KINECTIC THEORY OF GASES

The kinectic molecular theory of gases is employed to intepret the properties of gas molecule in a more quantitative manner. Anytime a theory is developed to account for experimental observations, the system (object of emphasis) is defined, in a case in which all properties of the system are not understood, a number of assumptions are made. Therefore, model for kinectic theory of gases is based on the following assumptions;

A gas is made up of a great number of atoms or molecules seperated by distance that are large compare to their size

Molecules have mass but volume is negligibly small, i.e, gases contain ~~[illegible]~~ point-like molecules.

Molecules are constantly in random motion

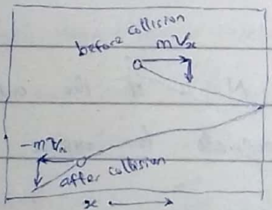
Collisions among molecules and between molecules and wall of container is elastic, i.e, Kinectic energy can be transferred from one molecule to another but it is not converted to other forms of energy.

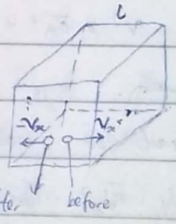
No inter-molecular attractions or repulsion between molecules

An ideal gas follows equation of state, i.e, $PV = nRT$

PRESSURE OF A GAS

Using the model for kinectic theory of gases, an expression can be derived for pressure of a gas in term of its molecular properties. Consider an ideal gas with N molecules, each of mass, m, confined in a ~~go~~ cubic box of lenght, L. As shown below





At any instant, the molecular motion in the container is completely random, ~~which~~ when a particle of mass, m, that is travelling with a component velocity V_x parallel to x-[illegible], [illegible]ides with wall on right it is immediately reflected because collision is elastic, i.e, [illegible] velocity after collision is same as before collision but in opposite direction. Hence,

~~Change in momentum = mV~~ Momentum of the molecule = mV_x

Change in momentum $= mV_x - (-mV_x) = 2mV_x$

Immediately after collision, the molecule will take l/V_x to collide with the second wall. To strike the same wall again, the molecule take $2l/V_x$ time (Note that this only apply to collision with wall alone not with any other molecules). Therefore, the freguency of collision, f, between the molecule and the containor's wall or the number of collision per unit time is $V_x/2l$, [illegible] $\frac{V_x}{2l}$

Change in momentum per unit time $= \cancel{2}mv_x \times \frac{v_x}{\cancel{2}l} = \frac{mv_x^2}{l}$

Therefore, force by one molecule on one of the ~~the~~ wall as a result of collision is given by;

$$F = \frac{mv_x^2}{l}$$

$$F_{Total} = \frac{Nmv_x^2}{l} \quad \text{for } N \text{ molecules}$$

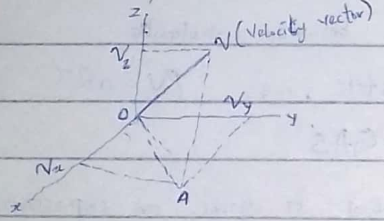
~~The~~ Total pressure on one wall is given as ~~hmyes~~ P_T and it is;

$$P_T = \frac{F_T}{A} \qquad \text{Recall } A = l^2$$

$$P_{Total} = \frac{Nmv_x^2}{l(l^2)} = \frac{Nmv_x^2}{l^3} = \frac{Nmv_x^2}{V}$$

$$\therefore PV = Nmv_x^2$$

If ~~the~~ motion of a molecule is analysed with v, since velocity is a vector quantity, i.e. it has both magnitude and direction therefore v can be resolved ~~measured~~ into three mutually perpendicular ~~perpendic~~ components v_x, v_y, v_z. These three components give the rate at which the molecule is moving along x, y and z direction respectively.



$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

The projection of the velocity of the x and y plane $\overline{OA}$ which by pythagoras is given by

$$\overline{OA}^2 = v_x^2 + v_y^2$$

Similarly, $v^2 = \overline{OA}^2 + v_z^2 = v_x^2 + v_y^2 + v_z^2$

When dealing with large collection of molecules when N is of the order of 6.023×10^{23}, there is tremendous trends of molecular velocity. It's more appropriate to replace v_x^2 with the mean or average quantity $\bar{v}_x^2$. Therefore,

$$\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2 \quad \text{and} \quad \bar{v}^2 = \frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}$$

The $\bar{v}^2$ is the mean square velocity

When N is a large number, it is correct to assume that molecular motion along the x, y and z directions ~~is~~ equally probable, i.e, $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$

$$\therefore \bar{v}^2 = 3\bar{v}_x^2 \Longrightarrow \bar{v}_x^2 = \frac{\bar{v}^2}{3}$$

$$\therefore PV = \cancel{mn}\bar{v}_x^2 \Rightarrow PV = Nm\bar{v}_x^2 \Longrightarrow PV = \frac{Nm\bar{v}^2}{3}$$

$$\therefore 3PV = Nm\bar{v}^2$$

for N molecules moving with mean ~~with~~ effective velocity $\bar{v}^2$

TRANSLATIONAL MOTION

This is the movement of an object from one place to another

Recall, $P = \frac{2N}{3V}\left(\frac{1}{2}m\bar{v}^2\right)$

Average kinectic energy of ~~an~~ ~~[illegible]~~ molecule $= \frac{1}{2}m\bar{v}^2$

$$\therefore P = \frac{2N}{3V}\bar{E}_{trans}$$

This shows that pressure is directly proportional to Pressure exerted by one molecule on one wall ~~[illegible] exerted by one molecules on one wall~~. ~~This~~ average translational energy or mean square velocity. Hence, the larger the velocity the more frequent the collision and the greater the change in momentum

KINECTIC ENERGY AND TEMPERATURE

Considering ideal gas equation, i.e, $PV = nRT = \frac{N}{N_A}RT$

Combining the pressure of an ideal gas and pressure due to kinectic energy

$$\frac{2N}{3V}\bar{E}_{trans} = \frac{NRT}{N_A V}$$

$$\bar{E}_{trans} = \frac{3RT}{2N_A} = \frac{3}{2}K_BT \quad \text{where } K_B \text{ is Boltsmann constant}$$

Therefore, the mean kinectic energy of one molecule is proportional to absolute temperature $\therefore$ So, when two gases (ideal) are at same temperature, T, they have same kinectic energy, i.e, average kinectic energy is independent of molecular properties of gas (such as size, molar mass and amount of gas pressure) as long as N is a large number

$$\therefore \bar{E}_{trans} = \frac{1}{2}m\bar{v}^2 = \frac{3}{2}\frac{RT}{N_A} = \frac{3}{2}K_BT \quad \text{(for any amount of N, i.e, independence of N)}$$

$$\text{if } \frac{1}{2}m\bar{v}^2 = \frac{3RT}{2N_A} \Rightarrow \bar{v}^2 = \frac{3RT}{mN_A} = \frac{3R_BT}{NM} = \frac{3K_BT}{m}$$

$$V_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3K_BT}{m}}$$

V_{rms} is the root mean square velocity, where $NM = mN_A$ and m is mass in kg of one molecules

Therefore, root mean square velocity is directly proportional to square root of temperature but inversely proportional to square root of molar mass. Hence, the heavier the molecule the lower its motion, the higher the temperature or ~~[illegible]~~ molecule the higher the motion

ILLUSTRATION QUESTION: The V_{rms} of methane is 846m/s. What is the temperature of the gas?

$$V_{rms} = \sqrt{\frac{3RT}{M}} \Rightarrow T = \frac{MV_{rms}^2}{3R} = \frac{846^2 \times 0.016}{3 \times 8.314} = 460K$$

Calculate the average for Nitrogen gas molecule and for 1 mole of Nitrogen gas at 20°C

$$\bar{E}_{trans} = \frac{3}{2}K_BT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 293 = 6.07 \times 10^{-21}J$$

~~Since, $\bar{E}_{trans}$ is independent of amount of gas~~ a ~~gas molecules, hence, the $\bar{E}_{tran}$ for~~ a ~~[illegible] mole of N_2 it~~ same. $\bar{E}_{tran} = 6.07 \times 10^{-21}J \times 6.02 \times 10^{23} = 3.65kJ$

To what temperature will Helium atom be cooled so that they have same V_{rms} as oxygen at 25°C

$$\sqrt{\frac{T_1}{T_2}} = \sqrt{\frac{M_1}{M_2}} \Rightarrow \sqrt{\frac{298}{T_2}} = \sqrt{\frac{32}{4}} \Rightarrow T_2 = \frac{298}{8} = 37.3K \text{ or } -235.7°C$$

IDEAL GAS LAW

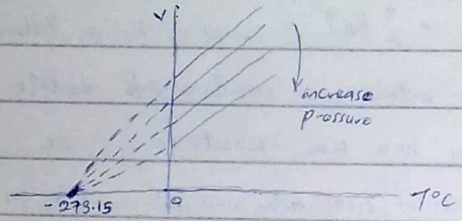
Studying the behaviour of gas has given rise to a number of chemical and physical theories

The molecule of ideal gas possess no intrinsic volume and they neither repel or attract each other. The equation of state, $PV = nRT$, relate state variables of gaseous system for an ideal gas

No ideal gas exist in nature but under relatively high temperature ($T \geq 25°C$) and low pressure ($P \leq 10 atm$), this equation roughly predict the behaviour of most gases. Ideal Gas Equation is accumulation of English Chemist, Robert Boyle (1627-1691) and French Physicists, Jacques Charles (1746-1823) and Joseph Gay-Lussac (1778-1850)

KELVIN TEMPERATURE SCALE

The relationship between Kelvin scale and degree Celsius is obtained by studying the variation of volume of a gas and temperature at constant pressure



At any given pressure, the plot of volume versus temperature yeilds a straight line, by extending the line to zero volume, we found the intercept on temperature axis to be -275.15°C. The plot above shows the amount of gas versus temperature at different pressure. All gases ultimate condenses if they are cooled to enough temperature, when these lines are extrapolate, they all converge at point representing zero volume and temperature of -273.15°C, this temperature is known as zero temperature which is the lowest attainable temperature. In 1848, the Scottish mathematician, William Thompson (known as Lord Kelvin 1824-1907) set up an absolute temperature scale now called Kelvin scale. The relationship between the two scale is;

$$T/K = t/°C + 273.15$$

	Kelvin Scale	Celsius
Absolute Zero	0	-273.15°C
Freezing point of water	273.15K	0°C
Boiling point of wate	373.15k	100°C

In most cases, 273 is used instead of 273.15 as term relating Kelvin and Celsius.

THE GAS CONSTANT

The value of gas constant, R, can be obtained as follow, experimentally it was found that 1mole of ideal gas occupies 22.414L at 1 atm and 273.15K, a condition known as standard temperature and pressure: Thus

$$R = \frac{PV}{nT} = \frac{(1 atm)(22.414L)}{(1 mol)(273.15K)} = 0.08206 L atm K^{-1} mol^{-1}$$

To express R in unit of $JK^{-1}mol^{-1}$, we use the conversion factors, which include;

1 atm = 1.01325×10^5 Pa ; 1Pa = $1 Nm^{-2}$; 1L = $1 \times 10^{-3} m^3$; 1Nm = 1J

$$\therefore R = \frac{1.01325 \times 10^5 Nm^{-2} \times 22.414 \times 10^{-3} m^3}{1\ mol \times 273.15 K} = 8.314\ Nm K^{-1} mol^{-1} = 8.314\ J K^{-1} mol^{-1}$$

From the two values of R, i.e, $0.08206\ L atm K^{-1} mol^{-1}$ and $8.314\ J K^{-1} mol^{-1}$

1Latm = 101.3 J and 1J = 9.822×10^{-2} Latm

To express R in unit of bar, we will use the conversion factor of 1atm = 1.01325 bar

Hence, $R = 0.08206\ L atm K^{-1} mol^{-1} \times 1.01325\ bar\ atm^{-1} = 0.08314\ L\ bar\ K^{-1} mol^{-1}$

ILLUSTRATION EXERCISE: Air entering lungs ends up in tiny sacs called alveoli from which oxygen diffuses into the blood. The average radius of the alveolus is 0.0050cm and the air inside contains 14 mol percent O_2. Assuming pressure in alveoli is 1.0atm and temperature is 37°C. Calculate the number of molecules in one of the alveoli

r = 0.0050 cm = 0.000050m P = 1atm T = 37°C = 310K

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \frac{0.000050}{l} = 5.24 \times 10^{-13} m^3 = 5.24 \times 10^{-10} L$$

$$PV = nRT \implies n = \frac{PV}{RT} = \frac{1 \times 5.24 \times 10^{-10}}{0.08206 \times 310} = 2.05 \times 10^{-11} mol$$

Because the air in alveolus is 14% oxygen, therefore

$$n_{O_2} = 2.05 \times 10^{-11} \times 14/100 = 2.87 \times 10^{-12} mol$$

$$N_{O_2} = n_{O_2} \times N_A = 6.02 \times 10^{23} \times 2.87 \times 10^{-12} = 1.7 \times 10^{12} molecules$$

DISTRIBUTION OF MOLECULAR SPEED IN IDEAL GAS

While deriving kinectic gas equation, it was assumed that all molecules in a gas has same velocity but it is not so. When any two molecules collide, one molecule transfers kinectic energy to other molecule, the velocity of molecule which gain energy increase but that of other decreases. In studying, for example, 1 mole of a gas, the velocity of each molecule is difficult to know because of large number of molecules and because velocities of molecule is changing constantly due to the large number of molecules. There is a continuous spread or distribution of velocity as a result of collision, so, instead of individual molecular velocity, it is convenient to consider the Number of molecules moving at velocity, v and v+dv at any moment for a given system at some known temperature, e.g how many molecules in a macroscopic gas sample have velocity between 407.4 and 407.5 at any moment.

The distribution of velocity approach was first employed by Scottish Physicist James Clerk Maxwell in 1860 and was later refined by Boltzmann. They showed that for a given system contain N molecules (ideal gas) at thermal equilibrium with surrounding, the fraction of molecule $\frac{dN}{N}$ moving at velocity V_x and $V_x + dV_x$ along x-direction is given by

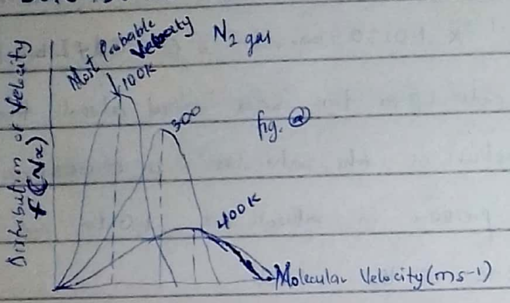
$$\frac{dN}{N} = \sqrt{\frac{m}{2\pi K_B T}}\, e^{-mV_x^2/2K_BT}\, dx = f(V_x)\, dV_x$$

Where m is the mass of the molecule, K_b is Boltzmann constant, T is absolute temperature.
The quantity $f(v_x)$ is Maxwell velocity distribution function in one direction

$$f(v_x) = \sqrt{\frac{m}{2\pi k_b T}}\, e^{-mv_x^2/2k_bT}$$

The relation above is called Maxwell's Law of distribution of velocity

DEPENDENCE OF VELOCITY DISTRIBUTION CURVE ON TEMPERATURE & MOLAR MASS



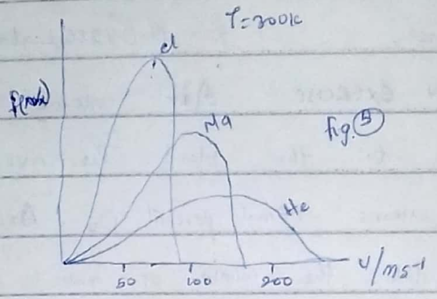


Figure ⓐ represent distribution of velocity in nitrogen gas, the ~~the~~ ~~the~~ figure show the distribution curve is influence by temperature, it can be seen that a very some ~~small~~ fraction of molecule have either very low or very high velocity. At low temperature, the distribution has a rather narrow range, as the temperature increase, the curve becomes flatter meaning that there are more fast moving molecules. This shows that at high temperature more molecules have high velocity and fewer has ~~high~~ low velocity

The speed corresponding to maximum value of f(v) is called called the most probable velocity, ~~speed~~. It is the speed possess by largest fraction of molecule.

In figure ⓑ, we see that heavier gases have a narrower range of speed distribution than light gases at same temperature. So, heavier gases move slower on average than lighter ~~oxygen~~ gases.
The usefulness of Maxwell speed distribution is that it enables us to calculate average quantities

Consider the mean speed, $\bar{c}$, of large collection of molecules at temperature, T the mean speed is calculated by multiplying each speed by fraction of molecules that have that speed and adding all product together because the fraction of molecule with a speed in the range c and c+dc is f(c)dc. The product of this fraction and the speed is cf(c)dc. Thus, the mean speed is obtained by evaluating the integral between the limits c=0 and c=∞, that is;

$$\bar{c} = \int_0^\infty c f(c)\, dc \qquad f(c) = 4\pi c^2\left(\frac{m}{2\pi k_bT}\right)^{3/2} e^{-mc^2/2k_bT}$$

$$\bar{c} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty c^3 e^{-mc^2/2k_BT}\, dc \qquad \int_0^\infty x^3 e^{-ax^2}\, dx = \frac{1}{2a^2}$$

$$\bar{c} = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} \times \frac{1}{2}\left(\frac{2k_BT}{m}\right)^2$$

$$\bar{c} = \sqrt{\frac{8k_bT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

This give the average velocity a average speed because the square of average velocity is a scalar quantity, it follows that $\bar{v}^2 = \bar{c}^2$, Hence, $V_{rms} = C_{rms}$. According to calculations made by Maxwell, most probable velocity is given by the expression;

$$V_{mp} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}}$$

RELATIONSHIP BETWEEN V_{RMS}, AVERAGE VELOCITY & MOST PROBABLE SPEED

$$\frac{\bar{V}}{V_{rms}} = \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}} = 0.9213$$

$$\bar{V} = 0.9213\, V_{RMS}$$

$$\frac{V_{mp}}{V_{rms}} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165$$

$$V_{mp} = 0.8165\, V_{RMS}$$

ILLUSTRATION EXERCISE: Calculate the value of most probable speed, average speed and root mean square velocity of oxygen at 300K. Given $R = 8.314\,JK^{-1}mol^{-1}$ $M = 32\,g/mol$

$$V_{rms} = \sqrt{\frac{3 \times 8.314 \times 300}{0.032}} = \sqrt{233831.25} = 484\,m/s$$

$$V_{mp} = 0.8165 \times V_{rms} = 0.8165 \times 484 = 395\,m/s \qquad \bar{V} = 0.9213 \times V_{rms} = 0.9213 \times 484 = 446\,m/s$$

CALCULATIONS ON MOLECULAR SPEEDS

Calculating the molecular speeds when temperature alone is given.

EXAMPLE: Calculate the root mean square velocity of CO_2 molecule at 1000°C

$$V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 1273}{0.044}} = \sqrt{721617.41} = 850\,m/s$$

Calculating molecular speeds when temperature and pressure are given.

In such cases, the equation below is used based on kinetic gas equation;

Since $PV = nRT$ $\qquad V_{rms} = \sqrt{\frac{3PV}{M}}$

Also, knowing that 1 mole of a gas at s.t.p occupies 22.414L/mol known as molar volume. But before using this relation, molar volume is reduced to given condition of temperature and pressure.

