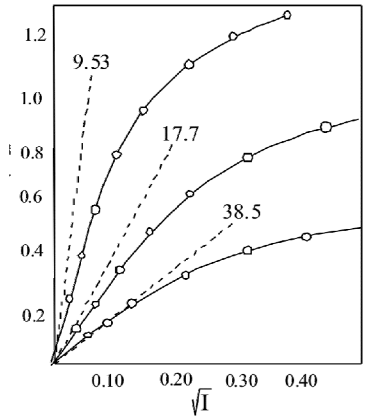
5.7.5 Verification of the Debye–Huckel equation

Activity coefficients can be determined from vapour pressure, freezing point and EMF measurements. Plots of $\log c_{\pm}$ against $\sqrt{I}$ should yield a straight line for aqueous solutions of electrolytes, if the limiting law is valid. The dotted lines in the figure are drawn with the theoretically expected slopes. The experimental curves are the full lines.



Test of the limiting Debye-Huckel equation

All cases the theoretical and experimental slopes agree for low values of $\sqrt{I}$ i.e. for quite low concentrations. The deviations at higher concentrations become more prominent for electrolytes other than uni-univalent electrolyte e.g. $CaCl_2$, a bi-univalent electrolyte and $ZnSO_4$, a bi-bivalent electrolyte. A second way of testing the theory is to plot $-\log c_{\pm}$ against $\sqrt{I}$ for the same electrolyte in solvents of varying dielectric constants. According to the limiting law a plot of $-\log c_{\pm}$vs $\sqrt{I}$ should give a straight line with a slope directly varying with $\frac{1}{(DT)^{\frac{1}{2}}}$



Limitting Debye-Huckel equation at different dielectric constants

The diagram above gives these plots as dotted lines (theoretical) and full lines (experimental). Again it may be seen that there is very good agreement for low values of √I.

5.7.6 The Debye- Huckel-Onsager Theory

The Theory was later on modified by **Onsager (1926)** to form the Modern Theory of Strong Electrolytes known as **Debye-Huckel-Onsager Theory** and the equation derived is known as **DHO equation**.

The **Debye-Huckel-Onsager (DHO)Theory for strong electrolyte showed**

How for strong electrolytes, the value of molar conductance at infinite dilution is much less than unity.

The fundamental idea underlying their work is based on the electrical attraction among the oppositely charged ions, which affect the speed of an ion in the electric field and arecalled **"inter ionic effects". There are two such effects**

(i) Relaxation effect and Asymmetry effect

(ii) Electrophoretic effect

Relaxation effect and Asymmetry effect

(a) In the absence of an applied field, **the ionic atmosphere is spherically symmetric** around the centre.

(b) But in presence of electric field is present, cations move towards cathode and anions move towards anode. This leaves a large number of oppositely charged ions behind than in the front. Thus, the **spherically symmetric ionic atmosphere is distorted** and the **centres of negative and positive charge no longer coincide.**

Overall effect:

The excess opposite charge left behind drags the moving ion backwards and slows the forward displacement of the centre of charge of the atmosphere a short distance behind the moving ion.The **attraction between the opposite charges retards the motion of the central ion.**

The **rate of formation of new ionic atmosphere is not the same** at which the **previous ionic atmosphere disperses and the later later takes more time.** This time is called the **Relaxation time.**

In the case of the moving ion there will always be an excess of ions of opposite charge. The ions will always be dragged back. **This effect** will **decrease the mobility of the ions** and hence **the conductivity** is known as the **Relaxation effect or Asymmetric Effect**

Electrophoretic Effect

We have seen that the ions moving under electric field experiences **a viscous drag**. When the **ionic atmosphere is present this drag is enhanced because the ionic atmosphere moves in an opposite direction to the central ion. The enhanced viscous drag,** called the **Electrophoretic effect, reduces the mobility of the ions and** hence also reduces their conductivities.

The **solvent molecules attach themselves to ionic atmosphere** and hence also reduces their conductivities.

The **solvent molecules attach themselves to ionic atmosphere** and **the ions move in the direction opposite to that of** central ion. It **produces friction due to which** the **mobility of the central ion is retarded.**

If the solution of electrolyte is not infinitely dilute, the motion of the ions is retarded.

