CHM 231 LECTURE NOTE

COURSE TITLE: BASIC PHYSICAL CHEMISTRY I (PART B)

CREDIT UNIT: 02

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COURSE SYNOPSIS

1. **The kinetic theory of gases**

   - ➢ **Postulates of kinetic theory**
   - ➢ **Derivation of Ideal gas equation from the kinetic theory**
   - ➢ **Deductions of gas laws from kinetic theory**

2. **Deviation from Ideal gas behavior**

   - ➢ **Causes of deviation**

   - ➢ **van der Waals equation**

3. **The distribution of molecular velocities**

   - ➢ **The most probable velocity, mean velocity and mean square velocity**

   - ➢ **Mean free path, collision frequency and collision density**

4. **Thermal energy and Heat capacity**

5. **Internal modes of motions**

   - ➢ **The equipartition principle**

6. **Phase equilibria**

   - ➢ **Phase rule, phase diagrams and triple points**

Recommended textbooks/References

1. Physical chemistry by K.K. Sharma and L.K. Sharma
2. Physical chemistry by A.J. Nee
3. Physical chemistry by Atkins
4. Principle of physical chemistry by J.M. Gross
5. Physical chemistry by R.A. Alberty and R.J. Silbey
6. Calculations in advanced physical chemistry by P.J.F. Griffiths and J.D.R Thomas
7. Physical chemistry by T. Engel and P. Reid
8. Essentials of physical chemistry by Bahl and Bahl
9. Chemistry: The central science by Brown, Lemay, Bursten and Murphy.

Kinetic theory of gases

Postulates of kinetic theory

1. Every gas consists of **identical** molecules which are considered as **non interacting point masses.**

2. Molecules are in constant random motion and the associated **translational kinetic energy** is determined only by the **absolute temperature.**

3. The pressure exerted by the gas is due to the bombardments by the gas molecules with the walls of the container.

4. The collisions of molecules with each other and with the walls of the container are **perfectly elastic.**

5. The molecules of a gas are small, hard sphere and **exert no forces on each other**, except at the instant of collision.

6. Since the molecules are very small compared to the distance between them, the volume occupied by the molecule is negligible compare to the total volume of the container.

7. There is **no effect of gravity** on the motion of the molecules of a gas.

Derivation of Ideal gas equation from the kinetic theory

Consider a cubic container of a gas of each side '*a*' containing N number of molecules. The velocity U of the gas can be resolved into 3 component velocities U_x, U_y and U_z.
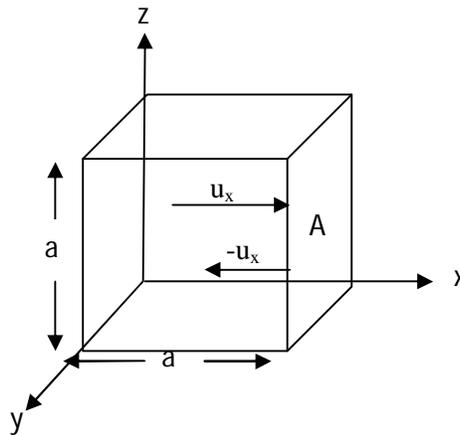
The magnitude of U is given by the Pythagoras' theorem as

$$U^2 = U_x^2 + U_y^2 + U_z^2$$ **(1)**

Consider 1 molecule of the gas in the cube, moving in the x-direction.

The distance travelled between successive collision on the surface of a=2a

The time between successive collisions is given by

$$\Delta t = \frac{2a}{U_x}$$

After each collision with surface A, there will be a change in momentum, i.e momentum before collision $= mU_x$ **(2a)**

and momentum after collision $= -mU_x$ **(2b)**

∴ **Change in momentum,** $\Delta \text{m}U_x = 2mU_x$ **(3)**

Rate of change in momentum, $\dfrac{\Delta mU_x}{\Delta t} = \dfrac{2mU_x}{2a/U_x} = \dfrac{mU_x^2}{a}$ **(4)**

From Newton's second law of motion, $F = \dfrac{\Delta mU_x}{\Delta t} = \dfrac{mU_x^2}{a}$

Area of surface A=a^2 and pressure, $P = \dfrac{Force}{Area}$ **(5)**

The pressure exerted by the molecule on surface A is P$_1$,

So, $P_1 = \dfrac{mU_x^2}{a \times a^2} = \dfrac{mU_x^2}{a^3}$ **(6)**

Let V represent the volume of the cubic box, then V=a^3

$$\therefore \quad P_1 = \dfrac{mU_x^2}{V}$$

So,

$$P_1 = \dfrac{mU_x^2}{V}$$ **(7)**

Since the collisions of molecule 1 with surface A are perfectly elastic, the velocity U$_x$ and mass of each molecule are constant. i.e. P$_1$=constant

Total pressure on surface A will be given by

P=P$_1$ + P$_2$ +P$_3$........+ P$_N$

$$\Rightarrow \qquad P = \sum_{i=1}^{N} P_i \qquad\qquad \textbf{(8)}$$

Recall that

$$P_1 = \frac{mU_x^2}{V}$$

$$P = \sum_{i=1}^{N} \frac{mU_{xi}^2}{V} = \frac{m}{V} \sum_{i=1}^{N} U_{xi}^2 \qquad\qquad \textbf{(9a)}$$