EXAMPLE: Calculate the root mean square velocity at 12°C and 780 torr of Cl_2

$P_1 = 760\,torr$ $\quad V_1 = 22.414\,L/mol$ $\quad T_1 = 273K$ $\quad P_2 = 780\,torr$ $\quad T_2 = 288\,K$ $\quad V_2 = ?$ $\quad P_2 = 780\,torr = 103991\,Nm^{-2}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{760 \times 22.414}{273} = \frac{780 \times V_2}{285} \Rightarrow V_2 = \frac{760 \times 285 \times 22.414}{780 \times 273} = 22.7[illegible]9\,L/$$

$$V_{rms} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 22.799 \times 10^{-3} \times 103991}{0.071}} = \sqrt{100178.48} = 317\,m/s$$

Calculating molecular speed at stp

EXAMPLE: Calculate the average speed of nitrogen gas at stp

$$\bar{V} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 273}{\pi \times 0.028}} = \sqrt{206421.42} = 454\,m/s$$

$$V = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8 \times 101325 \times 22.414 \times 10^{-3}}{\pi \times 0.028}} = \sqrt{206546.61} = 454\,m/s$$

Calculating molecular speed when molecular density and given pressure are given.

In such

cases, the following derived equation is used, i.e;

$$V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} \qquad \text{Recall } V = \frac{M}{D} \text{ where D is molecular density}$$

$$\therefore V_{rms} = \sqrt{\frac{3PM}{MD}} = \sqrt{\frac{3P}{D}}$$

~~Example~~ **EXAMPLE:** Oxygen at 1 atm and 0°C has a density of $1.4290 gL^{-1}$. Find the root mean square velocity of oxygen molecule and root mean square velocity at 12°C

$$D = 1.4290gL^{-1} = 1.4290gL^{-1} \times \frac{1kg}{1000g} \times \frac{1L}{0.001m^3} = 1.4290 kg/m^3$$

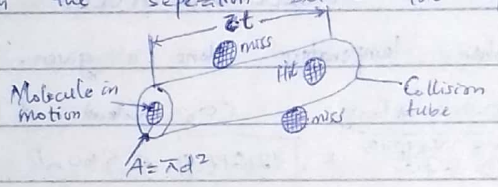
$$V_{rms} = \sqrt{\frac{3\times 101325}{1.4290}} = \sqrt{212718.68} = 461m/s$$

EXERCISE: Calculate the root mean square velocity of CH_4 at 370K. $(M = 16\times10^{-3}kg$

$$V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times8.314\times370}{0.016}} = \sqrt{576783.75} = 760m/s$$

MOLECULAR COLLISION

The collision frequence of the molecule of a gas depend on density of the gas and the molecular velocity and therefore on the temperature of the system. According to kinetic theory model, each molecule is assumed to be a sphere of diameter, d. A molecular collision is one in which the seperation between two sphere (measured from each center) is d.



If considering the motion of a particular molecule, let assume that at a given instance all other ~~molecules~~ molecules ~~at every~~ at every point are standing still except the molecule being considered, ~~at~~ in time, t. Thus, molecule move a distance $\bar{c}t$, where $\bar{c}$ is the average speed. The cross sectional area of the cylinder is πd^2. Therefore the volume, V, is given by;

$$V = A \times L = \pi d^2 \times \bar{c}t$$ i.e Volume of the molecule as it move in the tube

Any molecule whose centre lies within the cylinder will collide with the moving molecule. If N molecules is in volume V, the number density of the gas will be $\frac{N}{V}$. And number of collision in time, t, is N_c and is given by;

$$N_c = V \times \frac{N}{V} = \pi d^2 \bar{c} t \frac{N}{V}$$

The collision frequency (Number of collision per unit time), Z_1 is given by;

$$Z_1 = \pi d^2 c \left(\frac{N}{V}\right)$$

We assumed that all other molecules are frozen in position, if ~~we~~ we now assume the rest of the molecules are not frozen in position, then $\bar{c}$ should be replaced by average relative velocity

$$\bar{C}_{re} = \sqrt{2}\,\bar{V}$$

$$Z_1 = \sqrt{2}\,\pi d^2 \bar{V} \left(\frac{N}{V}\right)$$

This is the number of collision a single molecule makes in one second. Since there are N molecules in Volume V, each will make Z_1 collision per second, hence total number or binary collision (i.e, between two molecules) is Z_{11} ~~given~~ and it is expressed as;

$$Z_{11} = \frac{1}{2} Z_1 \left(\frac{N}{V}\right)$$

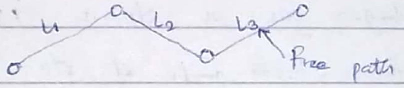
$$Z_{11} = \frac{\sqrt{2}\,\pi d^2 \bar{v}}{2} \left(\frac{N}{V}\right)^2$$

The unit of Z_{11} is collision $m^{-3} s^{-1}$

The fraction $\frac{1}{2}$ is introduce to ensure that we are counting collision between two molecule only once. The probability of three or more molecules colliding at once is very small except at high pressure.

MEAN FREE PATH

The distance travelled by molecule before collision is called the free path, but because the free path is different from time to time, mean is calculated. Mean free path is distance travelled by a molecule between successive collisions, i.e;



$$\lambda = \frac{L_1 + L_2 + L_3 + \ldots + L_N}{N}$$

Where N is the number of molecule's with which the molecule collide. It depends on pressure, density and viscosity of the gas and is expressed as;

$$\lambda = \eta \cdot \sqrt{\frac{3}{PD}}$$

where P is pressure of the gas, D is density, η is coefficient of viscosity of gas. Mean free path can also be expressed as;

λ = average velocity × average time between collision

average time between collision = the reciprocal of collision frequency

$$\lambda = \bar{v} \times \frac{1}{Z_1}$$

$$\lambda = \frac{\bar{v}}{Z_1} = \frac{\bar{v}}{\sqrt{2}\,\pi d^2 \bar{v} \left(\frac{N}{V}\right)} = \frac{1}{\sqrt{2}\,\pi d^2 \left(\frac{N}{V}\right)}$$

From equation above, it can be seen that mean free path is inversely proportional to number density. It can also be expressed in term of gas pressure, i.e;

$$PV = nRT \Rightarrow PV = \frac{N}{N_A} RT \Rightarrow \frac{N}{V} = \frac{PN_A}{RT}$$

$$\lambda = \frac{RT}{\sqrt{2}\,\pi d^2 P N_A} = \frac{K_B T}{\sqrt{2}\,\pi d^2 P}$$

ILLUSTRATION EXERCISE: The concentration of dry air at 1atm, at 298K is about 2.5×10^{19} molecule cm^{-3}. Assuming that air contain only nitrogen molecule, calculate the collision frequency, binary collision number and mean free path of nitrogen molecule. The collision diameter is 3.75Å.

$$\bar{V} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 298}{\pi \times 0.028}} = \sqrt{225324.5} = 475 m/s$$

$Z_1 = \pi d^2 \sqrt{2}\,\bar{v}\left(\frac{N}{V}\right) = \pi \times (3.75\times10^{-10})^2 \times \sqrt{2} \times 475 \times 2.5\times10^{25} = 7.42\times10^{9}$ collision s^{-1}

$Z_{11} = \frac{1}{2} Z_1 \left(\frac{N}{V}\right) = \frac{1}{2} \times 7.42\times10^{9} \times 2.5\times10^{25} = 9.3\times10^{34}$ collision $m^{-3}s^{-1}$

[illegible] $\lambda = \bar{v}/Z_1 = \frac{475}{7.42\times10^{9}} = 6.4\times10^{-8}$ m/collision [illegible]

Calculate the mean free path and binary collisions ~~number~~ between HI molecules at 300K and 1.0atm, the diameter being 5.10Å, assume idea gas behaviour.

$\bar{v} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times8.314\times300}{\pi\times0.128}} = \sqrt{50011.245} = 224$ m/s

$\lambda = \frac{K_B T}{\pi d^2 P\sqrt{2}} = \frac{1.38\times10^{-23}\times300}{\pi\times(5.10\times10^{-10})^2\times101325\times\sqrt{2}} = 3.54\times10^{-8}$ m/collision

$Z_{11} = \frac{\sqrt{2}\,\pi d^2\,\bar{v}}{2}\left(\frac{PN_A}{RT}\right)^2 = \frac{\sqrt{2}\times\pi\times(5.10\times10^{-10})^2\times224}{2} \times \left(\frac{101325\times6.02\times10^{23}}{8.314\times300}\right)^2 = 1.3\times10^{-16}\times5.98\times10^{50} = 7.8\times10^{34}$

At 0°c and 1 atm, the molecular diameter is 4Å. Calculate the mean free path of its molecule. If the molar mass is 28g/mol, what is the average speed of the gas

$\lambda = \frac{1}{\sqrt{2}\,\pi d^2 \frac{N}{V}} = \frac{22.414\times10^{-3}}{\sqrt{2}\times\pi\times(4\times10^{-10})^2\times6.02\times10^{23}} = \frac{0.022414}{427938.5} = 5.24\times10^{-8}$ m

$\bar{V} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times8.314\times273}{\pi\times0.028}} = \sqrt{206421.4} = 454.3$ m/s

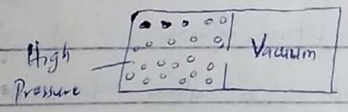
The root mean square velocity of hydrogen gas at stp is 1.83×10^{5} cms^{-1} and its mean free path is 1.78×10^{-5}cm. Calculate the collision number at stp

$\bar{v} = 0.9213 \times V_{rms} = 0.9213\times1.83\times10^{3} = 1.69\times10^{3}$ m/s

$Z_1 = \frac{\bar{v}}{\lambda} = \frac{1.69\times10^{3}}{1.78\times10^{-7}} = 9.5\times10^{9}$ collision s^{-1}

$Z_{11} = \frac{1}{2} Z_1\left(\frac{N}{V}\right) = \frac{1}{2}\times9.5\times10^{9}\times\frac{6.02\times10^{23}}{22.414\times10^{-3}} = 1.3\times10^{35}$ collision $m^{-3}s^{-1}$

EFFUSION



During effusion, a gas travels from high pressure region through a pin hole or origin. For effusion to occur, the mean free path of the molecule must be large compare with the [illegible] of the origin. The number of molecules passing through the origin equal to number of molecule that strike on the area of wall which equal to the area of the origin. Thomas Graham found experimentally that under same condition of temperature and pressure, the rate of diffusion of gases is inversely proportional to the square root of their molar masses. Thus, for two gases A and B:

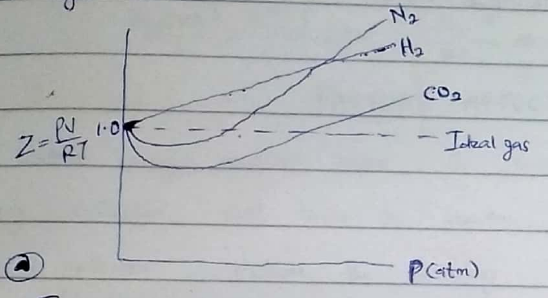
$$R \propto \sqrt{\frac{1}{M}} \Longrightarrow \frac{R_A}{R_B} = \sqrt{\frac{M_2}{M_1}}$$ where R_1 and R_2 is the rate of diffusion or effusion.

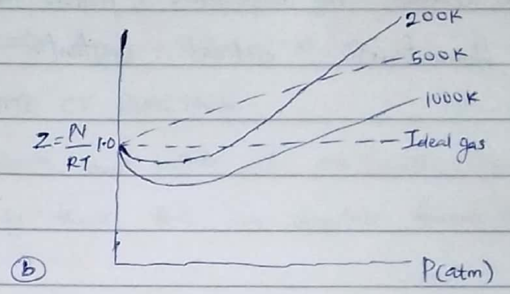
REAL GASES

An ideal gas is one which obey gas law or gas equation (PV=nRT) at all temperature and pressure. Experimental evidence as shown that very few gas obey ideal gas law and only at low pressure and high temperature. That most gases shows deviation from ideal gas behaviour at high pressure and low temperature, thus, all gases that do not obey ideal gas equation are called non-ideal gases or real gases. The extent to which a real gas deviate from ideal behaviour may be expressed in term of a new function called compressibility factor Z. It is defined as;

$$Z = \frac{PV}{RT}$$

A plot of compressibility factor againt pressure at constant temperature shows deviation from ideal gas behaviour.





For 1 mole of an ideal gas compressibility factor, Z, is unity (i.e, Z = 1) and it is independent of temperature and pressure. For real gases, Z is a function of both temperature and pressure and it varies from gas to gas. The amount by which the actual factor differ from unity give a measure of deviation from ideality for the gases. At low pressure and very high temperature for all gases, Compressibility factor is approximately unity (i.e $Z \simeq 1$). This indicate that at low pressure and high temperature, real gases exhibit ideal behaviour.

VANDER WAAL EQUATION.

Vanderwaal attribute the deviation of real gases from ideal behaviour to two erroneous postulates, which are;

The molecule in a gas are point mass and possess no volume

The molecule do not attract each other i.e no intermolecular attraction

Hence, the ideal gas equation derived from kinetic theory for real gases. Vanderwaal equation of state attempt to account for finite volume of individual molecules in a non-ideal gas and attractive forces between them. therefore we have

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

where a and b are Vanderwall constant (specific for each gas) and n is number of mole of gas

CRITICAL PHENOMENON

A gas can be liquified by lowering the temperature and increasing the temperature. At lower temperature, the gas molecule lose kinetic energy, the slow moving molecules aggregate due to attraction between them and are converted into liquid. The same effect is produced by increas of pressure

Critical Temperature (T_c): This is the temperature above which a gas can't be liquified no matter the pressure applied

Critical Pressure (P_c): This is the minimum pressure require to ~~liquefying~~ liquefy a gas at critical temperature.

Critical Volume (V_c): This is the volume occupied by a mole of a gas at its critical temperature and pressure.

Hence, critical ~~tap~~ temperature, pressure and volume are called critical phenomenon. All real gases have a characteristic critical constant.

CHEMICAL KINECTICS

~~An~~ As thermodynamic and free energy change answer the question of how feasible a chemical reaction is, so also, chemical kinectic answer the question of rate or how fast a chemical reaction. Therefore, Chemical kinectic is the branch of chemistry that explore the rate at which a chemical reaction occur as well as the pathways ~~through~~ which reaction occurs, i.e mechanism of chemical reactions. It has two broad division, ~~namely~~ viz; Rate and Mechanism.

IMPORTANCE OF CHEMICAL KINECTICS: It provides ways to optimize the rate of reaction

It helps to characterise and predict the rate of change and approach to equilibrium

It involves search for methods to slow down undesired reaction and methods to stive up desired reaction such as baking of bread and decomposition of garbage.

It also involve search for conditions that leads to maximum yield of product e.g Haber Process

It ~~also~~ is important in modelling complex chemical system and consequently to predict chemical change and rate of change e.g global climate change.

RATE OF REACTION

Considering the hypothetical reaction; $aA + bB \longrightarrow cC + dD$

The rate of reaction can be determined by measuring the change in concentration of any product or reactant with time, i.e rate of consumption of the ~~product~~ reactant ~~and~~ or formation of the product with time, as expressed below;

$$\text{Rate} = \frac{\Delta[\text{Product}]}{\Delta\,\text{time}} = \frac{-\Delta[\text{Reactant}]}{\Delta\,\text{time}}$$

Rate of reaction is always a positive quatity, hence the negative sign in the expression for rate in term of consumption of reactant. Since concentration is in mol/L or M, hence, ~~the~~ unit of Rate is ~~molar~~ $mol\,L^{-1}s^{-1}$ or $molecule\,mL^{-1}s^{-1}$

RATE OF REACTION AND STOICHIOMETRY

Consider these hypothetic reaction also; $aA + bB \rightarrow cC + dD$

$$Rate = -\frac{1}{a}\frac{\Delta[A]}{t} = -\frac{1}{b}\frac{\Delta[B]}{t} = \frac{1}{c}\frac{\Delta[C]}{t} = \frac{1}{d}\frac{\Delta[D]}{t}$$

ILLUSTRATION EXERCISE: For the reaction, $2N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2(g)}$, if at one point the rate of consumption of N_2O is $1.3 \times 10^{-3} Ms^{-1}$, what will be the rate of appearance of O_2 at that point?

$$\frac{R[N_2O]}{2} = \frac{R[O_2]}{1} \Rightarrow \frac{1.3\times10^{-3}}{2} = R[O_2] \Rightarrow R_{[O_2]} = 6.5\times10^{-4} Ms^{-1}$$

FACTORS AFFECTING RATE OF REACTION

Before any reaction occur, the reactant molecule must collide with one another, however, it is not every collision that leads to reaction, it is only those that are effective. Factors that increase frequency of collision include the following;

Concentration of reactant: Increase in concentration of reactant leads to increase in number of reactant molecules, consequently the greater the frequency of collision and higher rate of reaction. The dependent of rate of ~~concentration~~ reaction on the concentration of reactant can be expressed in term of the rate law equation, i.e

$$Rate = K[A]^n[B]^m \quad \text{For reaction; } aA + bB \rightarrow Product$$

where k is called specific rate constant, m and n are the order of reaction with respect to each reatant A and B respectively, The overall order of reaction is the sum of m and n

DETERMINATION OF ORDER OF REACTION: The order of reaction with respect to concentration of a reactant is an experimentally determined quantity. It has no correlation with stoichiometry co-efficients of the reactant in balanced equation for the reaction. In determining this quantity, ~~every method~~ methods that can be used include; initial rate method, Integrated rate law, etc

Initial rate method: This involve keeping constant the concentration of a reactant, say A, and varying the concentration of the other reactant, say B, at an instant to determine the order of reaction with respect to reactant B. and ~~any~~ same principle is used to determine order of reaction with respect to A, i.e keeping concentration of B constant [illegible] that of reactant B varies at an instant.

ILLUSTRATION EXERCISE: The following datas were obtained from reaction $2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$, where the rate is $\frac{-d[ClO_2]}{dt}$. Determine the rate law and value of rate constant.

$[ClO_2]$ M	$[OH^-]$ M	Rate Ms^{-1}
0.050	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.050	1.15×10^{-1}

Using Experiment 1, 2 $\frac{R_2}{R_1} = \frac{[ClO_2]_2^x [OH^-]_2^y}{[ClO_2]_1^x [OH^-]_1^y}$ Rate $= k[ClO_2]^x[OH^-]^y$ and $[OH^-]_2 = [OH^-]_1$

$\therefore \frac{R_2}{R_1} = \frac{[ClO_2]_2^x}{[ClO_2]_1^x} \Longrightarrow \frac{2.30\times10^{-1}}{5.75\times10^{-2}} = \frac{0.100^x}{0.050^x} \Rightarrow 4 = \left(\frac{0.100}{0.050}\right)^x \Longrightarrow 2^2 = 2^x \Longrightarrow x = 2$

Using Experiment 2, 3 $\frac{R_2}{R_3} = \frac{[ClO_2]_2^x [OH^-]_2^y}{[ClO_2]_3^x [OH^-]_3^y}$ $[ClO_2]_2 = [ClO_2]_3$.

$\therefore \frac{R_2}{R_3} = \frac{[OH^-]_2^y}{[OH^-]_3^y} \Longrightarrow \frac{2.30\times10^{-1}}{1.15\times10^{-1}} = \frac{0.100^y}{0.050^y} \Longrightarrow 2 = \left(\frac{0.100}{0.050}\right)^y \Longrightarrow 2^1 = 2^y \Longrightarrow y = 1$

$\therefore$ Rate law is, $R \propto [ClO_2]^2[OH^-]^1$

Using Experiment 3, $K = \frac{R_3}{[ClO_2]_3^2[OH^-]_3} = \frac{1.15\times10^{-1}}{(0.100)^2 \times 0.050} = \frac{11.5\times10^{-2}}{10^{-2}\times5\times10^{-2}} = 2.30\times10^2\,M^{-2}s^{-1}$

Note: If the solution for order of reaction can be solved with indices, use logarithm

Integrated rate law: This is a trial ~~Integrated~~ and error method. The order of reaction which is not known is ~~is not known~~ gotten by trying ~~using~~ different integrate rate law for different order of reaction and the one which comply with experimental data is the correct order of the reaction

First order reaction: Example of such reaction is the isomerization reaction e.g. Cyclopropane $\rightleftharpoons$ Propene. Considering this hypothetical reaction, $A \longrightarrow$ Product

$$-\frac{d[A]}{dt} \propto [A] \Longrightarrow -\frac{d[A]}{dt} = k[A] \Longrightarrow \frac{d[A]}{[A]} = -k\,dt$$ integrating both side

$$\int \frac{d[A]}{[A]} = -k\int dt \Longrightarrow Ln[A]_t = -kt + c$$ at $t = 0$ $[A]_t = [A]_o$

$$\therefore Ln[A]_o = -k(0) + c \Longrightarrow c = Ln[A_o]$$

$$\therefore Ln[A]_t = -kt + Ln[A]_o$$

If a reaction is first order reaction, plot the graph of the Logarithm of concentration of A at any time ~~with~~ against time, such that you have a negative slope, i.e.