Because of the **electrical attraction between ions of opposite sign (Relaxation or Asymmetry effect),** and

Because the positive and negative ions are moving in opposite directions each carrying some solvent (Electrophoretic effect).

Both the effects are intensified as the concentration of the electrolyte increases so that the **retarding forces** increase and the **conductivity decreases.**

5.8 Transport Number

5.8.1. Transport number

During the passage of electric current through an electrolyte, the total electric charge is carried by both the cations and the anions.

The ratio.

$\dfrac{\textit{Charge carried by the cations}}{\textit{total charge carried by cations and anions}}$ is known as the transport number of the cations ; similarly we can define the transport number of the anions. The transport number can also be expressed as the ratio of speeds and ratio of ionic conductances. Thus the transport number of cations or anions.

$$=\frac{\textit{speed of cations or anions}}{\textit{speed of cations} + \textit{speed of anions}}$$

$$\text{i.e.}\ \frac{u_+}{u_+ + u_-}\ \text{or}\ \frac{u_-}{u_+ + u_-} = \frac{\lambda_+}{\lambda_+ + \lambda_-}\ \text{or}\ \frac{\lambda_-}{\lambda_+ + \lambda_-}$$

The transport number is characteristic of the ionic species (H^+ and ^-OH have the largest transport numbers); for a given ionic species, the transport number depends upon concentration. The transport number may be experimentally determined by the classical Hittorf's method in which concentration changes around the cathode or the anode are measured. It can do be evaluated by directly measuring the absolute speed of an ionic species (moving boundary method). Potentiometric methods are also available for evaluating transport numbers.

5.8.2. EXPERIMENTAL DETERMINATION OF TRANSPORT NUMBER

The concept of ionic atmosphere in strong electrolytes : As we have seen earlier, the anomalous properties of a strong electrolyte are explained in terms of interionic attraction, which has been statistically treated through the concept of what is known as the ionic atmosphere. The presence of the ionic species in the immediate vicinity of a given ion, called the central ion, is governed by two factors. One is thermal agitation that leads to a random orientation of ions of both the species (positive and negative) around the central ion. The other factor is the attraction of the central ion towards ions of opposite charge. There is a dynamic compromise between these two factors and the probability of finding an oppositely charged ion in the immediate vicinity of the central ion is more than finding an ion of the same sign. The region immediately surrounding the central ion, with an excess of opposite charge density is known as the ionic atmosphere; the total charge of the ionic atmosphere is equal, but opposite to that of the central ion.

Asymmetry or Relaxation effect and Electrophoretic effect : These are retarding influences on the movement of ions of a strong electrolyte in an electrical field. As long as an ion is stationary, its ionic atmosphere is spherically symmetrical, but when it begins to move, the symmetry is lost. The reason is that as the ion moves to the front, the old ionic atmosphere that was associated with it in its previous position does not decay instantaneously, but lingers for some time. This, together with the new ionic atmosphere at the front, gives an asymmetric ionic atmosphere with a larger charge density (with sign opposite to that of the central ion) at the back of the central ion. Hence the moving ion suffers a retardation. This is known as asymmetry or relaxation effect. This retarding influence decreases with decrease in concentration.

The other retarding influence is the electrophoretic effect. As an ion move to the front, the oppositely charged ions in the ionic atmosphere are pulled in the opposite direction. Since the ions are solvated, the ion moving to the front has to swim upstream against a counter current of the solvent molecules. This retarding influence also decreased with decrease in concentration.

Dispersion of conductance and anomalous conductance.

(a) In the measurement of conductance of strong electrolytes, using an alternating current, with increasing frequency, the conductance suddenly shoots up at a particular frequency (of the order of several thousand cycles per second), called the threshold frequency, which depends on the nature of the electrolyte and its concentration. This is known as Debye-Falkenhagen effect. This sharp increase in conductance is due to the elimination of the asymmetry effect, discussed previously. At such high frequencies (threshold), the ion is practically stationary and the ionic atmosphere is spherically symmetrical.