Since it is not possible to measure the velocity of each of the molecule, the average velocity of all the molecules is given by

$$\bar{U}_x^2 = \frac{\sum U_{xi}^2}{N} \qquad\qquad \textbf{(9b)}$$

$$\Rightarrow \qquad \sum U_{xi}^2 = \bar{U}_x^2 N \qquad\qquad \textbf{Where I is a counter and } \bar{U}^2 \textbf{ is}$$

mean square velocity

$$\therefore \qquad P = \frac{mN\bar{U}_x^2}{V} \qquad\qquad \textbf{(10)}$$

For each molecule,

$$U_1 = U_{x1}^2 + U_{y1}^2 + U_{z1}^2$$

$$U_2 = U_{x2}^2 + U_{y2}^2 + U_{z2}^2$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$U_N = U_{xN}^2 + U_{yN}^2 + U_{zN}^2$$

Adding up:

$$\bar{U}^2 = \frac{\sum U_i^2}{N} \quad \text{where N is number of molecule}$$

$$= \frac{\sum U_{xi}^2}{N} + \frac{\sum U_{yi}^2}{N} + \frac{\sum U_{zi}^2}{N} \qquad \text{(11)}$$

Since the motion is entirely random and the 3 directions x, y and z are equivalent.

Then, $\qquad \bar{U}_x^2 = \bar{U}_y^2 = \bar{U}_z^2$

$$\therefore \quad \bar{U}^2 = 3\bar{U}_x^2$$

$$\Rightarrow \qquad \bar{U}_x^2 = \frac{\bar{U}^2}{3} \qquad \text{(12)}$$

$$\therefore \quad PV = \frac{1}{3} Nm \bar{U}^2 \qquad \text{(13a)} \quad \text{for N molecule of}$$
gas

For 1 mole, $\quad PV = \frac{1}{3} N_A m \bar{U}^2 \qquad \text{(13b)}$

But $N_A m = M$ **where** M **is molar mass and** m **is the relative molecular mass**

$$\therefore \qquad PV = \frac{1}{3} M \bar{U}^2 \qquad \text{(13c)}$$

For n mole, $\quad PV = \frac{1}{3} nM \bar{U}^2 \qquad \text{(13d)}$

Deductions of gas laws from kinetic theory

(1) Boyles law: According to the law, PV= constant at constant mass and temperature.

According to the postulate 2 of the kinetic theory, the translational kinetic energy for N molecule is directly proportional to the absolute temperature.

i.e
$$E_{trans} = \frac{1}{2} Nm \bar{U}^2 \; \alpha T$$

$$= \frac{1}{2} Nm \bar{U}^2 = KT \qquad \textbf{(14)}$$

Multiply both sides by 2/3

$$\Rightarrow \qquad \frac{1}{3} Nm \bar{U}^2 = \frac{2}{3} KT \qquad \textbf{(15)}$$

Recall that
$$PV = \frac{1}{3} Nm \bar{U}^2$$

$$\therefore \qquad PV = \frac{2}{3} KT \qquad \textbf{(16)}$$

$$\Rightarrow \qquad PV = \text{constant if T is constant}$$

2. Charles law: The law states that V α T at constant mass and pressure. Recall that $PV = \frac{2}{3} KT$

$$V = \frac{2}{3}\left(\frac{K}{P}\right)T \qquad \textbf{(17)}$$

Avogadro's law: To deduce this law, let there be 2 gases 1 & 2 existing at the same temperature and pressure.

$$PV_1 = \frac{1}{3}N_1 m_1 \bar{U}_1^{\,2}$$ ------- **For gas 1** **(18a)**

$$P_2V_2 = \frac{1}{3}N_2 m_2 \bar{U}_2^{\,2}$$ ------- **For gas 2** **(18b)**

But P and V for the 2 gases are the same

$$\therefore \qquad PV_1 = P_2V_2$$

Hence, $$\frac{1}{3}N_1 m_1 \bar{U}_1^{\,2} = \frac{1}{3}N_2 m_2 \bar{U}_2^{\,2}$$ **(19)**

Since the 2 gases are at the same temperature, the average kinetic energy per molecule will be the same.

i.e. $$\frac{1}{2}m_1 \bar{U}_1^{\,2} = \frac{1}{2}m_2 \bar{U}_2^{\,2}$$ **(20)**

Thus, the equation 19 is reduced to N$_1$=N$_2$ which authenticate the law.

Graham law: the law states that the rate of diffusion of a gas at a particular temperature and pressure is inversely proportional to the square root of its density.

i.e $$r \alpha \frac{1}{\sqrt{d}}$$ **(21)** **where r is rate of diffusion and d is the density**

Hence, $$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$ **(22)**

Applying the kinetic theory, $$PV = \frac{Nm\bar{U}^{\,2}}{3} = nRT$$ **(23)**

$$\bar{U} = \sqrt{\frac{3nRT}{Nm}}$$ **(24)**

When n=1 for each of the 2 or more gases at constant temp. But $N_A m = M$

$$\therefore \quad \bar{U}_1 = \sqrt{\frac{3RT}{M_1}} \quad \textbf{and} \quad \bar{U}_2 = \sqrt{\frac{3RT}{M_2}}$$ **(25)**

$$\therefore \quad \frac{\bar{U}_1}{\bar{U}_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\Longrightarrow \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \frac{\bar{U}_1}{\bar{U}_2} = \sqrt{\frac{M_2}{M_1}}$$ **(26)**