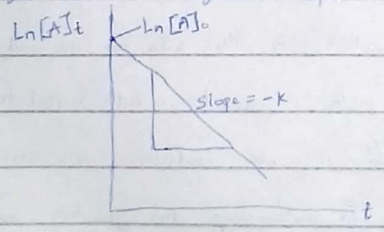


ILLUSTRATION EXERCISE: A certain reaction has the following general form; $aA \rightarrow bB$ at particular temperature. ~~The~~ initial concentration of A is 0.02M, concentration versus time data collected for this reaction was used to plot $Ln[A]$ versus time, this resulted in a straight line with a slope value of -2.97×10^{-2} min⁻¹. Determine the rate law, integrated ~~rate~~ rate law and value of rate constant for this reaction. How much time is required for concentration of A to decrease to 0.0025M

Rate law is $R \propto [A] \Longrightarrow R = k[A]$

Integrated rate law $-\frac{d[A]}{dt} \propto [A] \Rightarrow -\frac{d[A]}{dt} = k[A] \Longrightarrow Ln[A]_t = -kt + Ln[A]_o$

Rate constant Slope $= -k \Longrightarrow \cancel{-}2.97\times10^{-2} = \cancel{-}k \Longrightarrow k = 2.97\times10^{-2}$

$$Ln[A]_t = -kt + Ln[A]_o \Longrightarrow Ln\frac{[A]_o}{[A]_t} = kt$$

$$Ln\frac{0.02}{0.0025} = 2.97\times10^{-2}t \Longrightarrow t = \frac{Ln\,8}{2.97\times10^{-2}} = 70_{min}$$

The concentration of product ~~at~~ a time can be determined for a first order reaction, as shown below:

~~For~~ reaction $A \longrightarrow \text{Product}$

Using mass balance, $[A]_t + [P] = [A]_0 \implies [P] = [A]_0 - [A]_t \implies [A]_t = [A]_0 - [P]$

Recall, $[A]_t = [A]_0 e^{-kt} \implies [A]_0 - [P] = [A]_0 e^{-kt}$

$$[P] = [A]_0 - [A]_0 e^{-kt} = [A]_0(1 - e^{-kt})$$

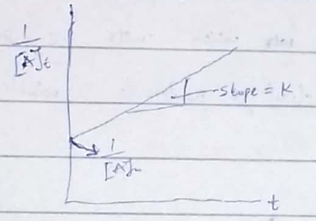
Second Order Reaction: A reaction can also be ~~a~~ second order reaction. It may involve only one reactant or two different reactants. For a second order reaction involving one reaction, ~~it~~ follows thus,

$$R \propto [A]^2 \implies R = k[A]^2$$

$$-\frac{dA}{dt} = k[A]^2 \implies \int \frac{dA}{[A]^2} = \int -k\,dt$$

$$\cancel{-}\frac{1}{[A]}\Bigg|_{[A]_0}^{[A]_t} = \cancel{-}kt \implies \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$



For second order reaction involving two different reactant, it follows thus

For hypothetical reaction: $A + B \longrightarrow \text{Product}$

$$R \propto [A][B] \implies R = k[A][B]$$

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

Using mass balance: $[A]_0 - [A] = [B]_0 - [B] \implies [B] = [B]_0 - [A]_0 + [A]$

$[B] = \Delta + [A]$ such that $\Delta = [B]_0 - [A]_0$

$$-\frac{dA}{dt} = k[A][\Delta + [A]] \implies \int \frac{dA}{[A][\Delta + [A]]} = \int -k\,dt$$

$$\int \frac{1}{[A][\Delta + [A]]}\,dA = -kt \xrightarrow[\text{fraction}]{\text{By partial}} \int \frac{1}{\Delta[A]} - \frac{1}{\Delta[\Delta + [A]]}\,dA = -kt$$

$$\frac{1}{\Delta}\left(\int \frac{1}{[A]} - \frac{1}{\Delta + [A]}\,dA\right) = -kt \implies \frac{1}{\Delta}\left(\int \frac{1}{[A]}\,dA - \int \frac{1}{\Delta + [A]}\,dA\right) = -kt$$

$$\frac{1}{\Delta}\left(\ln[A] - \ln[\Delta + [A]]\right)\Bigg|_{[A]_0}^{[A]_t} = -kt \implies \frac{1}{\Delta}\ln\frac{[A]}{\Delta + [A]}\Bigg|_{[A]_0}^{[A]} = -kt$$

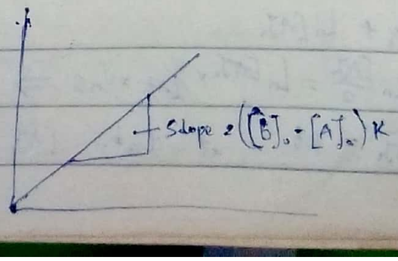
$$\frac{1}{\Delta}\left(\ln\frac{[A]}{\Delta + [A]} - \ln\frac{[A]_0}{\Delta + [A]_0}\right) = -kt$$

Since $\Delta = [B]_0 - [A]_0 = [B] - [A]$

$$\therefore \frac{1}{\Delta}\left(\ln\frac{[A]}{[B]} - \ln\frac{[A]_0}{[B]_0}\right) = -kt \implies \frac{1}{\Delta}\ln\left(\frac{[A]/[A]_0}{[B]/[B]_0}\right) = -kt$$

$$\cancel{-}\frac{1}{\Delta}\ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = \cancel{-}kt$$

$$\therefore \ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = \Delta kt = ([B]_0 - [A]_0)kt$$



For a reaction with unknown order of reaction, α, such that α ≠ 1, thus can be ~~chosen~~ gotten as a general equation for such, provided that there is only one reactant

For a hypothetical reaction: $A \longrightarrow$ Product

$$R \propto [A]^{\alpha} \Longrightarrow R = k[A]^{\alpha}$$

$$\frac{-dA}{dt} = k[A]^{\alpha} \Longrightarrow \int \frac{d[A]}{[A]^{\alpha}} = \int -k\,dt$$

$$\frac{[A]^{-\alpha+1}}{-\alpha+1} = -kt \Longrightarrow \frac{[A]^{1-\alpha}}{1-\alpha}\Bigg|_{[A]_0}^{[A]} = -kt$$

$$[A]^{1-\alpha}\Bigg|_{[A]_0}^{[A]} = (1-\alpha)-kt \Longrightarrow \frac{1}{[A]^{\alpha-1}}\Bigg|_{[A]_0}^{[A]} = (\alpha-1)kt$$

$$\frac{1}{[A]^{\alpha-1}} - \frac{1}{[A]_0^{\alpha-1}} = (\alpha-1)kt \quad \text{for } \alpha \neq 1$$

By simulation, order of reaction can be determined by inputting several possible value for α and the value for which the graph give a straight line will be the order of reaction.

Zeroth order of reaction: This involve a reaction ~~with~~ which rate is independent of concentration of reactant. An example is the decomposition reaction of dinitrogen pentoxide which is of ~~Tro~~ Tropospheric interest, that is;

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

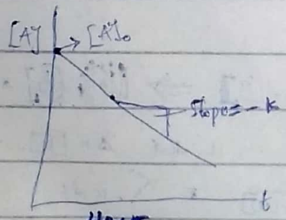
N_2O_5

$$R \propto [A]^0 \Longrightarrow R = k[A]^0$$

$$\frac{-dA}{dt} = k \Longrightarrow \int_{[A]_0}^{[A]} dA = \int -k\,dt$$

$$[A]\Big|_{[A]_0}^{[A]} = -kt \Longrightarrow [A] - [A]_0 = -kt$$

$$[A] = -kt + [A]_0$$



USING ~~[illegible]~~ HALF LIFE TO DETERMINE ORDER OF REACTION

Half life is the time taken for half of a given ~~reactant~~ amount of reactant to have been consumed in a reaction.

For Zeroth order reaction: $[A]_t = -kt + [A]_0$ at $t_{1/2}$; $[A]_t = \frac{[A]_0}{2}$

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$kt_{1/2} = [A]_0 - \frac{[A]_0}{2} = \frac{[A]_0}{2} \Longrightarrow t_{1/2} = \frac{[A]_0}{2k}$$

For First order reaction: $\ln[A]_t = -kt + \ln[A]_0$ at $t_{1/2}$ $[A]_t = \frac{[A]_0}{2}$

$$\ln\frac{[A]_0}{2} = -kt_{1/2} + \ln[A]_0$$

$$kt_{1/2} = \ln[A]_0 - \ln\frac{[A]_0}{2} = \ln [A]_0 \times \frac{2}{\cancel{[A]_0}} = \ln 2 \Longrightarrow t_{1/2} = \frac{\ln 2}{k}$$

For Second order reaction: $\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$ at $t_{1/2}$; $[A]_t = \frac{[A]_0}{2}$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$kt_{1/2} = \frac{2-1}{[A]_0} \Rightarrow t_{1/2} = \frac{1}{[A]_0 k}$$

For unknown reaction of order, α, in which $\alpha \neq 1$: $\frac{1}{[A]_t^{\alpha-1}} - \frac{1}{[A]^{\alpha-1}} = kt(\alpha-1)$ at $t_{1/2}$; $[A]_t = \frac{[A]_0}{2}$

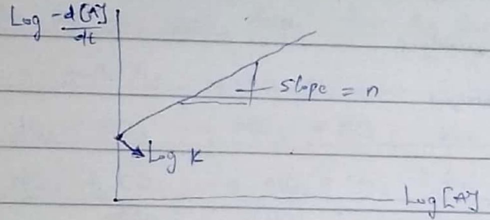
$$\frac{2^{\alpha-1}}{[A]_0^{\alpha-1}} - \frac{1}{[A]_0^{\alpha-1}} = kt_{1/2}(\alpha-1)$$

$$\frac{2^{\alpha-1}-1}{[A]_0^{\alpha-1}} = kt_{1/2}(\alpha-1) \Rightarrow t_{1/2} = \frac{2^{\alpha-1}-1}{[A]_0^{\alpha-1}(\alpha-1)k}$$

Differential rate law method: If a reaction is assumed to be n order of reaction with respect to a particular reactant A, Such that,

$$\frac{-d[A]}{dt} = k[A]^n$$

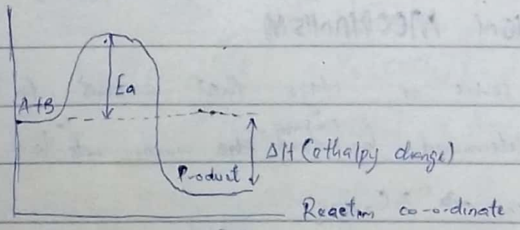
$$\text{Log}\,\frac{-d[A]}{dt} = \text{Log}\,k + n\,\text{Log}[A]$$

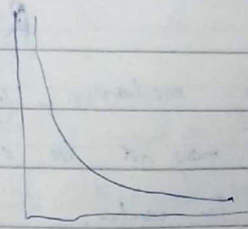


Effect of temperature on rate of reaction: The average kinetic energy of reacting molecule is a function of temperature, i.e $K \cdot E = \frac{3}{2}K_BT$. Such that as temperature increase, average kinetic energy increases, hence, frequency of collision increase leading to increase in rate of reaction. The rate constant K is constant all condition except temperature, ~~that~~ is, the only quantity that affect magnitude of K is temperature. The dependence of rate constant on temperature is expressed quantitatively using Arrhenius equation;

$$K = Ae^{-E_a/RT}$$ where A is

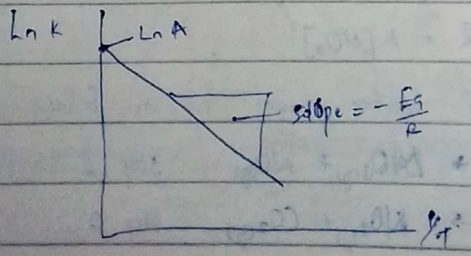
Where A is pre-exponential factor which is a measure of frequency of collision, Ea is known as activation energy, i.e the energy barrier that reactant molecule must overcome before forming product.





$$\text{Ln}\,k = \text{Ln}\,A - \frac{E_a}{RT}$$

$$\text{Ln}\,k = -\frac{E_a}{RT} + \text{Ln}\,A$$



The graph can be used to get the rate constant at a particular temperature, if we have an ~~experimen~~ experimental data. It can also be used to relate known rate constant and temperature to unknown ~~v~~value of rate constant ~~or~~ temperature; i.e,

$$\ln k_1 = \left(\frac{-E_a}{R}\right)\frac{1}{T_1} - \ln A \quad \text{— (i)} \qquad \ln k_2 = \left(\frac{-E_a}{R}\right)\frac{1}{T_2} + \ln A \quad \text{— (ii)}$$

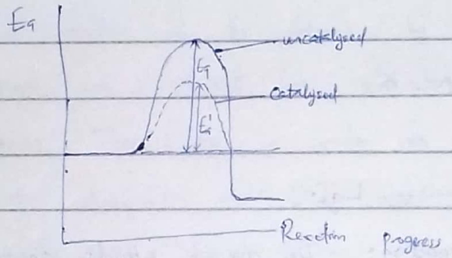
By substituting (ii) from (i)

$$\ln k_1 - \ln k_2 = \frac{-E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

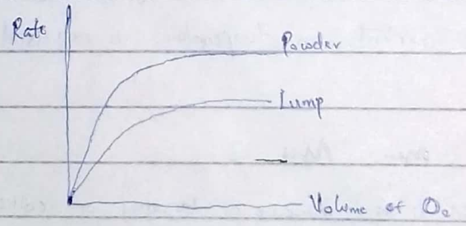
$$+\ln \frac{k_2}{k_1} = +E_a/R\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Effect of catalyst: Catalyst is a chemical compound that ~~is~~ used to alter the rate of reaction. A catalyst provides alternative pathway by lowering activation energy, as shown below



Nature of reactant: The nature of reactant also affect the rate of reaction. An increase in surface area of the reactant increases the rate of reaction. Reaction between $CaCO_3$ and HCl is an example, i.e.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$



REACTION MECHANISM

Reaction mechanism is a series of stage that account for a given reaction whose order of reaction may not be easily determined by ~~using~~ comparing the common rate laws ~~and~~ to experimental data. As we know

For reaction, $2O_{3(g)} \rightarrow 3O_{2(g)}$

The rate law is $R = k[O_3]/[O_2]$

Also, $NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$

The rate law is $R = k[NO_2]^2$

The proposed mechanism for the reaction above is as follows;

$NO_{2(g)} + NO_{2(g)} \longrightarrow NO_{3(g)} + NO_{(g)}$ step 1

$NO_{3(g)} + CO_{(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$ step 2

Such species as NO_3 which was not part of the original reaction which is produced in step 1 and consume in step 2 is called reaction intermediate, it is neither reactant nor product. Each of the step involved in mechanism is called elementary step which is defined as a reaction whose rate can be written from its molecularity, i.e number of species that must collide to produce the reaction indicated by that step, it can be unimolecular, bimolecular and rarely ter-molecular. For reaction ~~plane~~ mechanism, which is a series of elementary step, to be reasonable, it must satisfy two conditions;

Sum of elementary steps must give a balanced equation of the reaction

The mechanism must agree with experimentally determined rate law of the reaction

In a multi-step reaction, there is alway a step that is much slower than the other steps and there is no way a reaction can be much faster than the slowest reaction step, i.e rate determined step which is the slowest step in a multi-step reaction e.g

$$NO_2 + NO_2 \rightarrow NO_3 + NO \quad \text{slow}$$

$$NO_3 + CO \rightarrow NO_2 + CO_2 \quad \text{fast}$$

$$\frac{d[CO_2]}{dt} = \frac{d[NO]}{dt} = k[NO_2][NO_2] = k[NO]^2$$

A common type of reaction mechanism is that which involves a rapid equilibrium step, e.g reaction ~~is~~ between chlorine and chloroform, i.e

$$Cl_2 + CHCl_3 \longrightarrow HCl + CCl_4 \qquad Rate = k[Cl]^{1/2}[CHCl_3]$$

The proposed mechanism are;

$$Cl_2 \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2Cl \quad \text{rapid equilibrium}$$

$$Cl + CHCl_3 \xrightarrow{K_2} HCl + CCl_3 \quad \text{slow} \qquad CCl_3 + Cl \rightarrow CCl_4 \quad \text{fast}$$

$$Rate = K_2[CHCl_3][Cl]. \quad \text{from the ~~rate~~ determining step}$$

From rapid equilibrium step. $Rate = K_1[Cl_2]$ Forward reaction $\quad Rate = K_{-1}[Cl]^2$ Backward reaction

$$K_1[Cl_2] = K_{-1}[Cl]^2 \quad \text{~~rate~~ or forward reaction equal backward reaction}$$

$$[Cl]^2 = \frac{K_1[Cl_2]}{K_{-1}} \Longrightarrow [Cl] = \left(\frac{K_1}{K_{-1}}\right)^{1/2}[Cl_2]^{1/2}$$

$$Rate = K_2[CHCl_3][Cl] = K_2[CHCl_3]\left[\left(\frac{K_1}{K_{-1}}\right)^{1/2}[Cl_2]^{1/2}\right]$$

$$Rate = K_2\left(\frac{K_1}{K_{-1}}\right)^{1/2}[Cl_2]^{1/2}[CHCl_3] = K_{eff}[Cl_2]^{1/2}[CHCl_3] \quad \text{such that } K_{eff} = K_2\left(\frac{K_1}{K_{-1}}\right)^{1/2}$$

EXERCISES: Consider general reaction $aA + bB \rightarrow cC$ and the following average rate over a specific time; $\frac{-\Delta[A]}{\Delta t} = 0.0080$, $\frac{-\Delta[B]}{\Delta t} = 0.0120$, $\frac{\Delta[C]}{\Delta t} = 0.016$. Determine a set of possible co-efficients to balance the general reaction.

Recall, $\frac{1}{a}\frac{-\Delta[A]}{\Delta t} = \frac{1}{b}\frac{-\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} \Longrightarrow \frac{1}{a}0.008 = \frac{1}{b}0.012 = \frac{1}{c}0.016$

dividing through by ~~0.008~~;

$$\frac{a}{0.008} = \frac{b}{0.012} = \frac{c}{0.016}$$

~~Multiplying through by 0.016,~~ ~~2a + 1.5b → c~~

$$0.012a = 0.008b \Longrightarrow b = \frac{0.012a}{0.008} = 1.5a$$

$$\frac{a}{0.008} = \frac{c}{0.016} \Longrightarrow 0.016a = 0.008c \Longrightarrow c = \frac{0.016a}{0.008} = 2a$$

CLASS EXERCISES: Consider general reaction $aA + bB \rightleftarrows cC$ and the following rate data over a specific period of time, Δt; $\frac{-\Delta[A]}{\Delta t} = 0.008Ms^{-1}$, $\frac{-\Delta[B]}{\Delta t} = 0.012Ms^{-1}$, $\frac{\Delta[C]}{\Delta t} = 0.016Ms^{-1}$. Determine a set of possible co-efficient to balance the general reaction.

$$\frac{1}{a}\frac{-\Delta[A]}{\Delta t} = \frac{1}{b}\frac{-\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} \Longrightarrow \frac{0.008}{a} = \frac{0.012}{b} = \frac{0.016}{c}$$

$$\frac{0.008}{a} = \frac{0.012}{b} \Longrightarrow 0.008b = 0.012a \Longrightarrow b = \frac{\cancel{0.012a}}{\cancel{0.008}} = 1.5a$$

$$\frac{0.008}{a} = \frac{0.016}{c} \Longrightarrow 0.008c = 0.016a \Longrightarrow c = \frac{\cancel{0.016a}}{\cancel{0.008}} = 2a$$

$$aA + bB \rightarrow cC \Longrightarrow aA + 1.5aB \longrightarrow 2aC \Longrightarrow A + 1.5B \rightarrow 2C$$

$$\therefore \quad 2A + 3B \longrightarrow 4C$$

The following datas were obtained from gas phase decomposition of N_2O_5;

$[N_2O_5]$M	Initial rate Ms^{-1}
0.075	8.9×10^{-4}
0.190	2.26×10^{-3}
0.275	4.26×10^{-3}
0.410	4.85×10^{-3}

$$N_2O_{5(g)} \longrightarrow 2NO_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

Defining the rate as $\frac{-d[N_2O_5]}{dt}$, write the rate law and calculate the rate constant.