(b) If the conductance measurement is made with direct current and if the potential gradient is extremely large (of the order of several thousand volts cm^{-1}) again the conductance shoots up. At such high electrical fields, the ion moves with a speed that will take it away from the influence of the lingering ionic atmosphere at the back. This effect is known as the Wien effect. An increase in conductance due to the elimination of the retarding influence of the ionic atmosphere is sometimes referred to as dispersion of conductance.

(c) Another anomalous conductance behaviour is observed in the case of certain electrolytes of high valence type of solvents of low dielectric constant. For each electrolytes, the variation of equivalent conductance Λ_{eq} with concentration is anomalous. In the initial stages, an increase in concentration is accompanied by a decrease in Λ_{eq}, in accordance with the general trend. But at one stage, Λ_{eq} begins to increase with increase in concentration. This behaviour is rationalized as follows:

In the initial stages, with increase in concentration, the individual ions form more and more ion pairs, which do not contribute to electrical conductance. (This is of course in addition to the increase in the asymmetry and electrophoretic influences, which also lower the conductance). But at higher concentrations, ion – pairs are gradually converted to ion – triplets which contribute to conductance.

$$3(+-) \rightleftarrows (+-+) + (-+-)$$

ion pair ion-triplet ion-triplet

Apparent deviation from Ohm's law : According to Ohm's law , the current flowing through a conductor is directly proportional to the potential difference that drives it, that is $\frac{E}{C}$ is a constant $\frac{E}{C} = R$ the resistance of the conductor. Ohm's Law holds good, so long as the resistance remains constant. in the case of electrolytes, the resistance does not always remain constant during electrical measurements. This is illustrated by the following cases.

(a) With the possibility of polarisation at an electrode, say gas evolution at the electrode, current will begin to flow continuously only when a minimum potential is applied, which is referred to as the deposition potential. Till the commencement of continuous current flow,or continuous electrolysis, the resistance is not constant and so $\frac{E}{C}$ is also not a constant.

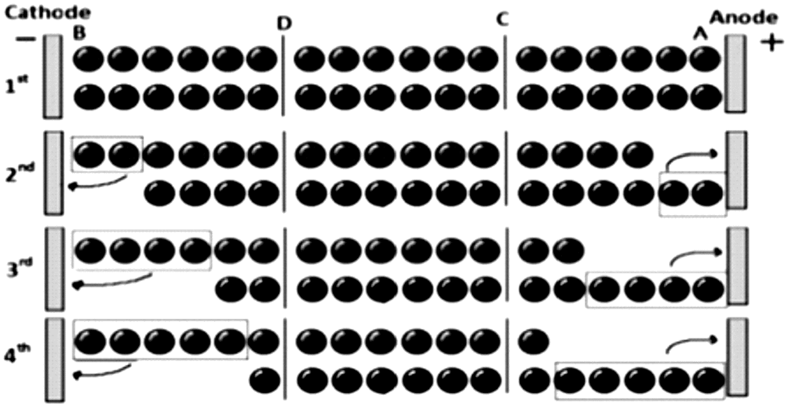
(b) During electrolysis, the resistance of the electrolyte solution changes due to a change in the concentration of the electrolyte.

(c) In connection with the Debye Falkenhagen effect we have seen that at the threshold frequency, the conductance shoots up. Similarly in Wien effect, the conductance sharply increases at a threshold potential gradient. Thus these are also cases of apparent deviation from **Ohm's law**.

Hittorf Method

Relative speed of ions during electrolysis

Let us consider electrolytic vessel containing two metal electrodes A and B. The vessel is divided into three compartments AC, CD and DB termed as aniodic central and cathodic compartments respectively.



Before electrolysis the position of the solution is represented as (1st) in the diagram. Now on applying potential, i.e. energy difference, only two of the cation move towards cathode. This condition will be represented in the (2nd) diagram . There will be two unpaired cations in the cathodic compartment. As unpaired ions always get discharged at the respective electrodes (by the gain or loss of electrons as the case may be), two cations will be discharged at the cathode and two anions will be discharged at the anode.