Dalton's law of partial pressure: consider N_1 molecules of a gas 1 with mass m_1 and velocity $\bar{U}_1$ occupying volume V, the pressure exerted by these molecules is given by

$$P_1 = \frac{1}{3}\frac{N_1 m_1 \bar{U}_1^2}{V}$$ **(27a)**

Under similar condition, N_2 molecules of gas 2 exerted pressure P_2, $P_2 = \frac{1}{3}\frac{N_2 m_2 \bar{U}_2^2}{V}$ **(27b)**

For the 3rd gas, $P_3 = \frac{1}{3}\frac{N_3 m_3 \bar{U}_3^2}{V}$ **(27C)**

Assuming that all the 3 gases are put together in a vessel of the same volume and at the same pressure, the total pressure is given by

$$P = \frac{1}{3}\frac{N_1 m_1 \bar{U}_1^{\;2}}{V} + \frac{1}{3}\frac{N_2 m_2 \bar{U}_2^{\;2}}{V} + \frac{1}{3}\frac{N_3 m_3 \bar{U}_3^{\;2}}{V} \qquad \textbf{(28a)}$$

$$\Rightarrow \qquad P = P_1 + P_2 + P_3 \qquad \textbf{(28b)}$$

N.B: from all the deductions of the gas laws from kinetic theory of gases, it follows that $PV = \frac{1}{3}Nm\bar{U}^{\;2}$ **is in agreement with the empirical (classical) ideal gas equation PV=nRT where n is the number of mole of gas.**

$$\therefore \quad PV = \frac{1}{3}Nm\bar{U}^{\;2} = nRT$$

Deviation from ideal gas behavior

Experimental evidences have shown that very few gases obey the ideal gas equation only at low pressure and high temperature, and that most gases show marked deviation from the ideal behavior at high pressure and low temperature.

A plot of PV against pressure shows that most gases behave ideally only in the limit of zero pressure.
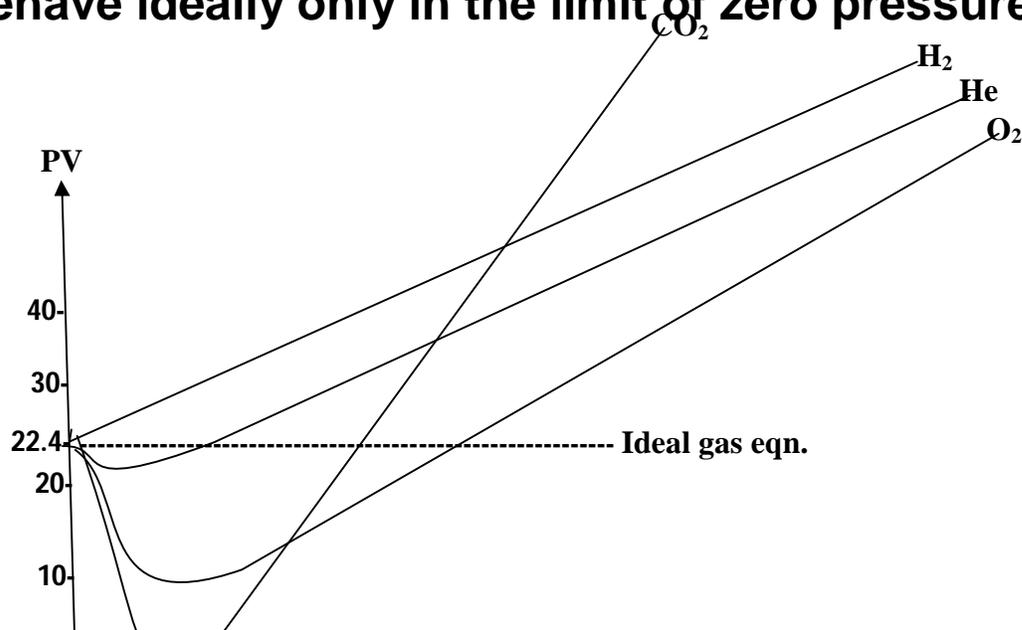
From the diagram,

(i) The smaller molecules like H_2 and He, the curve starts at the value of $PV_{(ideal)}$ and the value of PV increases with the pressure.

(ii) The larger molecules like O_2 and CO_2, the curve also start at the value of $PV_{(ideal)}$, shows a decrease in PV in the beginning, passes through a minimum and then begin to increase with increasing pressure.

Also, a plot of compressibility factor, **z** against the pressure at constant temperature shows deviation from ideal gas behaviour.

Meanwhile, compressibility factor is an index of deviation from ideality. i.e. $Z = \dfrac{PV}{RT}$

For 1 mole of an ideal gas, Z=1, and it is independent of pressure and temperature.