Let $\quad Rate = K[N_2O_5]^x$

From Ex 1 $\quad 8.9\times10^{-4} = K(0.075)^x$ —(i) $\quad$ From Ex. 2 $\quad 2.26\times10^{-3} = K(0.190)^x$ —(ii)

Dividing equation (i) by (ii) $\quad \frac{8.9\times10^{-4}}{2.26\times10^{-3}} = \frac{\cancel{K}(0.075)^x}{K(0.190)^x} = \left(\frac{0.075}{0.190}\right)^x$

$$\frac{89}{226} = \left(\frac{15}{38}\right)^x \Longrightarrow Log\frac{89}{226} = Log\left(\frac{15}{38}\right)^x \Longrightarrow x = \frac{Log\left(\frac{89}{226}\right)}{Log\left(\frac{15}{38}\right)} = 1.0025 \cong 1$$

Rate law is, $\quad Rate = K[N_2O_5]$

Using Ex 1 $\quad 8.9\times10^{-4} = K[0.075] \Longrightarrow K = \frac{8.9\times10^{-4}}{0.075} = 1.19\times10^{-2}s^{-1}$

The rate of decomposition of phosphene (PH_3) is given as $\frac{-d[PH_3]}{dt} = K[PH_3]$. It takes 120s for the concentration of 1M phosphene to decrease to 0.250M. How much time is required for 2M phosphene to decrease to 0.35M

Since the reaction is a first order reaction $\quad Ln[PH_3]_t = -kt + Ln[PH_3]_o$

$$Ln\frac{[PH_3]_o}{[PH_3]_t} = kt$$

when $[PH_3]_o = 1M$, $[PH_3]_t = 0.25M$ and $t = 120$, $\quad K = \frac{1}{t}Ln\frac{[PH_3]_o}{[PH_3]_t} = \frac{1}{120}Ln\frac{1}{0.25} = \frac{Ln\,4}{120} = 0.0116s^{-1}$

When $[PH_3]_o = 2M$, $[PH_3]_t = 0.35M$ and $t = ?$ $\quad t = \frac{1}{k}Ln\frac{[PH_3]_o}{[PH_3]_t} = \frac{1}{0.0116}Ln\frac{2}{0.35} = 150s$

The proposed mechanism for a reaction is given below. From the information given, find the rate law, the reaction intermediates and the overall reaction

$C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ $\quad$ slow $\quad$ Rate law is $\frac{-d[C_4H_9Br]}{dt} = K[C_4H_9Br]$

$C_4H_9^+ + H_2O \longrightarrow C_4H_9OH_2^+$ $\quad$ fast $\quad$ Reaction intermediates are $C_4H_9^+$, $C_4H_9OH_2^+$

$C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$

The overall reaction is $\quad C_4H_9Br + 2H_2O \longrightarrow C_4H_9OH + Br^- + H_3O^+$

A reaction has $k = 1.77 \times 10^{-6} M^{-1} s^{-1}$ at 25°C and an activation energy of 20.0kJ/mol. What is the order of reaction? What is the value of rate constant at 100°C?

Let the reactant be A, Rate = $k[A]^n$ when n is the order or reaction

$$Ms^{-1} = M^{-1}s^{-1}[A]^n \Rightarrow [A]^n = \frac{Ms^{-1}}{M^{-1}s^{-1}} = M^2 \Rightarrow [A]^n = M^2 \Rightarrow M^n = M^2 \Rightarrow n = 2$$

$$Ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{20000}{8.314}\left(\frac{1}{373} - \frac{1}{298}\right) = -1.623140607$$

$$\frac{k_1}{k_2} = e^{-1.623140607} = 0.1972781519 \Rightarrow k_2 = \frac{k_1}{0.1972781519} = \frac{1.77 \times 10^{-6}}{0.1972781519} = 8.972 \times 10^{-6} M^{-1}s^{-1}$$

Consider the decay of free neutron, i.e $^{1}_{0}n \rightarrow {}^{0}_{-1}e + {}^{1}_{1}H$, with half life of 10.3min, how long will it take for 1% of 1mol of free neutrons to decay. Note that all radioactivity reaction is first order reaction.

$$t_{1/2} = \frac{Ln\,2}{k} \Rightarrow k = \frac{Ln\,2}{t_{1/2}} = \frac{Ln\,2}{10.3} = 0.0673\,min^{-1}$$

$$Ln\frac{[A]_t}{[A]_0} = -kt \Rightarrow t = -\frac{1}{k}Ln\frac{[A]_t}{[A]_0} = -\frac{1}{0.0673}Ln\frac{0.99}{1} = 0.15min$$

Many organic reaction double their rate for an increase of only 10°C. Determine the approximate value of the activation energy that will lead to doubling of organic reaction rate when heat from 25°C to 35°C

$$R_1 = k_1[A]^n \qquad R_2 = 2R_1 = k_2[A]^n$$

$$\frac{2R_1}{R_1} = \frac{k_2[A]^n}{k_1[A]^n} \Rightarrow \frac{k_2}{k_1} = 2 \Rightarrow k_2 = 2k_1$$

$$Ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \Rightarrow E_a = Ln\frac{k_1}{2k_1} \times R \Big/ \left(\frac{1}{308} - \frac{1}{298}\right) = Ln\,0.5 \times 8.314 / -1.0895 \times 10^{-4} = 52.9kJ$$

THERMODYNAMICS

Thermodynamics is the science of heat and temperature in particular or the laws governing conversion of thermal energy into mechanical energy, electrical energy or other forms of energy. It is concerned with; how macroscopic world behave, how energy is transferred, how and under which condition equilibrium is achieve, also how and into which direction processes develop. For example a sealed fluid filled container on a burner to determine change of state or a solution in a container checking the change of state as pressure changes

RELEVANCE TERMS

System: All ~~specific~~ scientific study is carry out in a particular object, that is, the subject of the study. It is part of universe that can conveniently study with the method at hand e.g [illegible] as simple as container filled with water placed on heating plate. Systems can be grouped based on the boundary. Typically, 3 types of systems are considered;

Closed system: This allows exchange of energy between system and surrounding but disallow exchange of matter.

Open system: This allows exchange of energy as well as matter e.g between two compartment separated by semi-permeable membrane.

Isolated system: This can neither exchange matter or energy with its environment or surroundings. It, thus, can't ellicit any change in the surrounding nor can it be changed by its environment.

Surrounding: This is any part of the universe outside the system

Boundary: This seperate a system from its surroundings

Work: Thermodynamically, it is the transfer of energy from one mechanical system ~~and~~ to another. It encompasses ~~involving~~ a broad ~~way~~ range of processes including surface work, electrical work, work of magnetization, etc.

Heat: This is the transfer of energy between two bodies at different temperatures

Energy: This describes the capacity to do work and thus bring about change. It is measured in Joule.

THERMODYNAMIC VARIABLE

State variable are parameter that describe particular properties or co-ordinate of a system. They can be subdivided into two groups;

Extensive variables: These depends on amount of substance present in the system. The value of extensive ~~sys~~ variable can be calculated as sum of partial values when system is sub-divided into parts e.g volume mass

Intensive variables: These do not depend on amount of substance present in the system. The value of intensive parameter can be measured at any point within a system.

STATE OF A SYSTEM

The state of a perfect gas can be defined by ~~separation~~ specifying ~~parameter~~ pressure P, temperature T and Volume V. For a fixed mass of gas, $PV = nRT$ such that $P = f(V, T)$, $V = f(P, T)$ and $T = f(P, V)$, so if two variables are known, others can be determined. Such equation that relate P, V and T is called **equation of state**. Parameters such as P, T, V and U that defined the state of a substance are called ~~state~~ **state functions**. Important state ~~functions~~ variables in thermodynamics are; Temperature T, Pressure P, Volume V, Mass m, Internal energy U, Entropy S, Enthalpy H and Density ρ.

THERMOCHEMISTRY

This is the branch of thermodynamics that deals with heat change that occur during a chemical reaction in substance of a fixed composition. The main objective is the determination of quantity of energy emitted or absorbed as heat in various process and the deduction of the energy stored in chemical bond. At constant volume, the amount of heat q_v equals change in internal energy ΔU and at constant presure, the amount of heat q_p equals change in enthalpy ΔH, i.e

$$q_v = \Delta U \quad \text{at constant } V \qquad \text{and} \qquad q_p = \Delta H \quad \text{at constant } P.$$

The thermochemical quantity q therefore provides a means of evaluating thermodynamic paramete ΔH and ΔU. And this is the central line between thermodynamics and thermochemistry

STANDARD STATE

The standard state or a substance is the most stable form of it at 1atm and a specified temperature usually 25°C, e.g among the allotropes of sulphur, rhombic sulphur is the most stable at 25°C. The Standard enthalpy ΔH° of reactant is defined as the quantity of heat change that accompany formation of one mole of a substance from its elements in their standard state and the product at standard state. It can be measured from variety of processes, the process is specified by a subscript after the delta, i.e $\Delta_R H^\circ$, for enthalpy change that occur in a reaction. Reaction can be exothermic or endothermic based on the value of the standard enthalpy change for the reaction, i.e

$$\Delta_R H < 0 \quad \text{exothermic} \qquad \Delta_R H > 0 \quad \text{endothermic}$$

$$\Delta_R H = 0 \quad \text{thermoneutral}$$

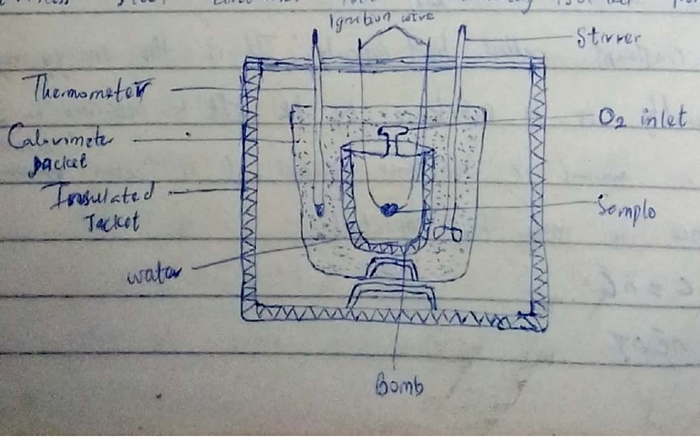
An increase in temperature favours product formation for endothermic reaction but disfavour the formation of product in exothermic

CALORIMETRIC MEASUREMENT & CALCULATION

The standard method for determining enthalpy change is Calorimetry method, i.e measurement of temperature rise after a known amount of material have reacted, the temperature rise is related to heat evolved, q, in ~~process~~ the process and heat capacity by the fundamental equation in calorimetry, i.e,

$$q = \int C\,dT = C\Delta T$$

A calorimeter must correspond as close as possible to a closed system (neither heat or matter must be exchanged. One most common calorimeter is constant-volume, adiabatic bomb calorimeter. This device enable to measure heat of ~~reaction~~ combustion of substance. It is a tightly sealed heavy walled, stainless steel container that is thermally isolated from its surrounding



The substance under investigation is placed inside the container which is filled with Oxygen at about 30atm. The combustion is started by an electrical discharge through a pair of wire that are in contact with the substance. The heat released by the reaction can be measured by ~~montoryn~~ monitoring the temperature rise of water filling inner jacket of calorimeter. The Change in Temperature, ΔT, of the calorimeter is proportional to energy that the reaction release or absorbed as heat. Using the heat capacity of calorimeter we can calculate the Change in energy as a result of combustion, i.e

$$\Delta U = q_v + W$$

$$\Delta U = q_v - P\Delta V \qquad W = -P\Delta V$$

$$\Delta V = 0 \quad \text{at constant volume}$$

$$\Delta U = q_v$$

ILLUSTRATION EXERCISE: A bomb calorimeter is built with heat capacity 1.58kJ/K. Calculate the molar internal energy change, if the combustion of 120mg of Naphthalene ($C_{10}H_8$) lead to a temperature rise of 3.06K. ($M_{C_{10}H_8}$) = 128.17g/mol). ~~Calculate the~~

$$\Delta U = q_v$$

The heat of combustion at constant volume, q_v is equal and opposite to energy transferred to calorimeter.

$$-q_v = q = C\Delta T = 1.58 \times 3.06 = 4.835\,kJ$$

$$q_v = -4.835\,kJ$$

$$\Delta U = \frac{q_v}{n} = \frac{-4.835}{\left(\frac{0.12}{128.17}\right)} = \frac{-4.835}{9.368 \times 10^{-4}} = -5164\,kJ/mol$$

The negative sign indicate the reaction is exothermic

HEAT CAPACITY

When heat is added to a substance, its temperature rises; how much temperature rise depends on; amount of heat delivered, amount of substance present, condition under which energy is added to the substance. The temperature rise is related to heat added by;

$$q = C\Delta T \Longrightarrow C = q/\Delta T$$

Where C is the proportionality constant called heat capacity. It is the energy required to raise the temperature of a given quantity of a substance by 1K. It is measure in J/K. Because the increase in temperature depends on amount of substance present, it is often considered the heat capacity, of one mole of a substance, i.e molar heat capacity.

$$\bar{C} = \frac{C}{n} \Longrightarrow C = n\bar{C}$$

$$q = C\Delta T = n\bar{C}\Delta T$$

Where n is the number of mole of substance present in a particular measurement. Note that heat capacity is a extensive property but molar heat capacity is an intensive ~~propey~~ property like all other molar quantity.

Heat capacity is a direct measurable quantity knowing amount of substance present, heat added and temperature rise. the value of molar heat capacity also using ~~using~~ the above equation. The calculated value depends on how the heating processes is carried out, heat absorbed equal internal energy, hence, for a constant volume, we have

$$C_v = \frac{q_v}{\Delta T} = \frac{\Delta U}{\Delta T} = \left(\frac{\partial U}{\partial T}\right)_v$$

$$dU = C_v dt$$

Similarly, for a constant pressure process $q_v = \Delta H$ where ΔH is enthalpy change, the heat capacity at constant pressure is,

$$C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T} = \left(\frac{\partial H}{\partial T}\right)_p$$

$$dH = C_p dT$$

From definition of C_v and C_p, we can calculate change in internal energy and change in enthalpy for processes carry out under constant volume or constant pressure condition, by integrating between T_1 and T_2

$$\Delta U = \int_{T_1}^{T_2} C_v\, dT = C_v(T_2 - T_1) = C_v \Delta T = n\bar{C}_v \Delta T$$

$$\Delta H = \int_{T_1}^{T_2} C_p\, dT = C_p(T_2 - T_1) = C_p \Delta T = n\bar{C}_p \Delta T$$

where n is number of moles of the substance present. ~~In~~ arriving at the relation above, we assumed that both C_v and C_p are independent of temperature which is not true.

The specific heat capacity of a substance is the energy required to raise the temperature of 1g of the substance by 1°C. It unit is $Jg^{-1}K^{-1}$. Heat capacity is given by product of specific heat capacity and mass of substance. There is a simple relation between the two heat capacities of an ideal gas, i.e

$$C_p - C_v = nR$$

The molar heat capacity of a perfect gas is about $8 JK^{-1}mol^{-1}$ larger at constant pressure than at constant volume, i.e;

$$\bar{C}_p - \bar{C}_v = R$$

ILLUSTRATION EXERCISES: Calculate internal energy change and enthalpy change for the heating of 55.40g of Xenon from 300K to 400K. The molar heat capacity of Xenon at constant volume and constant pressure are $12.47 JK^{-1}mol^{-1}$ and $20.79 JK^{-1}mol^{-1}$ respectively. Assuming that C_v and C_p are independent of temperature. $(M.M_{Xe} = 131.29 g/mol)$

$$n = \frac{m}{M} = \frac{55.40}{131.29} = 0.422\,mol \qquad \Delta T = 100$$

$$\Delta U = n\bar{C}_v \Delta T = 0.422 \times 12.47 \times 100 = 526J$$

$$\Delta H = n\bar{C}_p \Delta T = 0.422 \times 20.79 \times 100 = 877J$$

A 6.22kg piece of copper metal is heated from 20.5°C to 324.3°C, Given Specific heat of Copper is 0.385 $Jg^{-1}°C^{-1}$ calculate heat absorbed ~~by~~ in KJ by the metal

$$q = mC\Delta T = 6.22\times10^{3} \times 0.385 \times 303.2 = 727.5KJ$$

It takes 330J of energy to raise temperature of 24.6g of benzene from 21.0°c to 28.7°c at constant pressure, what is the molar heat capacity of benzene at constant pressure

$$q_p = \Delta H = n\bar{C}_p\Delta T$$

$$\bar{C}_p = \frac{\Delta H}{n\Delta T} = \frac{330}{\left(\frac{24.6}{78}\right)K\,7.7} = \frac{330}{2.43} = 135.9 J mol^{-1} °c^{-1}$$

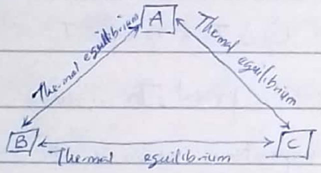
A 0.5122g sample of Naphthalene was burn in a constant volume bomb calorimeter consequently the temperature of water in inner jacket rose from 20.17°c to 24.09°C, if the effective heat capacity of the bomb calorimeter and water is 5267.8 JK^{-1}. calculate the internal energy for Combustion of naphthalene in KJ/mole

$$C_{10}H_8 + 12O_2 \rightarrow 10CO_2 + 4H_2O$$

$$\Delta U = \bar{C}\Delta T = \frac{C}{n}\Delta T = \frac{MC\Delta T}{m} = \frac{128.\,\times 5267.8 \times 3.91}{0.5122} = 5156KJ/mol$$

ZEROTH LAW OF THERMODYNAMIC

If two system are seperately in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.



The implication of this law is that one can determine if two system are in thermal equilibrium, by ~~bringing~~ introducing a third body, without bringing the two systems into contact. The third body can be thermometer, to compare temperature of other two system ~~of~~ if they have same temperature, then they will be in thermal equilibrium if they are place in contact. The Zeroth law give an operational definition of temperature

EXERCISE: Calculate the heat capacity at constant volume for Argon at room temperature (1mole) heat capacity ~~at~~ constant pressure ~~at~~ 20.8 $Jk^{-1}mol^{-1}$ and R is 8.3 $Jk^{-1}mol^{-1}$.