- Now suppose that if two cations move towards the cathode and two anions will move towards the anode in the same time as represented by 3rd . Now four cations and four anions will be discharged at the respective electrodes.
- Finally, if cations and anions move with different velocities so that two cations move towards the cathode and the three anions move towards the anode. In this case, five unpaired cations and five unpaired anions (i.e. same number) will be discharged at the respective electrodes as shown in the diagram.
- Thus if only cations are moving the same number of cations and anions will be discharged at the respective electrodes.
- It is based on the fact that during electrolysis " the loss in the amount of electrolyte around any electrode is proportional to the speed of the ion moving away from it."

$$\frac{loss\ around\ the\ cathode}{loss\ around\ the\ anode} = \frac{speed\ of\ anion}{speed\ of\ cation} = \frac{v}{u}$$

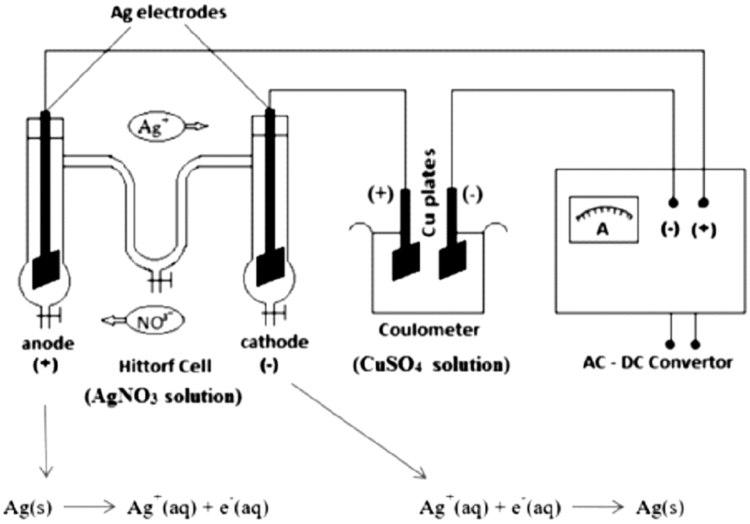
Adding 1 to both sides we get

$$1 + \frac{loss\ around\ cathode}{loss\ around\ anode} = 1 + \frac{v}{u}$$

$$\frac{loss\ around\ anode + loss\ around\ cathode}{loss\ around\ anode} = \frac{u+v}{u}$$

Taking reciprocal we get

$$\frac{loss\ around\ anode}{Total\ loss} = \frac{u}{u+v} = \mathrm{t}_+$$



The experimental setup for the determination of Transport number, Hittorf's Method.

Hittorf's apparatus consists of a two limbed vessel connected by a narrow U-tube in the middle. Both limbs as well as the tube are provided with stop-cocks at the bottom for the withdrawal of the solutions.

The two limbs are provided with Pt electrodes. To determine the transport numbers Ag^+ in $AgNO_3$. The electrodes are either Pt or pure Ag.

The apparatus is filled with a saturated solution of $AgNO_3$ (usually 0.1N) and the cells is connected in series with a source of direct current.

IONIC MOBILITIES

If an electric current is passed through a solution of an electrolyte, the anions and cations move with characteristic speeds toward the anode and cathode. These speeds vary with *magnitude of the applied voltage*, *temperature* and *nature of individual ions*. Among the factors associated with the nature of the ions are its *charge* and *size*. One type of ion does not affect the velocity of another type under a given set of conditions unless the concentration is sufficiently great to result in appreciable interionic attraction effects.

The mobility of an ion is defined as its velocity in the direction of an electric field of unit strength (i.e. V/m in SI units). The mobility of ions is generally quite small (in the order of 6×10^{-8} $m^2.s^1.V^{-1}$). The exceptions are hydrogen and hydroxyl ions with the abnormally high mobilities of 36.3×10^{-8} and 20.5×10^{-8} $m^2.s^{-1}.V^{-1}$, respectively.

Ionic mobilities are important factors in many electrochemical phenomena. However, it is more convenient to use a quantity called the transference number of an ion rather than the ionic mobilities in the formulas applicable to such phenomena. The *transference numbers* of the cation and anion are simply the numbers which gives the fraction of the current carried by each of the ions.