For real gases, Z is a function of both temperature and pressure and its value varies. The amount by

which the actual factor differs from unity gives a measure of deviation from ideality for the gas.
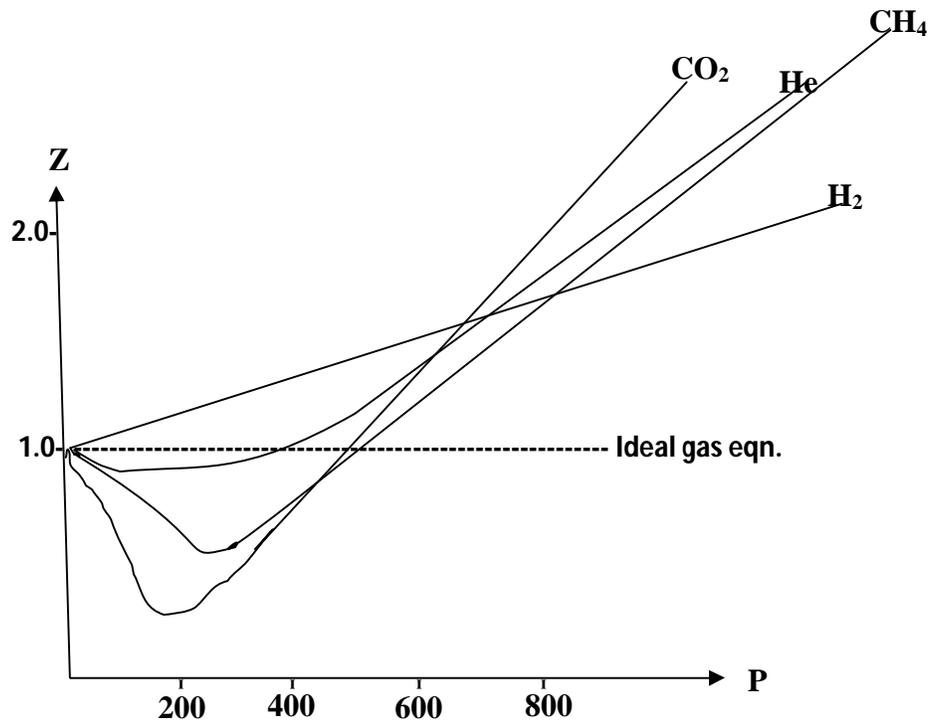
From the diagram above, for H_2, z increases continually but for N_2, CH_4 and CO_2, Z first decreases and then increases rapidly with increasing pressure. Experiments have shown that for those gases which can easily be liquefied (i.e. N_2, CH_4 and CO_2), z decreases sharply below the value of unity at low pressure.

Also, a plot of z against P for Nitrogen gas at different temperature shows that the dip in the curve becomes less pronounced with increasing temperature.
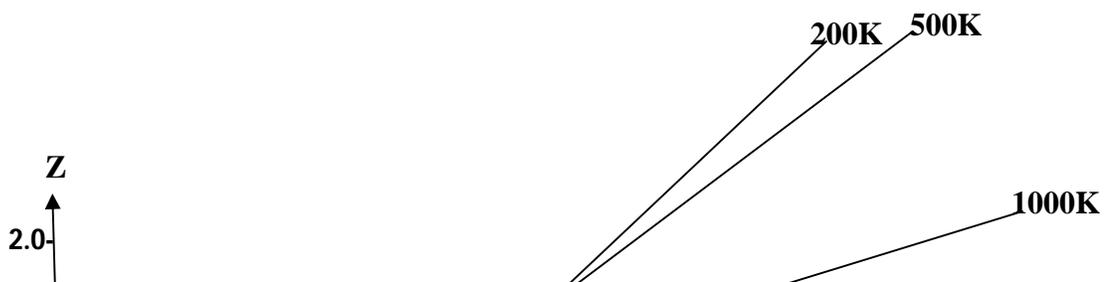
From the graph above, an increase in temperature causes the minimum to become smaller and at the same time, the position of the minimum moves toward lower pressure.

N.B: As temperature increases, the gas closely approaches ideal behaviour (represented by the dashed horizontal line). This confirms that deviation from ideality occur at high pressure and low temperature.

Causes of deviation

Deviation from ideality occurs because of the following weak assumptions in the postulates of kinetic theory of gases.

(i) The volume occupied by the molecule is negligible compare to the total volume of the gas. This is not true at lower temperature and high pressure where the molecules of the gas get so closed that the liquefaction and finally solidification of the gas occur. Since solids cannot be compressed, it confirms that molecules of the gas occupy some volume.

(ii) Molecules exert no force on each other. However, liquefaction occurs because there is force of attraction between the molecules of the gas.

The van de Waal's equation

This equation takes into consideration the effects due to finite size and intermolecular forces. Van der Waals introduces the correction term to the deviation from ideality. The equation is

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

But for n mole, the equation becomes

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

Where n is the number of mole of the gas, a & b are the van der Waals constants whose magnitudes depend on the type of the gas, and the units in which the pressure and volume are expressed.

Van der Waal and critical phenomenon

Critical temperature, T_c: critical temperature of a gas is that temperature above which it cannot be liquefied no matter how great the pressure the pressure applied. It is given by the expression $T_c = \dfrac{8a}{27Rb}$

Critical pressure, P_c: is the minimum pressure required to liquefy a gas at its critical temperature. It is given as

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

Critical volume, V_c: it is the volume occupied by 1 mole of it at its critical temperature and pressure. It is expressed as

$$V_c = 3b$$

The van der Waals constant a and b can be expressed in terms of critical constants by means of the following equations

(i) $b = \dfrac{1}{3} V_c$

(ii) $b = \dfrac{RT_c}{8P_c}$

(iii) $a = \dfrac{27 R^2 T^2}{64 P_c}$

The distribution of molecular velocities

While deriving the equation for pressure from the kinetic theory of gases, it was assumed that all molecules are moving with the same speed, i.e having the root mean square velocity $(\bar{U}^2)$. However, in practice, all the molecules cannot move with the same speed because they are frequently colliding with each other and walls of container leading to the interchange of momentum by the molecules. For example, consider 2 molecules with a given velocity moving in the same direction and collided. During collision, it is possible that one molecule may completely transfer its momentum to the other thereby causing the latter molecule to move off with

increased velocity and the former may stop completely and vice versa.