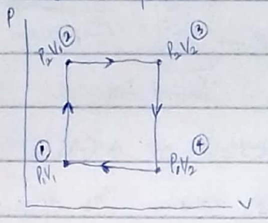
$$\bar{C}_p - \bar{C}_v = R \Rightarrow \bar{C}_v = \bar{C}_p - R = 20.8 - 8.3 = 12.5 Jk^{-1}mol^{-1}$$

$$C_v = n\bar{C}_v = 1 \times 12.5 = 12.5 Jk^{-1}$$

THERMODYNAMIC PROCESSES

The state of a thermodynamic system is changed as a result of interaction between the system and surrounding which can be mass or energy interaction. The mode in which the change of state of the system occur determine the kind of processes that take place in the system e.g the change may be at constant temperature, constant volume, etc. In order to ascertain that a thermodynamic process has taken place, the state must be defined before and after the process. The state is defined when certain values are specified for the minimum number of intensive variable e.g temperature, pressure, etc. For example, consider a system of a gas in a cylinder and being heated, the heating of the gas shall result in change in thermodynamic state of the system because, the pressure, temperature and volume of the system has increased. ~~The~~

Thermodynamic process may involve series of state changes called paths. Thermodynamic path refer to the loci of various intermediate state pass through by a system during a thermodynamic process. Sequence of thermodynamic processes may result in a thermodynamic cycle such that initial and final state of the system are identical. Series of thermodynamic processes through interconnected paths in closed loop will form a thermodynamic cycle.



1 → 2 → 3 → 4 → 1 ⇒ Thermodynamic cycle

1 → 2, 2 → 3, 3 → 4, 4 → 1 ⇒ Path

1 → 2, 3 → 4 Constant volume

2 → 3, 4 → 1 Constant pressure

A set of P-V processes showing Paths & Cycle

For a cyclic process, overall change in the state of system is zero, i.e

$$\oint dz = 0$$ where z is any thermodynamic property of the system

$$\int_1^2 dz + \int_2^3 dz + \int_3^4 dz + \int_4^1 dz = 0$$

Even though the integral for each thermodynamic path may not be zero, yet their sum equal zero. A thermodynamic process can be either chemical (involving reactions and chemical changes) or physical (involving change in physical parameters). A thermodynamic process may involve one or more of the following processes

A constant temperature, T, process ($dT = 0$) called Isothermal process

A constant volume, V, process ($dV = 0$) called Isochoric process or Isometric process

A constant pressure, P, process ($dP = 0$) called Isobaric or Isopiestic process

An adiabatic process in which case there is no net heat flow between system and surrounding

Reversible process in which case there is infinitesimal change in state variables (almost unnoticeable)

Irreversible process in which there is a large change in state variables

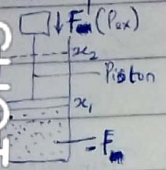
FIRST LAW OF THERMODYNAMICS

This has to do with energy in various forms e.g work, heat and internal energy. Heat is a form of energy that flow from one body to another as a result of temperature difference or gradient.

Work is done when a body is moved through a definite distance against certain force field by an apply force. Consider a gas expanding a piston, if the piston moves from position x_1 to x_2 against an opposing force F, the work done by the gas by expansion is given by:

$$W = \int_{x_1}^{x_2} -F\,dx = -\int_{x_1}^{x_2} F\,dx$$

From equation above, we have adopted that work done by a system is negative. If the opposing pressure or external pressure against which the gas is expanding is defined as force external per unit area of the cylinder, so that we have;

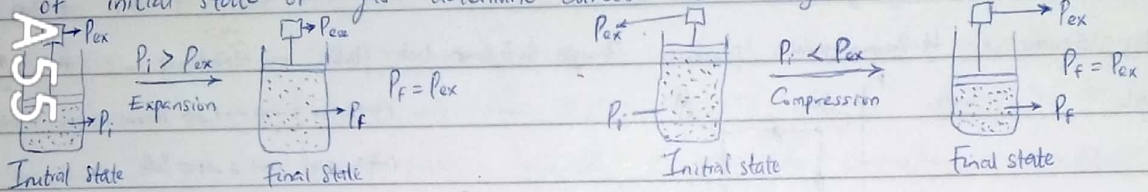


$$P_{ex} = \frac{F}{A} \qquad F = P_{ex} A$$

$$W = -\int_{x_1}^{x_2} F\,dx = -\int_{x_1}^{x_2} P_{ex} A\,dx \qquad \text{Since } dV = A\,dx$$

$$W = -\int_{V_1}^{V_2} P_{ex} dV$$

It is important to know that the relative magnitude of the external pressure compare to the pressure of initial state of gas determine direction of change.



P-V EXPANSION & COMPRESSION OF A GAS

At equilibrium, when no further change in gas volume is apparent, pressure of the system equal pressure external, so from equation above;

$$W = -\int_{V_i}^{V_f} P_{ex}\,dv = -P_{ex}\int_{V_1}^{V_2} dV = -P_{ex}(V_2 - V_1)$$

$$W = -P_{ex}\Delta V = -P_f \Delta V$$

Work is negative when $V_f > V_i$ (expansion) and work is positive whe $V_f < V_i$ (compression)

Internal energy is total sum of energy within the system. More appropriately, it is the sum of energy associated with molecule that constitute the system, thus may be translational, vibrational or rotational energy. It is denoted by U and it is a state function, i.e a quantity that change value as system change from one state to another. Work and heat are not state function because a state function is a property that depends only upon the state of the system and not upon how the system was brought to that state. As a state function, the total sum of infinitesimal change in U can be expressed as;

$$\int_1^2 dU = U_2 - U_1 = \Delta U$$

The internal energy of a system will change when a process is carried out on the system such that its state is change from a state (P_1, V_1, T_1, U_1) to another state (P_2, V_2, T_2, U_2), if such change is brought about by supplying heat energy, q, to the system such that the system does some work w, change in internal energy, ΔU, is sum of heat energy and work, i.e

$$\Delta U = q + w$$

Where q is the heat supplied to the system and w is the workdone by the system. This equation is the mathematical form of the First Law of Thermodynamics, which state that energy can neither be created nor destroyed but can be transformed from one form to another, i.e the total energy of a system is conserved. For the purpose of equation above, the convention that workdone on the system by surrounding or heat supplied to the system by surrounding is positive, that increase the internal energy of the system and workdone by system on surrounding or heat ejected by system to surrounding is negative, that decrease internal energy, shall be adopted.

INTERNAL ENERGY, HEAT CAPACITY & ENTHALPY

The internal energy, U, can be defined as function of volume and temperature $U = U(V,T)$ such that an infinitesimal change in internal energy, dU, can be expressed for an infinitesimal change in volume and temperature, i.e;

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

If the infinitesimal change is achieved by adding heat energy $đq$ and only P-V work is possible, then the first law of thermodynamics apply, i.e

$$dU = đq - P_{ex}\, dV$$

Suppose heat is added at constant volume, the equations above becomes,

$$dV = 0 \qquad dU = \left(\frac{\partial U}{\partial T}\right)_V dt = đq$$

The ~~form~~ $\left(\frac{\partial U}{\partial T}\right)_V$ is called heat capacity at constant volume; denoted by C_V. It is the amount of heat required to raise temperature of a system by 1K.

$$\int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} C_V\, dT$$

Assuming C_V is constant and independent of temperature

$$\int_{U_1}^{U_2} dU = C_V \int_{T_1}^{T_2} dT = \oint đq = q_V$$

$$\Delta U = C_V \Delta T = C_V (T_2 - T_1)$$

The equation above suggest for isothermal ~~or~~ isochoric process, $\Delta U = 0$.

Note: $C_V = \frac{3}{2}R$ for one mole of monoatomic ideal gas and $C_V = 3R$ for one mole of non-linear polyatomic gas.

ILLUSTRATION EXERCISES: Calculate change in internal energy when 1kg Argon is heated through a temperature difference of 75K, assuming $\bar{C}_V$ of Argon is $\frac{3}{2}R$ and molecular mass is 39.931g/mol.

$$\Delta U = C_V \Delta T = n\bar{C}_V \Delta T = \frac{1000}{39.931} \times \frac{3}{2} \times \frac{8.314}{1} \times \frac{75}{1}$$

$$\Delta U = 23.4\,kJ$$

Calculate work done by an ideal gas when it volume increase by factor of 10 in a reversible isothermal process that occur at 25°C

$$w = -nRT \ln\frac{V_f}{V_i} \quad \text{where } V_f = 10V_i$$

$$w = -1 \times 8.314 \times 298\,K \ln\frac{10V_i}{V_i}$$

$$w = -5.7\,kJ/mol$$

Calculate work required to compress 1 kg Methane reversibly isothermal from 1 to 10 atm at 400K

$$P_fV_f = P_iV_i \Rightarrow \frac{P_f}{P_i} = \frac{V_i}{V_f} \Rightarrow \frac{V_f}{V_i} = \frac{P_i}{P_f} = \frac{P_i}{10P_i} = \frac{1}{10}$$

$$w = -nRT\,Ln\frac{V_f}{V_i} = -\frac{1000}{16} \times 8.314 \times 400 \times Ln\,0.1$$

$$w = 478.6KJ$$

ISOTHERMAL PROCESS

Irreversible isothermal process: This process is irreversible and $dT = 0$, which implies $\Delta U = 0$

$$q = -w$$

Since the process is irreversible workdone is a PV work againt external pressure, i.e

$$w = -P_{ex}.\Delta V$$

For an ideal gas; $w = -P_{ex}(nRT)\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$

Reversible isothermal process: In this case, workdone is defined as the integral sum of all the infinitesimal pressure-volume work

$$w = -P_{ext}\int_{V_1}^{V_2} dv$$

The change in the system is very microscopic, it is nearly unnoticeable (i.e work is done infinitesimally). Since pressure of the gas will be infinitesimally greater than the external pressure, we have;

$$P = P_{ext} + dP$$

as $dP \to 0$ $\quad P \simeq P_{ext}$

For an ideal gas; $PV = nRT \Rightarrow P = \frac{nRT}{V}$

$$w = -P_{ext}\int_{V_1}^{V_2} dV$$

$$w = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$$

$w = -nRT\,Ln\,V_2/V_1$ This is the workdone in a isothermal expansion of ideal gas

Recall Boyle's law $\quad \frac{V_2}{V_1} = \frac{P_1}{P_2}$

$$w = -nRT\,Ln\,P_1/P_2$$

ISOCHORIC PROCESS

For an isochoric process, $dV = 0$, hence;

$$w = 0$$

$$\Delta U = q$$

ADIABATIC PROCESS

For this process, no heat energy transfer between system and surrounding, i.e

$q = 0$ and $\Delta U = w$

$$\Delta U = -P_{ext}\,dV$$

For an adiabatic expansion that begin on a state (P_1, V_1, T_1) and goes to a state (

T_2) for which only V_2 a perphap P_2 is known, the problem is to find T_2.

Suppose expansion is reversible and the gas is an ideal gas

$$P_{ext} = P(V,T)$$

$$n\bar{C}_v dT = -nRT\frac{dV}{V}$$

$$\bar{C}_v \frac{dT}{T} = -R\frac{dV}{V}$$

Note $\frac{P_2}{P_2} = \left(\frac{V_1}{V_2}\right)^{\alpha}$

$$Ln\frac{T_2}{T_1} = \frac{-R}{\bar{C}_v} Ln\frac{V_2}{V_1}$$

$$Ln\frac{T_2}{T_1} = Ln\left(\frac{V_2}{V_1}\right)^{-R/\bar{C}_v}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{-\left(\frac{R}{\bar{C}_v}\right)} = \left(\frac{V_2}{V_1}\right)^{-\left(\frac{\bar{C}_p-\bar{C}_v}{\bar{C}_v}\right)}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{-\left(\frac{\bar{C}_p}{\bar{C}_v}-1\right)} = \left(\frac{V_2}{V_1}\right)^{-(\alpha-1)} \quad \text{where } \alpha = \bar{C}_p/\bar{C}_v$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{(1-\alpha)} \text{ or } \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\alpha-1}$$

This is conveniently apply for system with a define state (V,T). However, if the system is defined by (P,V), (P,T), the enthalpy function will give a better expression, that is;

$$H = U + PV \Rightarrow dH = dU + d(PV)$$

$$dH = dU + PdV + Vdp$$

$$dH = đq + đw + PdV + Vdp$$

$$dH = đq - pdV + PdV + Vdp \qquad đq = 0 \quad \text{for adiabatic process}$$

$$dH = Vdp$$

If the system contains an ideal gas, in which $dH = n\bar{C}_p dT$ and $V = \frac{nRT}{P}$

$$n\bar{C}_p dT = \frac{nRT}{P}dp$$

$$\bar{C}_p dT = RT\frac{dp}{P}$$

$$\bar{C}_p \frac{dT}{T} = R\frac{dp}{P}$$

Integrating both sides ($\bar{C}_p$ being constant and independent on temperature)

$$\bar{C}_p Ln\frac{T_2}{T_1} = R Ln\frac{P_2}{P_1}$$

$$Ln\frac{T_2}{T_1} = \frac{R}{\bar{C}_p} Ln P_2/P_1$$

Since, $Ln\frac{T_2}{T_1} = \frac{R}{\bar{C}_p} Ln P_2/P_1 = -\frac{R}{\bar{C}_v} Ln\frac{V_2}{V_1}$

$$\frac{1}{\bar{C}_p} Ln P_2/P_1 = -\frac{1}{\bar{C}_v} Ln V_2/V_1$$

$$Ln P_2/P_1 = -\frac{\bar{C}_p}{\bar{C}_v} Ln V_2/V_1 \qquad \text{if } \frac{\bar{C}_p}{\bar{C}_v} = \alpha$$

$$Ln P_2/P_1 = -\alpha Ln V_2/V_1$$

$$Ln P_2/P_1 = Ln\left(\frac{V_2}{V_1}\right)^{-\alpha}$$

$$Ln P_2/P_1 = Ln\left(\frac{V_1}{V_2}\right)^{\alpha}$$

$$P_2/P_1 = \left(\frac{V_1}{V_2}\right)^{\alpha} \Longrightarrow P_1V_1^{\alpha} = P_2V_2^{\alpha}$$

$$T_1V_1^{\alpha-1} = T_2V_2^{\alpha-1}$$

SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics is only sufficient to know how much of heat change ~~accompany~~ accompanying a process ~~in~~ or ~~from~~ how much energy accompanies a process in form of heat energy and work. It provides quantitative reason of energy flow in a ~~in~~ system when it undergoes some process along a known path, however, the first law of thermodynamics do not provide information about spontaneity or non-spontaneity of the process, i.e no information about direction of change that occur effortlessly. However, many processes occur without extra driving forces e.g heat flows along a metal from region of high temperature to region of low temperature, water fall freely from hill tops, gas flows from region of high pressure to low pressure, all these processes are natural processes that occur without external forces and are said to be spontaneous. ~~Moreover~~ And the reverse form of these processes do not occur spontaneously in which first law of thermodynamics do not provide us with that information.

This implies that first law of thermodynamics can't be used to predict whether a chemical reaction will occur under a given set of conditions, it is therefore important to set a criterion for predicting spontaneity of a reaction or process, i.e a need for another thermodynamic function. The new thermodynamic function is entropy, which can't be defined in absolute term but it is convenient to define change in entropy. Entropy is a thermodynamic function denoted by S and the change in entropy by ΔS. Therefore, a statement of the second law is that entropy of a system will always increase in spontaneous process i.e ΔS is always positive. Thus,

$\Delta S > 0$ for spontaneous process $\Delta S < 0$ for non-spontaneous process

When a quantity of heat, q_{rev}, is absorbed ~~for~~ in a reversible process at temperature, T, change in entropy is defined as:

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

For series of such changes at constant temperature, the overall entropy change is given as;

$$\int_{S_1}^{S_2} ds = \int \frac{dq_{rev}}{T}$$

$$\Delta S = \frac{q_{rev}}{T}$$

When a system gains an amount of heat, q_{rev}, the surrounding loss same amount of heat $-q_{rev}$, hence, change in entropy of the surrounding is;

$$\Delta S_{surr} = \frac{-q_{rev}}{T}$$

The total change in entropy of the system and surrounding is given by

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = \frac{q_{rev}}{T} + \frac{-q_{rev}}{T} = 0$$ (This is typical of a cyclic process)

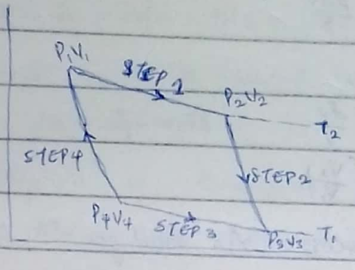
ENGINES

~~[illegible]~~

All engi[illegible]ork on a [illegible] that is, a fluid which is the working substance is heated and expand against the piston which does work. The fluid is discharge and the piston return to its position for another cycle. A typical example of engine that work based on this Principle is carnot engine and this principle of such engine is carnot cycle.

CARNOT CYCLE

A carnot cycle is an idealization of cyclic process. Assuming working substance is one mole of a idea gas, the diagram below depict a carnot cycle involving four steps;



Isothermal reversible expansion: This occurs as a result of amount of heat, q_2, at isothermal temperature, T_2 and the workdone is given as

$$w = -RT\,Ln\left(\frac{V_2}{V_1}\right)$$

$$q_2 = RT_2 Ln\left(\frac{V_2}{V_1}\right) \qquad \text{since} \quad \Delta U = 0$$

Adiabatic reversible expansion: This occurs from V_2 to V_3 and in this case, we have;

$$q = 0 \qquad w = \Delta U$$

$$\Delta U = \int_{T_1}^{T_2} C_v\,dT$$

Isothermal reversible compression: This occurs as a result of heat q_1 at temperature T_1 and the workdone is given as;

$$w = -RT\,Ln\left(\frac{V_4}{V_3}\right)$$

$$q_1 = RT_1 Ln\left(\frac{V_4}{V_3}\right)$$

Adiabatic reversible compression: This occurs from V_4 to V_1 and in this case, we have;

$$q = 0 \qquad w = \Delta U$$

$$\Delta U = \int_{T_2}^{T_1} C_v\,dT = -\int_{T_1}^{T_2} C_v\,dT$$

For the entire cycle, the following ~~given~~ are the total heat, work and change in internal energy:

$$q_T = q_1 + q_2 = RT_1 Ln\frac{V_4}{V_3} + RT_2 Ln\frac{V_2}{V_1}$$

$$w_T = -RT_2 Ln\frac{V_2}{V_1} - RT_1 Ln\frac{V_4}{V_3}$$

$$\Delta U_T = 0$$

The efficiency of the engine, E is given by: $E = \frac{-w}{q_2} = \frac{T_2 - T_1}{T_2}$?

For the carnot cycle, $\Delta S_T = \frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$

Therefore, for a carnot cycle, $\Delta S_T = 0$, $\Delta U_T = 0$

CALCULATIONS ON ENTROPY

For a constant volume process in which $\Delta U = q_v$

$$\Delta S = \int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{q_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_v dT}{T}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

For a constant pressure process in ~~which~~ which $\Delta H = q_p$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

For an isothermal expansion of a ideal gas in which $\Delta U = 0$ & $q = w$

$$ds = \frac{dq}{T} = \frac{PdV}{T}$$

$\frac{P}{T} = \frac{nR}{V}$

$$ds = \frac{nRdV}{V}$$

$$\int_{S_1}^{S_2} ds = \int_{V_1}^{V_2} nR \frac{dV}{V}$$

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

ILLUSTRATION EXERCISE ON ~~AN~~ ISOTHERMAL PROCESS: An ideal gas is compressed in a one litre cylinder with a movable piston under a pressure of 10^6 pa which comprises 9 blocks of equal weight, each exerting 10^5 pa and also 10^5 pa atmospheric pressure. Calculate expansion work in Joules when three blocks are removed at ~~once~~ once and calculate workdone when the three blocks are removed one after the other. What amount of heat energy flow between the system and surrounding, if expansion work, when the three block are removed at once, occur isothermally and what is the direction of flow of heat.