Hittorf's Method has been generally employed for the experimental determination of transference numbers and involves measurement of changes of concentration in the vicinity of the electrodes.

Current carried by the cations

$$I_+ = \frac{n_+ u z_+ e}{d}$$

where ;

n_+ = number of cations

u = velocity of the cation in the solution [cm/s] or mobilities of the cation

z_+ = charge of the cation

e = quantity of electricity associated with a unit charge [volts]

d = separation distance of the two plates

Current carried by the anions

$$I_- = \frac{n_- v z_- e}{d}$$

Total current carried by both ions, $I = I_+ + I_- = \frac{n_+ u z_+ e}{d} + \frac{n_- v z_- e}{d}$

The electro neutrality principle expresses the fact that all pure substances carry a net charge of zero ; $n_+z_+ = n_-z_-$

Thus total current becomes $I = \frac{n_+z_+e(u+v)}{d}$

The fraction of the total current for cation $t_+ = \frac{I_+}{I} = \frac{u}{u+v}$ and $\frac{I_-}{I} = \frac{v}{u+v}$

The sum of transference number is $t_+ + t_- = 1$

Although the speed of a particular ion does not dependent on the nature of the ion, the transference numbers depends on eachother.

Problem:

Discuss hittorf method of determination of transport numbers.

Solution :

The Hittorf Method

Every 1F of electricity causes dissolution and precipitation of 1 g-eq of metal, transfer $t_+ = (1 - t_-)$ cations to the cathode and transfer $t_- = (1 - t_+)$ anions to the anode.

As a result, in compartment I there is a loss of salt in quantity

$\Delta nI = t\text{-}Q/F$ in compartment III the same profit of salt, in compartment II the salt concentration is not changes.

Conditions for correct electrolysis:

(1) absence of adverse reactions at the electrodes (100% yield oncurrent)

(2) no transfer of solvent (dilute solutions)

(3) absence of diffusion equalization ofconcentration

(4) hydrostatic equilibrium, absence of electroosmosis and other phenomena (low current, short time).

Compartment I – negative electrode, cathode, cathodic reduction proceeds compartment III – positive electrode, anode, anodic oxidation proceeds

All three compartments are filled with a solution of the same concentration, and both electrodes are made of corresponding metal (for example, electrolyte CuSO4, electrodes – copper).

The definition is based on Faraday's laws:

(1) The amount of substance reacted on the electrodes, proportionally to the missed charge

(2) The mass of the reaction product is proportional to its molar mass / chemical equivalent n =Q / F

F = 96485 C mol^{-1}.

MOVING BOUNDARY METHOD

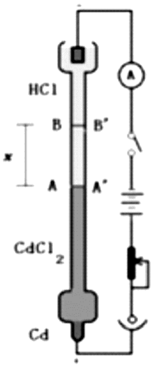
This method is based on the direct observation of migration of ions in an electric field. The conductivity cell in this method consists of a vertical tube filled with cadmium chloride and hydrochloric acid

HCl is the principle electrolyte and $CdCl_2$ serves as the indicator electrolyte to enable formation of boundary.

The concentration of solution is so adjusted that HCl floats over cadmium chloride. Since HCl is lighter than the $CdCl_2$.

A sharp boundary appears between the two solutions . The selection of the indicator electrolyte is done carefully, so that its cation do not move faster than the cation whose transport number is determined and it should have the same anion as the principle electrolyte. Cadmium Chloride fulfils both requirements.

The mobility of cadmium ions is less than that of hydrogen ions and it has a common anion with HCl.



The anode is a stick of Cd metal inserted at the bottom, while the cathode at the top is platinum foil. When a small current is made to flow through the conductivity cell the anions (Cl^-)move towards the anode while cations (H^+) move towards cathode.

The boundary separating the two solution also move upwards and the boundary moves through length , L (distance cm) ($AA^{/}$ to $BB^{/}$) . Then the volume of the solution V cm^3 = L ×A.