The molecules can experience collisions in all the possible direction. The net result is that, for a fixed number of molecules at a fixed temperature, a distribution of molecular velocities varying from zero to very high value will be attained. A plot of fraction molecules having a given velocity n_u against the velocity U at a definite temperature represent the distribution of molecular velocities and the graph is known as Maxwell-Boltzmann distribution of molecular velocities.
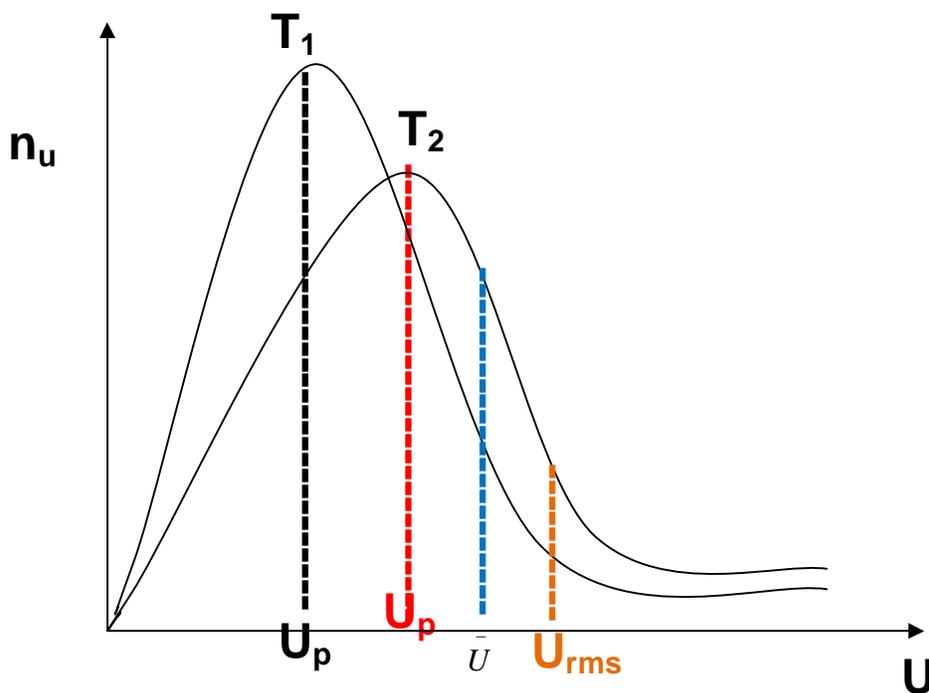
Total area under the curve = total number of molecules in the collection, i.e. total number of molecules having all velocities.

The most probable velocity U_p of the molecules is the velocity possessed by the greatest number of molecule which is given by the maximum in the curve. It varies linearly with the temperature, i.e. at higher temperature; a greater fraction of molecules is expected to have higher velocities. Hence, the maximum of the curve at T_2 shifts to higher velocity as compared to that of T_1.

Since the kinetic energy is proportional to $\bar{U}^2$, the mathematical expression that relate the number of molecule n_i having an energy E_i at a given temperature is

$$n_i = ce^{-E_i/kT}$$

but c=n$_T$, i.e. the total number of molecules of gas and k is Boltzmann's constant.

$$\Rightarrow \qquad n_i = n_T e^{-E_i/kT}$$

The average (mean) velocity, $\bar{U}$ of the molecule of a gas is defined as

$$\bar{U} = \frac{1}{n_T}\left(U_1 + U_2 + U_3 + \ldots\ldots\ldots U_i\right) = \frac{1}{n_T}\sum_{i=1}^{n_T}\bar{U}_i$$

Therefore, the mean square velocity is given by

$$\bar{U}^2 = \frac{1}{n_T}\left(U^2_1 + U^2_2 + U^2_3 + \ldots\ldots\ldots U^2_i\right) = \frac{1}{n_T}\sum_{i=1}^{n_T}\bar{U}_i^2$$

Hence, the root means square velocity, U $_{rms}$ is given by

$$\left(\bar{U}^2\right)^{1/2} = \bar{U}_{rms} = \frac{1}{n_T} \sum_{i=1}^{n_T} (\bar{U}_i^2)^{1/2}$$

Relating the root mean square to the molar mass

$$PV = \frac{nM \bar{U}^2}{3} = nRT$$

$$\frac{M \bar{U}^2}{3} = RT \qquad \textbf{for 1 mole}$$

$$\bar{U}^2 = \frac{3RT}{M}$$

$$\bar{U}_{rms} = \sqrt{\bar{U}^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}} = 1.7\sqrt{\frac{RT}{M}}$$

Also, $\bar{U}_p = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{D}} = 1.4\sqrt{\frac{RT}{M}}$ **and**

$$\bar{U} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8P}{\pi D}} = \sqrt{\frac{5RT}{2M}} = 1.6\sqrt{\frac{RT}{M}}$$

Ratio of different velocities is

$$\bar{U}_{rms} : \bar{U} : \bar{U}_p = 1.7 : 1.6 : 1.4$$

Collision properties

1. **Mean free path; λ: It is the distance travelled by a molecule between two successive collisions. It can be expressed as follow**

   (a) **In term of the coefficient of viscosity of gas,**

   $$\eta \qquad \lambda = \frac{3\eta}{mnu_{rms}} = \frac{3\eta}{du_{rms}} \qquad \text{where } \lambda \text{ is the}$$

   mean free path, n is the number of molecules per m³, m is the mass and d is the density

   (b) **In term of molecular diameter, δ**

   $$\lambda = \frac{1}{\sqrt{2}\pi\delta^2 \bar{n}} \qquad \text{where } \bar{n} \text{ is the}$$

   average number of molecules per cubic centimeter and it is expressed as $\bar{n} = \dfrac{\bar{P}}{RT}N_A$.