$W_{at\ once}$ is an irreversible workdone

$$W_{at\ once} = -nRT\left(\frac{1}{P_2} - \frac{1}{P_1}\right)P_{ext} \quad \text{where } P_{ext} = P_f$$

$$= -7\times10^5 \times 8.314 \times \left(\frac{1}{7\times10^5} - \frac{1}{10^6}\right)$$

$$= -2.494\ J mol^{-1} K^{-1}$$

$W_{not\ at\ once}$ is an reversible workdone

$$W_{not\ at\ once} = -nRT \ln \frac{P_1}{P_2}$$

$$= -8.314 \ln \frac{10^6}{7\times10^5}$$

$$= -2.965\ J mol^{-1} k^{-1}$$

$q_{flow} = -w$ ~~for~~ isothermal process where $\Delta U = 0$

$q_{flow} = -W_{at\ once} = -(-2.494) = 2.494\ J mol^{-1} K^{-1}$

Since q_{flow} is positive, the heat flow from surrounding into the system.

FREE ENERGY

The natural tendency of an object to fall from higher point to lowe level might be assumed to occur in order to minimise energy, however, this can not be the only condition for some behaviour of substance at molecular level eg the spontaneous mixing of ideal gas involves no energy change but increase in entropy. The tendency of energy to ~~cn~~ go to minimum and entropy to maximum for a system in which both can change will determine direction of spontaneity. Therefore, a new state function can be defined which combine both energy and entropy, which is called Helmholtz free energy denote by A. This new function is given by;

$$A = U - TS$$

For an infinitesimal change $dA = dU - d(TS)$

$$dA = dU - TdS - SdT \qquad dU = \text{đ}q - pdV$$

$$dA = \text{đ}q - pdV - TdS - SdT$$

If this change occurs at constant volume and temperature

$$dA = \text{đ}q - TdS$$

According to the second law of thermodynamics, the RHS of the equation above must be negative for a spontaneous change. Therefore, the criterion for a spontaneous change at constant volume and temperature is $dA \le 0$, ~~there~~ such that, $dS \ge \frac{\text{đ}q}{T}$.

Since most reaction occur at constant pressure then a corresponding free energy parameter that takes p as an independent variable ~~must~~ seem to be convenient, thus, a new thermodynamic variable which is called Gibbs free energy denoted by G, given by;

$$G = H - TS$$

For an infinitesimal change $dG = dH - TdS - SdT \qquad$ since $dH = dU + pdV + Vdp$

$$dG = dU + pdV + Vdp - TdS - SdT$$

~~If this change occurs at constant pressure and temperature~~

$$dG = \text{đ}q - \cancel{pdV} + \cancel{pdV} + Vdp - TdS - SdT$$

$$dG = \text{đ}q + Vdp - TdS - SdT$$

If this change occurs at constant pressure and temperature

$$dG = \text{đ}q - TdS$$

From the second law of thermodynamics, the RHS of the equation above must be less than zero for spontaneous process, that is $dG \le 0$. This implies that Gibbs free energy is a function that will decrease in any system at constant pressure and temperature and that this function is minimum at equilibrium where $dG = 0$. For a final change in a process at constant pressure and temperature leading to final change in entropy and Gibbs free energy,

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G < 0$ when a process proceed spontaneously in forward direction

$\Delta G = 0$ when process is at equilibrium

$\Delta G > 0$ when the process proceeds spontaneously in reverse direction.

multiply through by -1 $\quad -\Delta G = -\Delta H + T\Delta S$

This equation above explain the driving force for spontaneous process which is the decreasing tendency of ΔG, which depend on two factors $-\Delta H$ and $T\Delta S$. $-\Delta H$ is the tendency of a system to attain a minimum energy while $T\Delta S$ is tendency of a system to attain a maximum ~~minimum~~ disorder. At equilibrium, the two factors balances and $\Delta G = 0$. At normal temperature, ΔH is greater that $T\Delta S$, that is, most reactions are exothermic. Since $T\Delta S$ increases with temperature more quickly than ΔH, $T\Delta S$ becomes significantly high at high temperature and though ~~so~~ ΔH becomes ~~becomes~~ negative.

RELATIONSHIP BETWEEN ΔG AND EQUILIBRIUM CONSTANT

Consider a hypothetical reaction $\quad aA + bB \rightleftharpoons cC + dD$

$$\Delta G_{\text{Reaction}} = \Delta G_{\text{product}} - \Delta G_{\text{reactant}}$$

$$\Delta G = cG(C) + dG(D) - aG(A) - bG(B)$$

For a non-ideal system $\quad G = G^\circ + RT\ln a \quad$ where a is activity of the system and G° is free energy of ideal system

$$\Delta G = [cG^\circ(C) + cRT\ln a_c + dG^\circ(D) + dRT\ln a_d] - [aG^\circ(A) + aRT\ln a_a + bG^\circ(B) + bRT\ln a_b]$$

$$\Delta G = cG^\circ D + dG^\circ D - bG^\circ(B) - aG^\circ(A) + RT\ln a_c^c + RT\ln a_d^d - RT\ln a_a^a - RT\ln a_b^b$$

$$\Delta G = \Delta G^\circ + RT\ln\frac{a_c^c a_d^d}{a_a^a a_b^b} \qquad \text{where} \quad \frac{a_c^c a_d^d}{a_a^a a_b^b} = K$$

$$\therefore \Delta G = \Delta G^\circ + RT\ln K$$

at equilibrium, $\Delta G = 0$

$$\Delta G^\circ = -RT\ln K$$

CHEMICAL EQUILIBRIA

Under suitable condition, nitrogen react with hydrogen to give ammonia, conversely ammonia decomposes at high temperature to yield nitrogen and hydrogen. This kind of reaction that will go back and forth under suitable condition is said to be reversible and equation of reaction can be written as;

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

All reversible process tends to attain a state of equilibrium. For a reversible reaction, an equilibrium state is attained when the rate at which chemical reaction is proceeding to the forward direction equal to the rate at which the reverse reaction is proceeding and at equilibrium, the concentration of all substances are constant. In the concept of chemical equilibrium, rate of reaction are taken to be proportional to concentration and this is known as law of mass action (mostly for a single step reaction). Consider an hypothetical chemical reaction below;

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} M + N$$

$$\text{Rate}_f = k_f[A][B] \qquad \text{Rate}_b = k_b[M][N]$$

At equilibrium, $Rate_f = Rate_b \Longrightarrow K_f[A][B] = K_b[M][N]$

$$\frac{K_f}{K_b} = \frac{[M][N]}{[A][B]}$$

$$K = \frac{[M][N]}{[A][B]}$$

For a more general formulation for reversible chemical reaction, ~~as~~

$$aA + bB \rightleftharpoons mM + nN$$

$$K = \frac{[M]^m[N]^n}{[A]^a[B]^b}$$

The constant, K, is known, in this context, as mass action equilibrium constant expressed in term of concentration of the species. The problem with mass action approach is that reaction rate is not expressed based on simple mass action law of the overall reaction but rather depends on detailed reaction path or mechanism. Therefore, equilibrium constant, K, expressed in term of concentration is an approximation, the application of thermodynamics that deals with initial and final state, ~~Thermichdam~~ Chemical equilibrium seperate the subject from that of chemical kinectic. The exact definition of K based on ~~they~~ thermodynamics treatment uses the activity of the species, a_i, such that

$$K = \frac{a_M^m a_N^n}{a_A^a a_B^b} \quad \text{where} \quad a_i = \gamma_i x_i \text{ or } a_i = \gamma_i c_i$$

where γ_i is activity coefficient and x_i is the mole fraction and c_i is molality or molar concentration

$$K = \frac{(\gamma_M C_M)^m(\gamma_N C_N)^n}{(\gamma_A C_A)^a(\gamma_B C_B)^b} = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \cdot \frac{C_M^m C_N^n}{C_A^a C_B^b}$$

$$K = K_\gamma K_c$$

With assumption that K_γ is approximately one, i.e $K_\gamma = 1$, then

$$K \simeq 1 \times K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b}$$

GAS PHASE EQUILIBRIUM

For reaction involving gas, the equilibrium constant is better expressed in term of fugacity, f_i, given as;

$$f_i = \gamma_i P_i$$

$$K = \frac{(\gamma_M P_M)^m(\gamma_N P_N)^n}{(\gamma_A P_A)^a(\gamma_B P_B)^b} = \frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \cdot \frac{P_M^m P_N^n}{P_A^a P_B^b}$$

$$K = K_\gamma K_p \qquad \text{if } K_\gamma \simeq 1$$

$$K \simeq K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b}$$

Assuming gas behave ideal, we can relate K_c and K_p

$$PV = nRT \Longrightarrow \frac{n}{V} = \frac{P}{RT}$$

$$K_c = \frac{[M]^m[N]^n}{[A]^a[B]^b} = \frac{\left(\frac{P_M}{RT}\right)^m\left(\frac{P_N}{RT}\right)^n}{\left(\frac{P_A}{RT}\right)^a\left(\frac{P_B}{RT}\right)^b} = \frac{P_M^m P_N^n}{P_A^a P_B^b} \cdot \frac{\left(\frac{1}{RT}\right)^{m+n}}{\left(\frac{1}{RT}\right)^{a+b}}$$

$$= K_p(RT)^{-(m+n)+((a+b))} = K_p(RT)^{-[(m+n)-(a+b)]} = K_p(RT)^{-\Delta n}$$

where [illegible]

where Δn is the difference between the species at RHS and those at LHS

$$\therefore K_c = K_p(RT)^{-\Delta n}$$

Recall Dalton's law of partial pressure; $P = \sum_{i=1}^{n} P_i$ $\quad P_i = x_i P$ when x_i is mole fraction

Thus, $$K_p = \frac{(x_M P_M)^m (x_N P)^n}{(x_A P)^a (x_B P)^b} = \frac{x_M^m x_N^n}{x_A^a x_B^b} \cdot \frac{P^m P^n}{P^a P^b} = \frac{x_M^m x_N^n}{x_A^a x_B^b} \cdot \frac{P^{m+n}}{P^{a+b}}$$

$$K_p = K_{x_i} P^{\Delta n}$$

$$N = \sum_{i=1}^{n} n_i \qquad x_i = \frac{n_i}{N}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{\Delta n} \qquad K_n = \frac{n_M^m n_N^n}{n_A^a n_B^b}$$

EFFECT OF INERT GAS ON EQUILIBRIUM

Consider an equilibrium mixture of gases in a vessel, addition of an inert gas will increase 'N, i.e total number of molecules and ~~pressure~~ P, i.e, total pressure proportionately but P/N will remain same, likewise n_i which is number of molecules of reacting species will not change, i.e K_n will be same, such that

$$K_n = \frac{n_M^m n_N^n}{n_A^a n_B^b}$$

Therefore K_p will not be affect by adding inert gas. If however, the inert gas is added while keeping P constant, only N will increase (not P) ~~thus, and~~ K_n will increase if Δn is positive and decrease if Δn is negative. Physical expression of Kp for some reaction are given as follow:

$$2H_{2(g)} + O_2 \rightleftharpoons 2H_2O \text{ — ① } \qquad K_p = \frac{P_{H_2O}^2}{P_{H_2}^2 P_{O_2}}$$

$$H_{2(g)} + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \text{ — ② } \quad K_p' = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}}$$

The reaction 2 was achieved by dividing reaction 1 by 2, ~~thus~~.

$$K_p' = (K_p)^{1/2}$$

If a reaction equation is obtained by multiplying a reaction of known Kp by n Kp' of the new reaction is;

$$K_p' = (K_p)^n$$

If a reaction equation is obtained by addition of two or more equation of known Kp, Kp' for new equation is the product of Kp of the reactions whose equation are added, i.e;

$$K_p' = \prod_{i=1}^{n} K_{p_i}$$

For example:

$$2CO + \tfrac{1}{2}O_2 + H_2O \rightleftharpoons 2CO_2 + H_2 \qquad K = \frac{P_{CO_2}^2 P_{H_2}}{P_{O_2}^{2} P_{CO}^2 P_{H_2O}}$$

$$2CO + O_2 \rightleftharpoons 2CO_2 \quad K_1 = \frac{P_{CO_2}^2}{P_{CO}^2 P_{O_2}} \qquad H_2O \rightleftharpoons H_2 + \tfrac{1}{2}O_2 \quad K_2 = \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}}$$

$$\therefore K = K_1 K_2$$

ILLUSTRATION EXERCISE: Consider the reaction: $N_2O_4 \rightleftharpoons 2NO_2$, if 9.2g of NO_2 is introduced into 32L flask at 25°C, the equilibrium pressure is 0.1atm. Find Kp assuming ideal behaviour of the system.

$$N = \frac{PV}{RT} = \frac{0.1 \times 36}{0.082056 \times 298.15} = 0.147 \text{ mol}$$

$$n_{NO_2} = \frac{9.2}{46} = 0.2\,mol$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

	N_2O_4	$2NO_2$
Initially	–	0.2
During reaction	x	$2x$
At equilibrium		$0.2-2x$

$$n_{NO_2} + n_{N_2O_4} = 0.2$$

$$n_{NO_2} + n_{N_2O_4} = 0.147 \qquad n_{N_2O_4} = 0.053 \qquad n_{NO_2} = 0.094$$

$$K_p = \frac{0.094^2}{0.053}\left(\frac{0.1}{0.147}\right) = 0.113$$

If 0.0600 mol of SO_3 is placed in 1L container at 1000K, 36.7% of SO_3 is dissociated when equilibrium is established. What are the equilibrium concentalion of SO_3, SO_2 and O_2

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

	$2SO_3$	$2SO_2$	O_2
Initially	0.06	–	–
~~At~~ equilibrium	0.367×0.06	$0.367\times\cancel{0}.06$	$\frac{0.367}{2}\times0.06$

?

$$[SO_3] = 0.022M \qquad [SO_2] = 0.022M \qquad [O_2] = 0.011M$$

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{\cancel{0.022^2}\times0.011}{\cancel{0.022^2}} = 0.011$$

For the equilibrium reaction $H_2O + CO \rightleftharpoons H_2 + CO_2$ at 750°C, K_c is 1.30, If 0.600 mole of H_2O and 0.600 mole of CO are mixed in a 1L container at 750°C, What are the concentration of all the ~~four~~ species when equilibrium is estabished.

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

	H_2O	CO	H_2	CO_2
Initially	0.60	0.60	–	–
Reaction	x	x	x	x
At equilibrium	$0.6-x$	$0.60-x$	x	x

$$K_c = \frac{x^2}{(0.60-x)^2} = \left(\frac{x}{0.60-x}\right)^2$$

$$\frac{x}{0.60-x} = \sqrt{1.3} = 1.14$$

$$x = 0.684 - 1.14x$$

$$2.14x = 0.684 \Rightarrow x = \frac{0.684}{2.14} = 0.319$$

$$[H_2O] = 0.281M \qquad [CO] = 0.281M \qquad [H_2] = 0.319M \qquad [CO_2] = 0.319M$$

For the equilibrium reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 425°C, K_c is 54.8. If 1.00 mole of H_2, and 1.00 mole of I_2 and 1.00 mole of HI are placed in 1L container at 425°C. What are the concentration of all the three species when equilibrium is established

$$H_2 + I_2 \rightleftharpoons 2HI$$

	H_2	I_2	$2HI$
Initially	1	1	1
Reaction			$2x$
Equilibrium	$1-x$	$1-x$	$1+2x$

$$K_c = \frac{(1+2x)^2}{(1-x)^2} = \left(\frac{1+2x}{1-x}\right)^2$$

$$\frac{1+2x}{1-x} = \sqrt{54.8} = 7.403$$

$$1+2x = 7.403 - 7.403x \Longrightarrow 9.403x = 6.403$$

$$x = 0.681\,mol$$

$[I_2] = 0.319M$ $[H_2] = 0.319M$ $[HI] = 2.362M$

GENERAL SITUATIONS

For the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$, starting with n moles of N_2O_4, let degree of dissociation by α at equilibrium, hence;

	N_2O_4	$\rightleftharpoons 2NO_2$
Initially	n	–
Reaction	αn	$2\alpha n$
At equilibrium	$(1-\alpha)n$	$2\alpha n$

Total number of mole at equilibrium is; $n_T = n - \alpha n + 2\alpha n = n + \alpha n = n(1+\alpha)$

Mole fraction of N_2O_4 at equilibrium $= \frac{n(1-\alpha)}{n(1+\alpha)} = \left(\frac{1-\alpha}{1+\alpha}\right)$ Mole fraction of NO_2 at equilibrium $= \frac{2\alpha n}{n(1+\alpha)} = \frac{2\alpha}{1+\alpha}$

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}} \qquad P_{NO_2} = X_{NO_2}P \quad \text{and} \quad P_{N_2O_4} = X_{N_2O_4}P$$

$$K_p = \frac{(X_{NO_2}P)^2}{X_{N_2O_4}P} = \left(\frac{2\alpha}{1+\alpha}\right)^2 P^2 \div \frac{1-\alpha}{1+\alpha}P = \frac{4\alpha^2P^2}{(1+\alpha)^2} \times \frac{(1+\alpha)}{(1-\alpha)P}$$

$$K_p = \frac{4\alpha^2}{(1+\alpha)(1-\alpha)} = \frac{4\alpha^2}{1-\alpha^2}P$$

$$\therefore K_p = \left(\frac{4\alpha^2}{1-\alpha^2}\right)P \quad \text{and} \quad \cancel{\alpha}$$

$$K_p = \frac{4\alpha^2 P}{1-\alpha^2} \Longrightarrow K_p - \alpha^2 K_p = 4\alpha^2 P \Rightarrow K_p = \alpha^2(K_p + 4P)$$

$$\alpha = \left(\frac{K_p}{K_p + 4P}\right)^{1/2}$$

~~Also for the equilibrium reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$, based on this stoichiometry combination, at equilibrium, one~~ ~~fraction~~ ~~0.5x~~ ~~1.5x~~ ~~x~~ ~~n-0.5x~~ ~~n+1.5x~~ ~~x~~

Also, For the equilibrium reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$ based on this stoichiometry combination, at equilibrium; $P_{H_2} = 3P_{N_2}$ and if $P = P_{N_2} + P_{NH_3} + P_{H_2}$

$$P_{NH_3} = P - (P_{N_2} + P_{H_2}) = P - 4P_{N_2}$$

$$P_{N_2} = \frac{1}{4}(P - P_{NH_3}) \quad + \quad P_{H_2} = \frac{3}{4}(P - P_{NH_3})$$

$$K_p = \frac{P_{NH_3}}{P^{1/2}_{N_2}P^{3/2}_{H_2}} = \frac{P_{NH_3}}{\left[\frac{1}{4}(P-P_{NH_3})\right]^{1/2}\left[\frac{3}{4}(P-P_{NH_3})\right]^{3/2}} = \frac{P_{NH_3}}{\left(\frac{1}{4}\right)^{1/2}\left(\frac{1}{4}\right)^{3/2}3^{3/2}(P-P_{NH_3})^{1/2}(P-P_{NH_3})^{3/2}}$$

$$K_p = \frac{16P_{NH_3}}{3\sqrt{3}(P-P_{NH_3})^2} = \frac{16P_{NH_3}}{3\sqrt{3}\,P^2} \quad \text{since } P_{NH_3} << P$$

$$P_{NH_3} \simeq \frac{3\sqrt{3}K_pP^2}{16} \simeq 0.325K_pP^2$$

$$P_{NH_3} = 0.325K_pP^2$$

HETEROGENOUS EQUILIBRIA

For equilibrium involving more than one phase, the concentration of pure solid or liquid is constant, hence, it is embedded in K_c or K_p such that they do not appear explicit in expression for equilibrium constant. e.g decomposition of $CaCO_3$