Suppose the HCl acid solution contains C gm equivalent of HCl per dm^3 as one HCl molecules forms one H^+ ion. Hence

1 dm^3 or 1000 $cm^3$of HCl solution = C gmequivalent of H^+

1 cm^3 of HCl solution = $\frac{c}{1000}$ gm equivalent of H^+

Vcm^3 of HCl solution = $\frac{c}{1000} \times$ V gm equivalent of H^+

Now, 1 gm Equivalent of H^+ ions carry current of 1 Faraday

$\frac{c}{1000} \times$ V gm equivalent of H^+ carry current $1\times \frac{c}{1000}\times$ V Faraday

The quantity of electric current passed through the cell is indicated by silver coulometer and for Q faraday.

The transport number, $t_+ = \frac{cV}{1000}\times\frac{1F}{Q}$

Since this number of equivalents is carried toward the cathode by H^+ ions, and as the total current carried is q, so, the quantity is Q\F.

T_+ = *Transport number of the ion*

$$T_+ = \frac{V.C.F}{1000Q}$$

5.9. Conductometric Titrations

Types of conductometric titration

1. Acid – base or neutral titrations
2. Replacement or displacement titrations
3. Redox titrations precipitation titrations
4. Complexometric titrations
5. Non – Aqueous titrations

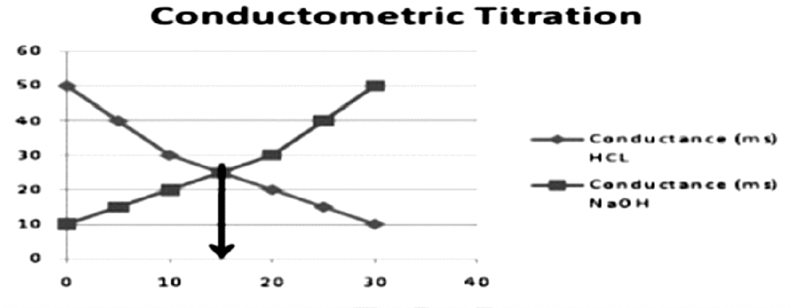
The Acid – base or neutral titration are again of four types

(a) Strong acid vs strong base eg. HCl vs NaOH

- Fall in conductance due to replacement of high conductivity H^+ ions by relative less conductive OH^-ions.

- Rise in conductance due to increase in hydroxyl ions

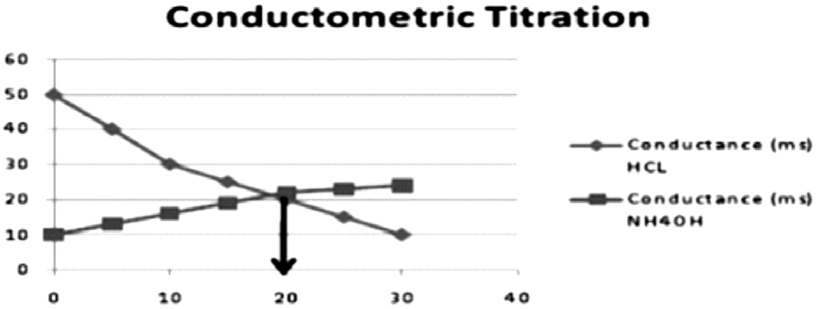
Plot of Conductance vs Volume of NaOH (no. of drops of NaOH)



(b) strong acid vs weak base eg. HCl vs NH_4OH

- Fall in conductance due to replacement of high conductivity H^+ ions by ammonium (NH_4^+) ions.
- Conductance remain constant due to suppression of NH_4OH by NH_4Cl.

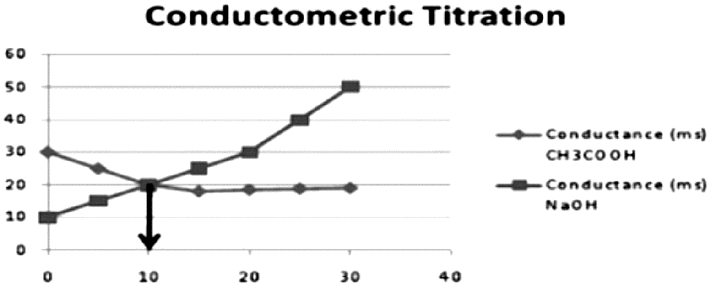
Plot of Conductance vs Volume of NH_4OH (no. of drops of NH_4OH)



(c) weak acid – strong base eg CH_3COOH vs NaOH

- Initial decrease in conductance followed by increase due to NaOH.
- Steep rise due to excess of NaOH.