2. **Collision frequency, z: it is the number of molecular collisions taking place per second per**

unit volume of the gas. It is denoted by z and given by the relation

$$z = \sqrt{2}\pi\delta^2\, \bar{n} <\bar{u}>$$

Where $<\bar{u}>$ is the average velocity and it is given as $<\bar{u}> = \sqrt{\dfrac{8RT}{\pi M}}$

3. Collision diameter, Z: It is the number of collisions per unit time per unit area. It is given by

$$Z = \frac{1}{\sqrt{2}}\pi\delta^2\, \bar{N}^2 <\bar{u}> \quad \text{where} \quad \bar{N} = \frac{N_A}{RT}P = \frac{P}{kT}$$

THERMAL ENERGY AND HEAT ENERGY

Recall that $\quad nRT = \dfrac{1}{3}Nm\bar{U}^2 \quad$ and $\quad R = N_A k$

Since $N = nN_A$,

$$N = nN_A = \frac{1}{3}nN_A m\bar{u}^2$$

$$kT = \frac{1}{3}m\bar{u}^2$$

Translational energy, $E_{trans} = \frac{1}{2}mu^2$

$$E_{trans} = \frac{1}{2}m\sum u_i^2 \qquad \textbf{(For all molecules)}$$

$$\bar{u}^2 = \frac{1}{N}\sum u_i^2$$

$$\Rightarrow \qquad N\bar{u}^2 = \sum u_i^2$$

$$\therefore \quad E_{trans} = \frac{1}{2}Nm\bar{u}^2$$

But $\qquad nRT = \frac{1}{3}Nm\bar{U}^2$

Multiply both sides by $\frac{2}{3}$

$$E_{trans} = \frac{2}{3}nRT \quad \textbf{for n moles}$$

$$E_{trans} = \frac{3}{2}NkT \quad \textbf{for N molecules}$$

The heat supplied to the system tends to increase the translational energy.

For monoatomic gases (e.g. He, Ne, Kr, Xe,Rn, Hg and Na vapour). Let E be the thermal energy for n moles.

$$\therefore \qquad E=nRT$$

For a small quantity of heat supplied, $dE = dq = nRdT$

The heat capacity at constant volume (C$_v$) is given by

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

$$\therefore \quad C_v = \frac{3}{2}nR$$

But   R=8.314JK^{-1}mol^{-1}

$$\bar{C_v} = \frac{3}{2}nR = 12.47 \text{ Jmol}^{-1}$$

Comment: The fact that heat capacity can be predicted is the justification that for the equation

$$nRT = \frac{1}{3}Nm\bar{U}^2$$

Internal Modes of Motions

Since molecules have bonds, they can rotate, vibrate and thermal energy can be absorbed. Degree of freedom is a mode of motion e.g. for translational motion, D.O.F=3

For a molecule containing A atoms, A atom will contribute 3A D.O.F.

Then how is the 3A D.O.F distributed?

According to classical mechanics, there are linear and non-linear molecules.

(i) For linear molecule, there are 2 D.O.F rotational
(ii) For non-linear molecule, there are 3 D.O.F rotational

For a linear molecules containing A atoms

Total D.O.F = 3A

Translation D.O.F = 3

Rotational = 2

Vibrational= (3A-5)

For non-linear molecules containing A atoms

Total D.O.F = 3A

Translation D.O.F = 3

Rotational = 3

Vibrational= (3A-6)

The equipartition principle

The principle of equipartition of energy states as follow:

(a) **Each translational and rotational D.O.F contributes ½kT to the thermal energy of 1 molecule (i.e. ½RT to the thermal energy of 1 mole).**

(b) **Each Vibrational mode contributes kT per molecule or per mole.**

Predicting the thermal energy, the following expressions are considered using classical mechanics.

> **For monoatomic gas:** $\bar{C_v} = 3 \bullet \dfrac{1}{2} R$

> **For linear molecules :**

$$\bar{C_v} = 3 \bullet \frac{1}{2}R + 2 \bullet \frac{1}{2}R + (3A - 5)R = \left(3A - \frac{5}{2}\right)R$$

> **For non- linear molecules:**

$$\bar{C_v} = 3 \bullet \frac{1}{2}R + 3 \bullet \frac{1}{2}R + (3A - 6)R = (3A - 3)R$$

N.B: This predictions are not accurate for linear and non-linear molecules because the principle of equipartition of energy were all based on classical mechanics which are not applicable to the molecular systems. To treat the heat capacities and thermal energy of molecules, it is therefore necessary to

replace the classical mechanics with quantum mechanics (which assumes that energies are quantized)