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

$$K = \frac{P_{CO_2} P_{CaO}}{P_{CaCO_3}} \qquad \frac{P_{CaCO_3}}{P_{CaO}} = \text{Constant} = K^x$$

$$K \cdot K^x = P_{CO_2}$$

$$\therefore K_p = P_{CO_2}$$

TEMPERATURE DEPENDENCY ON EQUILIBRIUM CONSTANT

Equilibrium constant is only constant at a fixed temperature, a change in temperature will change the magnitude of equilibrium constant, such that we have,

$$\Delta G = \Delta G^\circ + RT \ln K_p \qquad \text{at equilibrium } \Delta G = 0$$

$$\therefore \Delta G^\circ = -RT \ln K_p$$

$$\ln K_p = \frac{-\Delta G^\circ}{RT} \qquad \frac{d \ln K_p}{dT} = \frac{-1}{R} \frac{d(\Delta G^\circ/T)}{\partial T}$$

But $$\frac{\partial(G/T)}{\partial T} = \frac{-1}{T^2} G + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p$$

$$G = H - TS \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\frac{\partial(G/T)}{\partial T} = \frac{-1}{T^2} G + \frac{1}{T}(-S) = \frac{-1}{T^2}(G + TS) = \frac{-1}{T^2} H$$

$$\frac{\partial(G/T)}{\partial T} = \frac{-H}{T^2}$$

$$\int \frac{d \ln K_p}{dT} = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2}$$

$$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \text{ — Van't Hoff equation}$$

IONIC EQUILIBRIUM

Consider a chemical species HA in aqueous solution that dissociate to H^+ and A^-, i.e

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

$$\begin{array}{llll} \text{Initially} & a & - & - \\ \text{equilibrium} & a-x & x & x \end{array}$$

$$K_a = \frac{x^2}{a-x} \qquad \text{for } x << a$$

$$K_a = \frac{x^2}{a} \Rightarrow x = \sqrt{aK_a} \qquad \text{since } x = [H^+]$$

$$[H^+] = \sqrt{aK_a} \text{ — For weak acid dissociation}$$

Similarly, $$RNH_{2(aq)} + H_2O_{(l)} \rightleftharpoons RNH^+_{3(aq)} + OH^-_{(aq)}$$

$$\begin{array}{llll} \text{Initially} & C_b & - & - \\ \text{equilibrium} & C_b - x & x & x \end{array}$$

$$K_b = \frac{x^2}{C_b - x} \qquad \text{if } x << C_b$$

$$K_b = \frac{x^2}{C_b} \Rightarrow x = \sqrt{C_b K_b} \qquad \text{since } x = [OH^-]$$

$$[OH^-] = \sqrt{C_b K_b} \text{ — For weak bases}$$

$$[H^+][OH^-] = 1 \times 10^{-14} \text{ at } 25^\circ C \text{, i.e, ionic product of water}$$

For a weak acid and its salt eg in buffers, i.e. $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$CH_3COONa \rightarrow CH_3COO^- + Na^+$ $\quad$ $CH_3COO^- + H_2O \xrightleftharpoons{K_h} CH_3COOH + OH^-$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

multiply both denominator and numerator by $[H^+]$

$$K_h = \frac{[CH_3COOH][OH^-][H^+]}{[CH_3COO^-][H^+]}$$

$$K_h = \frac{[CH_3COOH]K_w}{[CH_3COO^-][H^+]} \qquad K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_h = \frac{K_w}{K_a} \Longrightarrow K_a K_h = K_w$$

BUFFER SOLUTION

Buffer solution is one that resist change in its pH upon addition of small amount of an acid or base. It is made up of a weak acid and a salt of the weak acid. or a weak base and its salt e.g CH_3COOH/CH_3COONa and NaH_2PO_4/Na_2HPO_4

Sodium dissociate completely in solution, such that; $CH_3COONa \rightarrow CH_3COO^- + Na^+$

But acid dissociates partially, such that; $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$-\log H^+ = -\log K_a \cancel{+} \log\frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = pK_a + \log\frac{\text{Salt}}{\text{acid}}$$

ILLUSTRATION EXERCISE: Dissociation of 0.1M acetic acid solution is 1.33%. Calculate the acid dissociation constant, Ka.

	CH_3COOH	$\rightleftharpoons CH_3COO^-$	$+ H^+$
Initial	0.1M	—	—
Reaction	0.0133(0.1)	0.00133	0.00133
Equilibrium	0.1-0.00133	0.00133	0.00133

$$K_a = \frac{(0.00133)^2}{0.1} \qquad \text{Since } 0.00133 << 0.1$$

$$\therefore K_a = 1.77 \times 10^{-5}$$

Using formic acid and sodium formate, suggest a recipe for a buffer at pH 3.0, given that Ka is 1.8×10^{-4}

$$pH = pK_a + \log\frac{\text{salt}}{\text{acid}}$$

$$\log\frac{\text{salt}}{\text{acid}} = pH - pK_a = 3.0 - (-\log 1.8\times10^{-4})$$

$$\log\frac{\text{salt}}{\text{acid}} = 3.0 - 3.745 = -0.745$$

$$\frac{\text{Salt}}{\text{acid}} = 10^{-0.745} = 0.18$$

Hence [Salt] : [acid] = 18 : 100

ILLUSTRATION EXERCISE: For a particular reaction the ΔH is 92kJ and R is 8.314. If Kc at 200°C is 9.6 what is Kc at 600°C

$$\ln\frac{K_{c_2}}{K_{c_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] = \frac{\Delta H}{R}\left[\frac{1}{573}-\frac{1}{873}\right]$$

$$\ln\frac{K_{c_2}}{9.6} = \frac{92400}{8.314}\left[\frac{873-573}{(873)(573)}\right] = \frac{92400\times300}{8.314\times873\times573} = 6.67$$

$$\frac{K_{c_2}}{9.6} = e^{6.67} = 788.4$$

$$K_{c_2}\ (\text{at } 600°) = 7.57\times10^{3}$$

For the reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ at equilibrium $K = 0.63$ at 700°C and 1.29 at 900°C calculate ΔH for the reaction

$$\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] = \frac{\Delta H}{R}\left[\frac{1}{973}-\frac{1}{1173}\right]$$

$$\ln\frac{1.29}{0.63} = \frac{\Delta H}{8.314}\left[\frac{1173-973}{(973)(1173)}\right] = \frac{\Delta H}{8.314}\left[\frac{200}{973\times1173}\right]$$

$$0.7167 = \frac{200\,\Delta H}{8.314\times973\times1173}$$

$$\Delta H = \frac{0.7167\times8.314\times973\times1173}{200} = 34\,kJ$$

For the equilibrium $N_2 + O_2 \rightleftharpoons 2NO$, $k_c = 4.08\times10^{-4}$ at 2000K and 3.60×10^{-3} at 2500K, Is the reaction exothermic or endothermic

$$\ln\frac{3.60\times10^{-3}}{4.08\times10^{-4}} = \frac{\Delta H}{8.314}\left[\frac{1}{2500}-\frac{1}{2000K}\right]$$

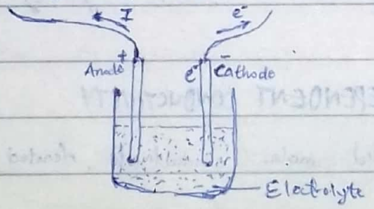
$$2.17 = \frac{\Delta H}{8.314}\left[\frac{2000-2500}{5000000}\right]$$

$$\Delta H = \frac{2.17\times8.314\times5000000}{-500} = -180.4\,kJ$$

Hence, the reaction is exothermic

ELECTROCHEMISTRY

ELECTROLYTIC CONDUCTION



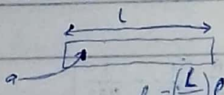
Electrolytic conduction is the conduction of an electrolyte which may be solid or solution. It is known for a long time that metallic conductor, such as copper wire, obeys ohm's law, i.e

$$E = IR$$

This implies that current I is directly proportional to emf E, which produces it. R is proportionality constant called resistance. The unit of current is Ampere, resistance is ohms and emf is volt. It has been shown that electrolyte also obeys ohm's law. And the ability of a solution to conduct electricity is called conductance [illegible] L. Conductance is defined as reciprocal of R, i.e

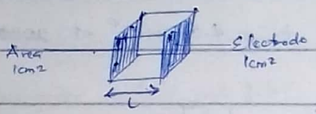
$$L = \frac{1}{R} \qquad L = \frac{I}{E} \quad \text{since } R = \frac{E}{I}$$

The conductance of a solution depends on; ~~the~~ nature of electrolyte, size of the electrode and distance between the electrode. Resistance of electrolyte between the two electrode is directly proportional to the lenght of electrolyte in between the two electrodes and inversely proportional to cross-sectional area. This implies that electrolyte can be viewed as a three dimensional conducting object, as shown below;



$$R = \left(\frac{L}{a}\right)\rho$$

a is the cross sectional area of the container (in most cases, electrodes are close to containers wall) and ρ is proportionality constant, called resistivity. Resistivity is measured in ohmsmeter. Therefore, the resistivity may be defined ~~is measured~~ as the resistance between electrode of 1cm² area which are 1cm distance apart, like a cube, i.e



Thus resistivity is the resistance of a cube of solution. The reciprocal of resistivity is called conductivity, denoted by κ, it is given as;

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\left(\frac{l}{a}\right) = L\left(\frac{l}{a}\right)$$

$$\kappa = L\left(\frac{l}{a}\right) \qquad L = \kappa\left(\frac{a}{l}\right)$$

$$\left(\frac{l}{a}\right) = \kappa R$$

The term $\left(\frac{l}{a}\right) = \kappa R$ is called cell constant, it depends on geometry of the electrolyte cell. κ depends on nature of electrolyte. The cell constant is usually evaluated by ~~used to~~ measuring resistance of electrolyte whose conductivity is known. KCl is then usually used as a standard electrolyte solution, one cell constant is known, the cell is filled with a solution whose conductivity is not known, using equation above, i.e

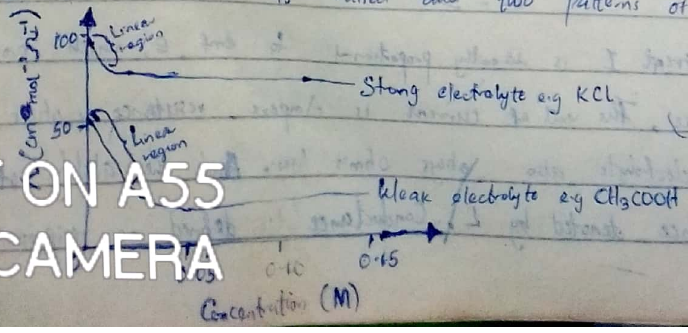
$$L = \kappa\left(\frac{a}{l}\right) = \frac{1}{R}$$

CONCENTRATION DEPENDENT CONDUCTIVITY

The concentration dependent conductivity is called molar conductivity, denoted by Λ. It is defined as;

$$\Lambda = \frac{\kappa}{c}$$

Molar conductivity was formally known as the equivalent conductivity. It is important because it give information about conductivity of ions produced in solution by one mole of the substance. In all cases, molar conductivity diminishes as the concentration is raised and two patterns of behaviour can be distinguished as shown below;



In this figure above, it is shown the dependence of molar conductivity and concentration. The dependence of molar conductivity on concentration may be expressed as;

$$\Lambda = \Lambda^{\circ} - bC$$

The intercept in figure above is equivalent to Λ° and it is molar conductivity at infinite dilution when the concentration is very very low. The ideal behaviour should be a straight line with a negative slope as against what is presented in figure above which shows the real behaviour. From figure above, it can be seen that that for strong electrolyte, molar ~~concentration~~ conductivity falls only slightly as concentration is raised. On the other hand, the weak electrolyte which produces fewer ion exhibit a much more pronounced form of Λ with increasing concentration. ~~The relationship~~ CH_3COOH is reversible ~~for~~, hence have low bend while KCl is irreversible hence have a ~~sharp~~ sharp bend.

The relationship between degree of dissociation and molar conductivity is given as;

$$\alpha = \frac{\Lambda}{\Lambda^{\circ}}$$ where α is degree of dissociation

ILLUSTRATION EXERCISE: The electrolytic conductivity of a 0.1M solution of acetic acid (corrected for conductivity of water) was found to be $5.3 \times 10^{-4}\,\Omega^{-1}cm^{-1}$ at 25°C. Calculate molar conductivity.

$$\Lambda = \frac{\kappa}{c} = \frac{5.3 \times 10^{-4}}{0.1 \times 10^{-3}} = 5.3\,cm^2 mol^{-1}\Omega^{-1}$$

A conductivity cell was filled with 0.0100M KCl which was known to have a conductivity of $0.001413\,\Omega^{-1}cm^{-1}$ at 25°C; its measured resistance was 94.3Ω. When the cell was filled with $AgNO_3$, its resistance was 50.3Ω. Calculate conductivity of $AgNO_3$ solution.

$$\frac{L}{a} = \kappa R = 0.001413 \times 94.3 = 0.133246\,cm^{-1}$$

$$\kappa = \left(\frac{L}{a}\right)\frac{1}{R} = 0.133246 \times \frac{1}{50.3} = 2.65 \times 10^{-3}\,\Omega^{-1}cm^{-1}$$

A conductivity cell whose constant is $22.81\,cm^{-1}$ was filled with 0.0025M K_2SO_4 solution. The resistance of the solution is 326.0Ω. If the K_2SO_4 dissociate completely in solution, what is molar conductivity of K_2SO_4.

$$\Lambda = \frac{\kappa}{c} = \left(\frac{L}{a}\right)\frac{1}{RC} = 22.81\,cm^{-1} \times \frac{1}{326.0 \times 0.0025 \times 10^{-3}} = 2.8 \times 10^{2}\,cm^2 mol^{-1}\Omega^{-1}$$

OSTWALD DILUTION LAW

Consider an electrolyte, A and B exist in solution party as undissociated species AB and partly as the ion A^+ and B^-, i.e

$$AB \rightleftharpoons A^+ + B^-$$

The equilibrium constant on the assumption of ideality, we can write the expression as;

$$K_c = \frac{[A^+][B^-]}{[AB]}$$

Suppose that an amount n of the electrolyte is present in the volume V and that the fraction dissociated is α. The fraction not dissociated will be $1-\alpha$. The amount of the three species present at equilibrium and the corresponding concentration will therefore be;

$$AB \rightleftharpoons A^+ + B^-$$

	AB	A^+	B^-
Amount present @ equilibrium	$n(1-\alpha)$	$n\alpha$	$n\alpha$
Concentration @ equilibrium	$\frac{n(1-\alpha)}{V}$	$\frac{n\alpha}{V}$	$\frac{n\alpha}{V}$

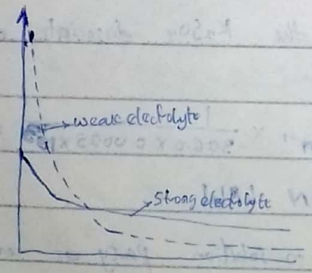
So the equilibrium constant is given as;
$$K_c = \frac{(n\alpha)^2}{V^2} \div \frac{n(1-\alpha)}{V} = \frac{(n\alpha)^2}{V^2} \times \frac{V}{n(1-\alpha)}$$
$$K_c = \frac{n\alpha^2}{V(1-\alpha)}$$

Thus, when given amount of substance, the degree of dissociation α must vary with volume as follow;
$$\frac{c\alpha^2}{1-\alpha} = K_c$$

Thus, the larger the volume, V, the lower the concentration, c and the large the degree of dissociation because ~~then~~ $c = \frac{n}{V}$. If 1 mole of electrolyte is diluted, the degree of dissociation increase and amount of ionized species increase, as V becomes very large concentration tends to zero and degree of dissociation approach unity at finite dilution, i.e molar conductivity Λ becomes molar conductivity at infinite dilution Λ°. The experimental value of Λ° corresponds to complete dissociation or AB which is the electrolyte. The dilution law can therefore be expressed as;
$$K = \frac{c\Lambda^2}{\Lambda^\circ(\Lambda^\circ - \Lambda)} \quad \text{because} \quad \alpha = \frac{\Lambda}{\Lambda^\circ}$$
and this is true for weak electrolyte.

INDEPENDENT MIGRATION OF IONS

In principle, plot of molar conductivity versus concentration, which ~~we~~ have as shown in the ~~diag~~ graph diagram before, can be extrapolated back to zero concentration to give the molar conductivity at infinite dilution giving the Λ° value. In practice, this extrapolation can satisfactorily be made ~~for~~ strong electrolyte, with weak electrolyte there is a strong dependent of molar conductivity on concentration at low concentration and therefore the ~~exp~~ extrapolation do not lead to reliable Λ° value.



The first graphical diagram is theoretical stipulation but in reality this second graphical diagram is valid.
Molar conductivity at infinite dilution of various Sodium ~~NaCl~~ and Potassium salt in various solution at 25°C is shown in table below;

Electrolyte	$\Lambda^\circ (\Omega^{-1} cm^2 mol^{-1})$	Electrolyte	$\Lambda^\circ (\Omega^{-1} cm^2 mol^{-1})$	Difference $(\Omega^{-1} cm^2 mol^{-1})$
KCl	149.9	NaCl	126.5	23.4
KI	[illegible]	NaI	126.9	23.4
[illegible]	[illegible]	Na_2SO_4	130.1	23.4

The table shows that the difference between Λ of Na and K salt of same anion is independent of nature of anion. Similar result were obtained for a variety of pair of salt with common cation or anion in both aqueous and non-aqueous solvent. This was explained in term of Kohlrausch's law of independent migration of ion given as;

$$\Lambda^\circ = \Lambda^\circ_+ + \Lambda^\circ_-$$

Thus, assuming that each ion make it own independent contribution to molar conductivity at infinite dilution, irrespective of nature of ~~atom~~ other ion with which it is associated, so for KCl, Λ° is given as,

$$\Lambda^\circ = \Lambda^\circ_{K^+} + \Lambda^\circ_{Cl^-} = 149.9$$

$$\Lambda^\circ = \Lambda_{Na^+} + \Lambda^\circ_{Cl^-} = 126.5$$

ILLUSTRATION EXERCISE; Calculate the molar conductivity at infinite dilution for acetic acid at 298K given the following data obtained by extrapolation from graph of molar conductivity against concentration. ($\Lambda^\circ_{HCl} = 426 \times 10^{-4} m^2 \Omega^{-1} mol^{-1}$; $\Lambda^\circ_{AcNa} = 91.0 \times 10^{-4} m^2 \Omega^{-1} mol^{-1}$; $\Lambda^\circ_{NaCl} = 126.5 \times 10^{-4} m^2 \Omega^{-1} mol^{-1}$)

$\Lambda^\circ_{H^+} + \Lambda^\circ_{Cl^-} = 426.1 \times 10^{-4}$ $\quad$ $\Lambda^\circ_{Ac^-} + \Lambda^\circ_{Na^+} = 91.0 \times 10^{-4}$ $\quad$ $\Lambda^\circ_{Na^+} + \Lambda^\circ_{Cl^-} = 126.5 \times 10^{-4}$

$$\Lambda^\circ_{H^+} - \Lambda^\circ_{Na^+} = 426.1 \times 10^{-4} - 126.5 \times 10^{-4} = 299.6 \times 10^{-4}$$

$$\Lambda^\circ_{AcH} = \Lambda^\circ_{Ac^-} + \Lambda^\circ_{H^+} = 299.6 \times 10^{-4} + 91.0 \times 10^{-4} = 390.6 \times 10^{-4}$$

Molar conductivity of a 0.001028M acetic acid solution is 48.15×10^{-4}, from molar ~~conductivity~~ ~~from Ab.~~ conductivity gotten from Above question, calculate degree of dissociation of acetic acid at this concentration and it ionization constant

$$\alpha = \frac{\Lambda}{\Lambda^\circ} = \frac{48.15 \times 10^{-4}}{390.6 \times 10^{-4}} = 0.1233 = 12.33\%$$

$$K_c = \frac{C\alpha^2}{1-\alpha} = \frac{0.001028 \times (0.1233)^2}{1 - 0.1233} = \frac{1.56 \times 10^{-5}}{0.8768} = 1.78 \times 10^{-5} M$$

IONIC MOBILITY & TRANSPORT NUMBER

The ability of an electrolyte to conduct electric current is dependent on product of the total charge carried by the ion and its velocity under the influence of electric field between the electrode. If the electro-chemical valence (n_e) and concentration of two ions are same, then at infinite dilution when all the molecule are completely dissociated, the conductivity of ions depends solely on their velocity (as this will be the only different behaviour). Since ion behave independently, it follows that

$$\Lambda^\circ_+ = Fu^\circ_+ \quad \text{and} \quad \Lambda^\circ_- = Fu^\circ_-$$

where u is velocity or ionic mobility of the cation or anion and F is the faraday constant. The mobility of an ion, u, is defined as the speed with which the ion move under a potential gradient. Thus, ~~From~~ ~~equate~~ we can write molar conductivity at infinite dilution to be;

$$\Lambda^\circ = \Lambda^\circ_+ + \Lambda^\circ_- = F(u^\circ_+ + u^\circ_-)$$

$$\frac{\Lambda^\circ_+}{\Lambda^\circ} = \frac{Fu^\circ_+}{F(u^\circ_+ + u^\circ_-)} = \frac{u^\circ_+}{u^\circ_+ + u^\circ_-} = t_+$$

$$\frac{\Lambda^\circ_-}{\Lambda^\circ} = \frac{u^\circ_-}{u^\circ_+ + u^\circ_-} = t_-$$

Transport or transference number is the fraction of the current carry by each ion present in solution. The experimental methods for determination of transport number are available in many physical textbooks.