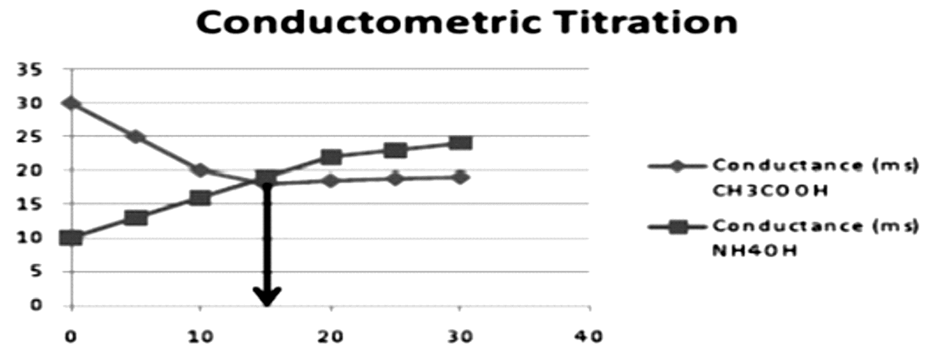
Plot of Conductance vs Volume of NaOH (no. of drops of NaOH)



(d) weak acid weak base. eg. CH_3COOH vs NH_4OH

- Increase in conductance due to excess of acetic acid
- constant conductance due to suppression of NH_4OH by CH_3COOH.

Plot of Conductance vs Volume of NH_4OH (no. of drops of NH_4OH)



Advantage

Does not require indicators since change in conductance is measured by conductometer, suitable for coloured solutions ; end point is determined by graphical means accurate results are obtained with minimum error.

Very dilute solutions provide better results.

Disadvantage

Increased level of salts in solution masks the conductivity changes – ;

Application of conductometric titration to redox systems is limited because high concentration of hydronium ions masks change in conductance.

Applications

- Check water pollution in river and lakes
- Alkainity of fresh water
- Salinity of Sea water
- Deuterium ion concentration in water deuterium mixture
- Food microbiology for tracing microorganisms
- Tracing antibiotics
- Estimate ash content in sugar juices
- Purity of distilled and deionised water
- Solubility of sparingly soluble salts, like $BaSO_4$, Ag Cl

5.10 Summary

In this unit we learned about viscosity and its measurement with focus on viscosity of liquids. Then we discussed electrolyte conductance including conductance measurement. We saw that their exists different theories for strong and weak electrolytes since their behaviour in solution can be very different from one another. At last the application of conductance for titration was also discussed.

5.11 Questions and Answers

Problem

Calculate the cell constant from the following data: The specific conductance κ of 0.1 N solution of KCl is 0.0112 $\mathrm{Scm^{-1}}$; the resistance of the cell containing the above solution is 55ohms.

Method

Cell constant = $\kappa R = 0.0112 \times 55 = 0.616\ \mathrm{cm^{-1}}$

Problem

The cell constant of a conductance cell is $0.367\mathrm{cm^{-1}}$ 0.100M NH_4Cl solution was taken in the cell and the resistance was measured as 28.5 ohms. Calculate the molar conductance of NH_4Cl solution at this concentration.

Method

$$\kappa = \frac{\text{cell constant}}{\text{resistance of electolyte}} = \frac{0.367}{28.5} = 0.01288\ \mathrm{Scm^{-1}}$$

$$\Lambda = \kappa\frac{1000}{C} = \frac{1000 \times 0.01288}{0.100} = 128.8\ \mathrm{cm^2mol^{-1}}$$

Problem

The resistance of a conductance cell with 0.01N KCl solution is 150 ohms at 25°C. The resistance of 0.01N HCl solution in the same cell is 51.4 ohms. Assuming the specific conductances of 0.01N KCl to be $0.0014088\mathrm{ohm^{-1}cm^{-1}}$, calculate the equivalent conductance of 0.01N HCl.