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translational   **rotational**   **vibrational**
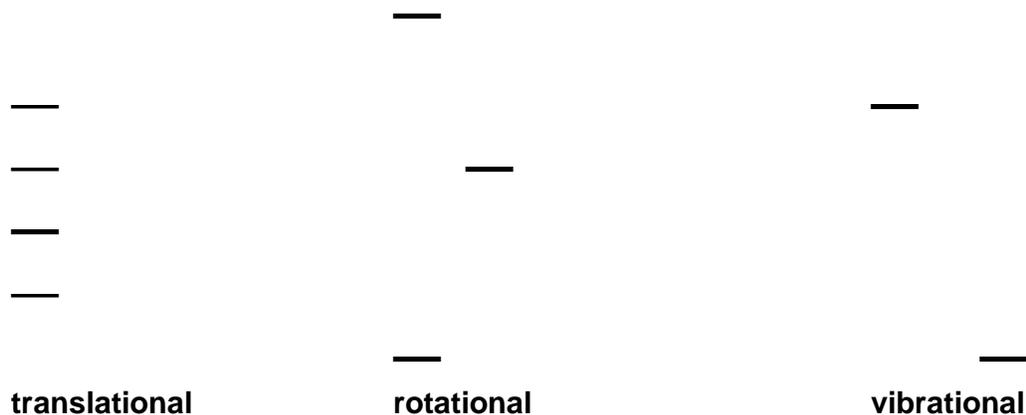
PHASE EQUILIBRIA

<u>Introduction</u>: **phase equilibria is a primarily concerned with systems in which one phase is converted to another. A system is said to experience phase equilibrium if a number of phases co-exist and there is no net conversion of one phase to another.**

<u>Phase rule</u>

Phase rule is the general law governing the phase equilibria. It is expressed in the form: $F = C - P + 2$

Where F is the number of degree of freedom, C is the number of component and P, the number of phases in a heterogeneous system.

A phase: a phase is a region having uniform properties and is separated from other phases by a boundary. Any gas or mixture of gases always constitutes a single phase, as does a homogeneous liquid or solid solution.

A mixture of water and ether constitutes a two-phase system since two liquid layers are obtained (i.e. one containing a saturated solution of ether in water, the other containing a saturated solution of water in ether), which are separated from each other by a definite boundary surface.

Under normal conditions, water constitutes a three-phase equilibria system (i.e. ice, water and water vapour). However, at a very high pressure, six different crystalline forms of ice exist, each of which constitutes a separate phase, since each is clearly separated from the other by a definite boundary.

Component: The number of components in a system is the minimum number of independent chemical constituents necessary to describe the composition of

each phase present either directly or in the form of a chemical equation.

The composition of each of the three phases present in water can be expressed in terms of one component (i.e. water), even though the molecular arrangement is different in the 3 phases.

Consider this equation

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

Phase 1   phase 2   phase 3

The equation involves 3 phases but only 2 components. To specify the composition of the gas phase, specie CO_2 is needed. Also, to specify the composition of solid phase, either $CaCO_3$ or CaO is needed.

N.B: The reaction above must be given sufficient time to reach equilibrium, otherwise the system contains 3 components.

Degree of Freedom: is the number of independent intensive variables (e.g. temperature, pressure, concentration, density etc) which must be fixed in order to completely define the system at equilibrium. For instance, in a single-component, single-phase

system (i.e. C=1, P=1), the pressure and temperature may be changed independently without changing the number of phases. So, F=2 (a bi-variant system i.e. a system with 2 degree of freedom)

APPLICATION OF THE PHASE RULE TO WATER

Though water is a three-phase, one-component system under normal conditions. However, the number of phase may be varied as follow:

   (i)One-phase region: is a region where only a single phase is present. F=1-1+2=2

i.e. each single phase has 2 degree of freedom which implies that both the temperature and pressure must be specified in order to define the condition of the phase.

   (ii)   Two-phase regions: is a region where 2 phases are   present in equilibrium.   F=1-2+2=1

i.e. two-phases in equilibrium have 1 degree of freedom implying that only one of the two variables

(temperature or pressure) needs to be specified in order to define the system.

(iii) Three-phase regions: is a region where 3 phases are present in equilibrium.

F=1-3+2=0

i.e. if the 3 phases co-exist in equilibrium, no variable is needed to be specified in order to define the system.

Phase Diagram

Phase diagram of a substance is a graphic representation of the equilibria among the solid, liquid and gaseous phases of a substance as a function of temperature and pressure. It shows the regions of pressure and temperature at which its various phases are thermodynamics stable. The lines separating the regions (i.e. phase boundaries) show the values of pressure and temperature at which two phases co-exist in equilibrium.