Method

Cell constant = Specific conductance of KCl × Resistance

$= 0.0014088 \times 150 = 0.2113\ \mathrm{cm^{-1}}$.

Specific conductance of 0.01N HCl = $\dfrac{0.2113}{51.4} = 4.111 \times 10^{-3}\mathrm{ohm^{-1}cm^{-1}}$.

$$\Lambda \text{ of } 0.01\text{N HCl} = \kappa\frac{1000}{C} = \frac{1000\times 4.111\times 10^{-3}}{0.01} = 411\,\text{ohm}^{-1}\text{cm}^{2}\text{equiv}^{-1}.$$

Problem

1. Calculate K_b of aqueous NH_3, given its degree of dissociation to be 0.042 in 0.01N solution. What is the pH of the solution ?

$$K_b = \frac{\alpha^2 c}{1-\alpha} = \frac{(0.042)^2\times 10^{-2}}{1-0.042} = 1.84\times 10^{-5}$$

$[OH^-] = \alpha c = 0.042\times 10^{-2} = 4.2\times 10^{-4}$

${}_pOH = -\log_{10} [OH^-] = 3.3768$

${}_pH = 10.6232.$

Problem

Dissociation constant of water from ionic product.

Method $H_2O(l) \rightleftharpoons H^+ + OH^-$

Ionic product of water 10^{-14} at 25°C.

$$\text{Dissociation constant of water} = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-14}}{55.5} = 1.8\times 10^{-16}$$

2. The equivalent conductance Λ of 1.028×10^{-3}M aqueous solution of acetic acid is 48.2 $\Omega^{-1}cm^2equiv^{-1}$ Calculate the degree of dissociation and the dissociation constant of the acid.

$$\text{Method} \quad \alpha = \frac{\Lambda}{\Lambda_0} = \frac{48.2}{39.1} = 0.1233$$

$$K_a = \frac{\alpha^2 c}{1-\alpha} = \frac{(0.1233)^2\times 1.028\times 10^{-3}}{1-0.1233} = \frac{0.01563\times 10^{-3}}{0.8767} = 1.78\times 10^{-6}$$

Polytropic acids: These are acids from which several protons are lost in successive stages. Ostwald's dilution law can be applied to each stage of equilibrium. The values of the dissociation constants of the successive stages of dissociation always decrease steadily. Example H_3PO_4

First stage

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$ $K_1 = 7.52 \times 10^{-3}$ (at 25°C)

Second stage

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}, K_2 = 6.22\times10^{-8}$

Third stage

$HPO_4^- + H_2O \rightleftharpoons H_3O^+ + PO_4^-, K_3 = 4.8\times10^{-13}$

In the first stage, the proton is removed from an uncharged molecule; in the second stage it is removed from a negative ion and hence the removal is more difficult; in the third stage the proton is removed from a di negative ion and hence the removal is still more difficult.

Questions

1. The velocity of a boundary of HCl with LiCl is followed in aqueous solution. It moves 15cm in a tube 1cm diameter in 22min when the current is 11.54amp. if the concentration of the HCl is 0.01065N, what is the transport number of the H^+ ?
2. Discuss other two methods to determine transference number.
3. What will be the change in the mass of the copper plates (increase/decrease)? Explain
4. What will be the change in the mass of the silver plates in the Hittorf cell (increase/decrease)? Explain.
5. How would the concentration of middle compartment change? Explain briefly.
6. Discuss factors influencing the transportnumber.
7. Discuss the function of the coulometer in thisexperiment.
8. Explain the function of middle compartment in this experiment.
9. Associate electrophoretic effect and relaxation effect with this experiment.

5.12. Recommended Books

(1) An Introduction to Electrochemistry by Samuel Glasstone

(2) Modern Aspects of Electrochemistry: by J. O'M. Bockris,ý B. E. Conway

(3) Text-Book of Electrochemistry by Svante Arrhenius

(4) Analytical Electrochemistryby Joseph Wang

(5) Handbook of ElectrochemistryCynthia G. Zoski