Phase diagram of water

P

C

A

Solid

Liquid

O

vapour

A

B

T

T_c
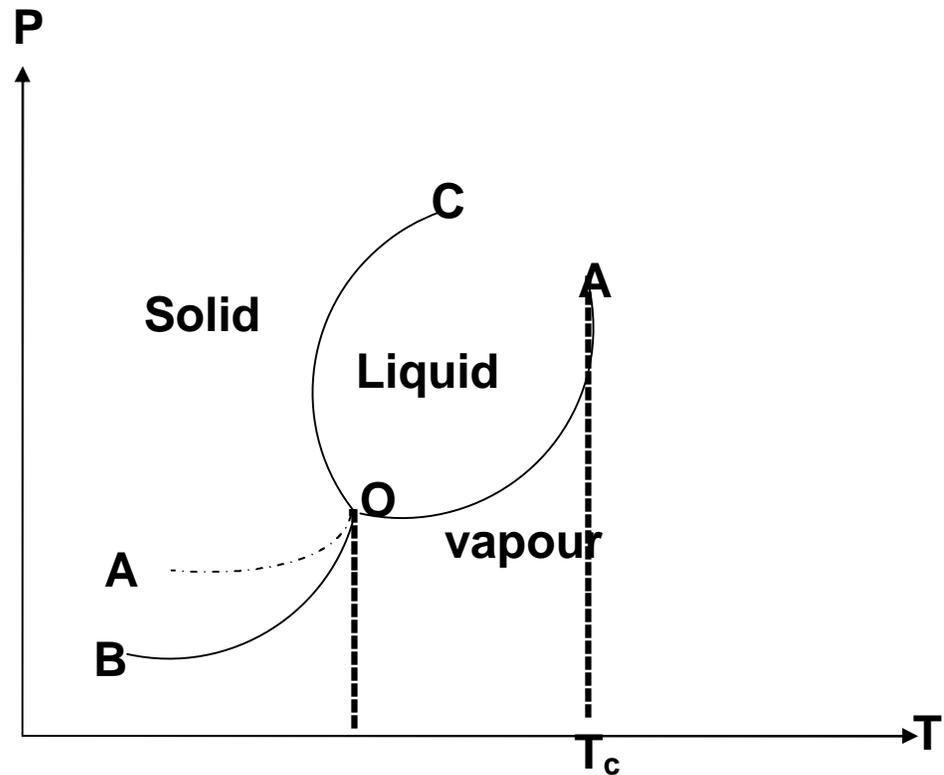
OA-   equilibrium between liquid-vapour

OB- equilibrium between solid-

OA and OB represent the variation of the vapour pressure of solid and liquid with temperature. OA continues to the critical temperature T_c(where liquid and vapour becomes indistinguishable) and OB continues down to zero Kelvin.

Triple point (OA, OB and OC):- Triple point is the point where all the three phases are in equilibrium. The triple point for water occurs at 0.0098^{o}C at an equilibrium vapour pressure of 611Nm^{-2} (4.58mmHg).

Metastable equilibrium: It is a specific equilibrium which is not the most stable equilibrium under the given conditions. In the diagram, the vapour pressure curve of the liquid is extended past the triple point to A' (represented by the broken lines). The liquid-vapour system along OA' is said to be in a metastable equilibrium.

Phase diagram of Sulphur

P

G

F

Liquid

D

Rhombic

Monoclinic

C

Vapour

E

B

A

T
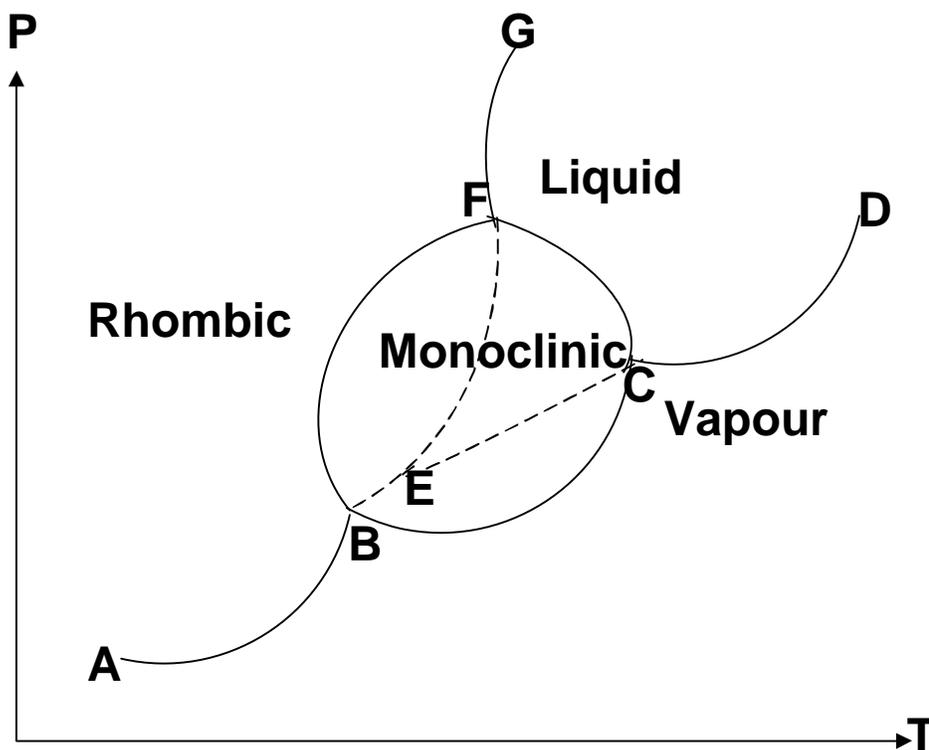
There are 4 triple points, they are:

F- Triple point for Rhombic-Monoclinic-Liquid sulphur

B- Triple point for Rhombic-Monoclinic-Vapour sulphur

E- Triple point for Rhombic- Liquid- Vapour sulphur (metastable)

C- Triple point for Monoclinic-Liquid- Vapour sulphur

One phase regions: Each sample phase is represented by an area. Since there are 4 phases (rhombic, monoclinic, liquid and vapour), there will be four of such areas. The slopes of the lines BF and CF are such that the monoclinic form can exist only in the triangular region BCF.

Two-phase regions: Two phases in equilibrium are represented by a line. Since there are 6 ways of choosing two phases from four, there should be 6 lines.