ILLUSTRATION EXERCISE: The molar conductivity at infinite dilution, at 25°C for KCl is 150 $cm^2\Omega^{-1}mol^{-1}$ and transport number of K at infinite dilution is 0.459. Calculate the molar conductivity at infinite dilution for K^+ and Cl^- at same temperature.

$$t_+ = \frac{\Lambda^\circ_+}{\Lambda^\circ} \Longrightarrow \Lambda^\circ_+ = 150 \times 0.459 = 68.85 cm^2\Omega^{-1}mol^{-1}$$

$$\Lambda^\circ_{KCl} = \Lambda^\circ_{K^+} + \Lambda^\circ_{Cl^-} \Longrightarrow \Lambda^\circ_{Cl^-} = \Lambda^\circ_{KCl} - \Lambda^\circ_{K^+} = 150.00 - 68.85 = 81.15 cm^2\Omega^{-1}mol^{-1}$$

EFFECT OF SOLVENT DRAG ON MOVING ION

The effect of solvent drag on moving ion is represented by Stoke's law as;

$$U_i = \frac{Z_i e}{6\pi\eta r_i}$$ where Z_i is valency number and r_i is ionic radius and η is viscosity.

Recall $\Lambda^\circ = \Lambda^\circ_+ + \Lambda^\circ_- = F(U^\circ_+ + U^\circ_-)$

$$\Lambda^\circ = \frac{Fe}{6\pi\eta}\left(\frac{Z_+}{r_+} + \frac{Z_-}{r_-}\right)$$

$$\Lambda^\circ\eta = \frac{Fe}{6\pi}\left(\frac{Z_+}{r_+} + \frac{Z_-}{r_-}\right) = \text{Constant} \qquad \text{(Walden's rule)}$$

ILLUSTRATION EXERCISE: The mobility of sodium ion in water at 25°C is $5.19 \times 10^{-4} cm^2V^{-1}s^{-1}$. Calculate the molar conductivity of the sodium ion

$$[illegible] \quad \Lambda_{Na^+} = F U_{Na^+}$$

$$\Lambda_{Na^+} = 96500 \times 5.19 \times 10^{-4} = 50.18 cm^2\Omega^{-1}mol^{-1}$$

Walden's rule holds for large ions only because of the complication of hydration which affect the small ions (are highly hydrated). The Stokes law can be used to molar conductivity at infinite dilution of cation and anion before by seperating the stoke's law as follows;

$$\Lambda^\circ_+ = \frac{FeZ_+}{6\pi\eta r_+} \qquad \Lambda^\circ_- = \frac{FeZ_-}{6\pi\eta r_-}$$

Since $\frac{Fe}{6\pi\eta}$ is a constant, it follows that the molar conductivity of cation will be proportional to r_+

$$\Lambda^\circ_+ \propto \frac{1}{r_+}$$

From experiment, it was shown that the relationship as consistent with the experimental data given below;

cations :	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+
$\Lambda^\circ_+ (cm^2\Omega^{-1}mol^{-1})$:	349.8	38.66	50.15	73.52	77.80	77.30

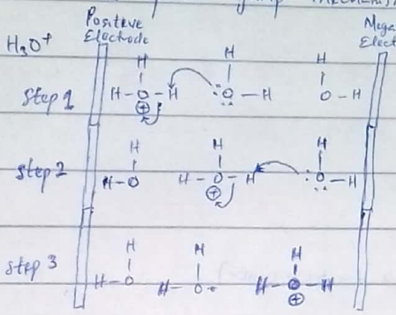
Anions :	OH^-	Cl^-	Br^-	I^-	ClO_3^-	BrO_3^-	IO_3^-
$\Lambda^\circ_- (cm^2\Omega^{-1}mol^{-1})$:	198.6	76.35	78.20	76.90	64.60	55.80	40.50

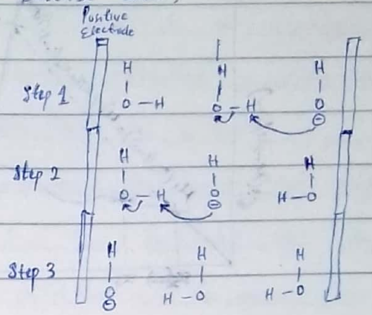
Small positive ion are known to be more highly hydrated than large positive ion, hence large ion are more conducting than small ions. Hydration number is number of solvent molecule attach to an ion. The hydration [illegible] Li^+ is [illegible] Na^+ [illegible] 4 [illegible] K^+ is 2 and Rb^+ is 1. This implies that the hydration number decreases as ion size increase and so, the effective ionic radius is very large for small ions due to their large hydration number.

The case of negatively charged ion can be understood, since it is generally agreed that they are less hydrated because of electron cloud. So small ion moves more faster than large ions, therefore large ion means less conductivity.

Molar conductivity of hydroxyl ion and hydrogen ion are much larger than the others, those large value can be explained on the basis of proton pump mechanism, which is describe below;

Since H^+ exist as H_3O^+





Thus process of hydrogen ion transfer result in more rapid movement of positively charged ion from one region to another. Hence, the high value of molar conductivity than will be possible if the ion have to push their way through the solution.

ACTIVITY & STANDARD STATE

The thermodynamics of ions in solution depends on the chemical potential, μ, the basic expression for chemical potential of ion i is given by;

$$\mu_i = \mu_i^\circ + RT\ln a_i$$

where μ_i° is the standard chemical potential, i.e chemical polarity at 1mol/kg, 298K and 1atm pressure; R is gas constant; a_i is the activity of the ionic species, which is defined as,

$$a_i = \gamma_i m_i \quad \text{(unitless)}$$

For ideality, at infinite dilution activity coefficient of an ionic species tends to one, activity tends to molality as molality of ionic species tends to zero.

If chemical potential of a monovalent cation is denoted by μ_+ and of a monovalent anion μ_-, the chemical potential of the solute is given by;

$$\mu_+ + \mu_- = \mu_+^\circ + \mu_-^\circ + RT\ln a_+ + RT\ln a_-$$

$$\mu_+ + \mu_- = \mu_+^\circ + \mu_-^\circ + RT\ln(m_+) + RT\ln(m_-) + RT\ln\gamma_+\gamma_-$$

The electrostatic interaction responsible for the deviation from ideality is contained in the last term of the equation above. This part can not be seperated into positive and negative ion but at best the mean activity coefficient can be introduced i.e $\gamma_\pm$ which is given by; $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$

$$\mu_+ = \mu_+^\circ + RT\ln(m_+) + RT\ln\gamma_\pm$$

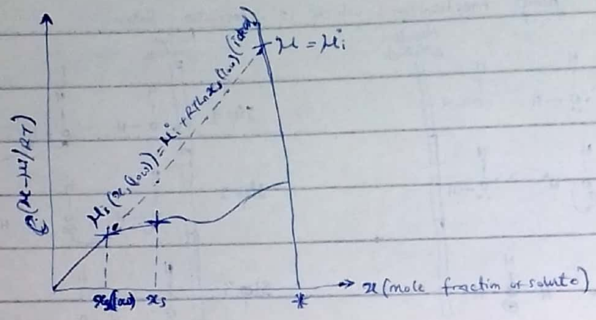
$$\mu_- = \mu_-^\circ + RT\ln(m_-) + RT\ln\gamma_\pm$$

When the salt is M_pX_q which dissolves to give a solution containing the ions, $M^{+|Z+|}$ and $X^{-|Z-|}$, ~~with~~ ~~ratio~~ p:q, the mean activity co-efficient will be given by;

$$\gamma_\pm = (\gamma_+^p \gamma_-^q)^{1/n} \quad \text{where } n = p+q$$

And the chemical potential of either species is given by;

$$\mu_i = \mu_i^\circ + RT\ln(m_i) \ \cancel{+RT\ln\gamma_\pm}$$



QUANTIZATION

By the end of 19th century, classical physics assumptions seems to be the solution to every physical proble ~~the~~ assumption of classical physics include;

Atoms are basic constituent of matter Newton's laws applies universally

The world is deterministic, i.e knowing initial position and velocity of any body, future velocity and position can be known, i.e

Given: $\vec{r}_0, \vec{v}_0$ $\quad \vec{V}(r) = \int_{\vec{v}_0}^{\vec{v}'} dv = \int_{t_0}^{t'} \frac{\vec{F}}{m}\,dt$ and $\vec{r}(t) = \int_{\vec{r}_0}^{\vec{r}'} dr = \int_{t_0}^{t'} \vec{v}\,dt$

With these ~~assumptions~~ assumptions, physics was complete, except for some exceptions because of the following reasons ~~which include the~~

Newtonian mechanics explain macroscopic behaviour of matter e.g planetary motion, fluid flow, elasticity, etc.

Also thermodynamics has its first and second laws and its consequencies

Basic statistical mechanics have been applied to chemical system ~~because light~~

Light was explained as an electromagnetic wave

However, there were several experiments that can't be explained by classical physics, ~~which~~ include; Black body radiation, Photo electric effect, Discrete atomic spectra and Electron as a subatomic molecule. There are some inescapable conclusion from these aforementioned problems, which are,

Atoms are not the most macroscopic object

Newton laws do not apply to the microscopic world of electron

Hence, a need for a new rule and this start the begining of quantum mechanics. Quantum mechanics describe rules that apply to small particles as electron in atoms and molecules. Quantum mechanic is not deterministic but probabilistic. It explained unsolved problems of late 19th century. It explains [illegible] structure and reactivity in chemistry e.g quantum mechanics was used to explain why cyclobutadiene can't be synthesized, which is because the Resonance Stabilization Energy (RSE) of cyclobutadiene is zero.

ELECTRON AS SUBATOMIC PARTICLE

Electron was discovered accidentally by J.J Thompson during a cathode ray experiment where he noticed a ~~charged~~ ray of ~~p~~ charged particle which are deflected to the positive pole of magnetic field. By ~~varing~~ varying magnetic field, he determined the ~~mass~~ charge to mass ratio (e/m) of electron. He also used different cathode and residual gas which give same e/m was same. Hence, he concluded that electron is a fundamental particle of atoms. He then, proposed a model that an atom ceonsist a uniformly distributed positively charged bodies with electron embedded in it called the water melon model (he won noble price in 1901)

Rutherford, Thompson's student, perform an alpha particle experiment, He observed that some particles pass through the metal foil while some were scattered backward, so, he concluded that atoms contain a centrally densed positively charged nucleus and that electrons are revolving round the nucleus like a planet. Though the model is correct but he could not explain the stability of his model atom, because electron at a point in revolution should lose its energy and stop.

The first model about quantization of energy was given by Niel Bohr. He ~~[illegible]~~ explained the stability of Rutherford's atom. Niel Bohr assumptions include the following;

(i) Atoms can exist in a stable state without radiating energy because each stable state has discrete energy

(ii) Transition between state can be made, with absorption or emission of a photon of frequency, ν

$$\nu = \frac{\Delta E}{h}$$

E_{n+1} ↓Emission ↑Absorption

E_n

The first two assumptions explain discrete spectrum of atomic vapour emission. Each line of its spectrum correspond to a transition between two particular levels. These two assumptions are the origin of modern spectroscopy

(iii) Angular momentum is quantized, i.e, it is the integral multiple of planck's constant

$$l = n\hbar = \frac{nh}{2\pi} \qquad K.E = \tfrac{1}{2}mv^2 = \frac{p^2}{2m} \qquad l = mvr = I\omega$$

$$mvr = I\omega \Rightarrow m^2v^2r^2 = I^2\omega^2 \Rightarrow \tfrac{1}{2}mv^2 = \tfrac{1}{2}\frac{I^2\omega^2}{mr^2} = \tfrac{1}{2}\frac{I^2\omega^2}{I} = \tfrac{1}{2}I\omega^2 = \tfrac{1}{2}\hbar\omega$$

(iv) There are two force acting on electron in an atom and they are equal, i.e centrifugal force equal the centripetal force.

$$\text{Centripetal force} = \frac{-e^2}{4\pi\varepsilon_0 r^2} \qquad \text{Centrifugal force} = \frac{mv^2}{r}$$

$$\frac{-e^2}{4\pi\varepsilon_0 r^2} + \frac{mv^2}{r} = 0 \Rightarrow \frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \Rightarrow mv^2 = \frac{e^2}{4\pi\varepsilon_0 r} \Rightarrow r = \frac{e^2}{4\pi\varepsilon_0 mv^2} \; \& \; V^2 = \frac{e^2}{4\pi\varepsilon_0 mr}$$

Also, $mvr = \frac{nh}{2\pi} \Rightarrow v = \frac{nh}{2\pi mr} \Rightarrow V^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \; \& \; r^2 = \frac{n^2h^2}{4\pi^2m^2V^2}$

$$r = \frac{e^2}{4\pi\varepsilon_0 mv^2} \times \frac{4\pi^2 m^2 r^2}{n^2h^2} = \frac{e^2\pi mv}{n^2h^2\varepsilon_0} \Rightarrow n^2h^2\varepsilon_0 = \pi mve^2$$

$$r = \frac{n^2h^2\varepsilon_0}{\pi me^2} = n^2\left[\frac{h^2\varepsilon_0}{\pi me^2}\right]$$

Hence, position of electron is also quantized

$$r^2 = \frac{n^2h^2}{4\pi^2(mv)^2}$$

$$n^2\left[\frac{h^2\varepsilon_0}{\pi me^2}\right]$$

$$\boxed{r = 0.0529n^2\,\text{nm}}$$

This implies that there are discrete position, within the atom round the nucleus, where electrons occupy.

(v) Total energy of electron is the sum of potential and kinectic energy, i.e

$$E_T = K.E + P.E \qquad K.E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{ke^2}{4\pi\varepsilon_0 r} = \frac{ke^2}{8\pi\varepsilon_0 r} \quad \& \quad P.E = \frac{-ke^2}{4\pi\varepsilon_0 r}$$

$$E_T = \frac{ke^2}{8\pi\varepsilon_0 r} - \frac{ke^2}{4\pi\varepsilon_0 r} = \frac{ke^2 - 2ke^2}{8\pi\varepsilon_0 r} = \frac{-ke^2}{8\pi\varepsilon_0 r}$$

$$E_T = \frac{-ke^2}{8\pi\varepsilon_0 r} = \frac{-ke^2}{8\pi\varepsilon_0} \times \frac{\pi m e^2}{n^2h^2\varepsilon_0} = -\left(\frac{\cancel{\pi} m e^4}{8\cancel{\pi} h^2\varepsilon_0^2}\right)\frac{1}{n^2}$$

$$E_T = -\left(\frac{me^4}{8h^2\varepsilon_0^2}\right)\frac{1}{n^2} = -2.18\times10^{-18}\frac{1}{n^2} = \frac{-13.60}{n^2}\,\text{eV} \quad \text{where } n = 1, 2, 3, 4, \ldots$$

Conclusively, energy of an atom is also quantized. Neil Bohr model, although good, is limited by the following;

The electron is too tiny to be located accurately and also effort to monitor position of an electron (by astrological microscope which uses light) alters the position, hence, there is always uncertainty in position or momendum of the electron

Lack of explanation for the complex spectrum of multi electron system.

WAVE - PARTICLE DUAL NATURE

Electron was believed to be a particle in the beginning but it was found that electron emit radiations which is not suppose to be ~~as~~ a particle, since it is not light. With this observation, electron was assumed to behave as light, i.e as a wave, ~~which~~ and this forms the basis of De Broglie's research work. Using Einstein and Planck's equation for energy, he showed that electron behave as wave and also as particle, i.e

$$E = mc^2 \quad \& \quad E = h\nu = h\frac{c}{\lambda}$$

$$mc^2 = \frac{hc}{\lambda} \Longrightarrow mc = \frac{h}{\lambda} \Longrightarrow P = \frac{h}{\lambda}$$

P give the particle property & λ give the wave property

An explanatory observation was made ~~at~~ using the atomic spectrum of hydrogen, showing that when an electron is excited, electron tend to go back to the ground or stable state, during which, it emit radiation which can be seperated by a glass prism. This phenomenon was first discovered by Balmer, which is ~~about~~ for electrons moving from $n = \infty$ to $n = 2$. After his first discovery, other scientists show other spectra of hydrogen atom, which are;

n = 1, 2, 3, ... Lyman

n = 2, 3, 4, ... Balmer

n = 3, 4, 5, ... Paschen

n = 4, 5, 6, ... Brackett

n = 5, 6, 7, ... Pfund

After sometimes, Rydberg then showed that the wavelenght of the radiation emitted by electron can be written as;

$$\frac{1}{\lambda} = R_H\left[\frac{1}{n^2} - \frac{1}{\infty^2}\right] = \frac{R_H}{4} \quad \text{when } n = 2$$

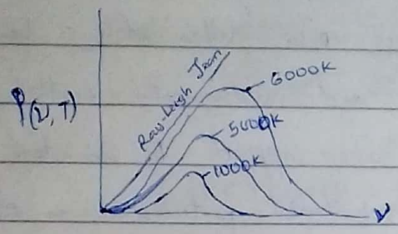
$$\text{Recall} \quad \Delta E = \frac{hc}{\lambda} \Longrightarrow \frac{1}{\lambda} = \frac{\Delta E}{hc}$$

$$\frac{\Delta E}{hc} = R_H\left(\frac{1}{n^2} - 0\right) \Longrightarrow \Delta E = R_H hc \frac{1}{n^2} \Longrightarrow \frac{R_H hc}{n^2}$$

For absortion, ΔE is negative and for emission, ΔE is positive. So, sign of the energy tells if the radiation is absorbed or emitted.

BLACK BODY RADIATION

This [illegible] important [illegible] quantization of energy, which was first explained by Max Planck. He talked about the black body radiation. When light or radiation fall on a surface, som of the light is reflected, some are absorbed while some are being transmitted through the surface. Differeat surface absorb, reflect or transmit light depending on the nature & material of the surface. For a black body, it was assumed that a black body is one that absorb all radiation that fall on it. A Black body is a model surface, for there is no such surface in nature. The experimental behaviour is such that spectrum intensity change as shown below;



$$\rho(\nu,T)d\nu = \frac{8\pi\nu^2}{c^3}\bar{E}_{osc}\, d\nu \qquad \bar{E}_{osc} = K_BT$$

$$\rho(\nu,T)\,d\nu = \frac{8\pi K_BT\nu^2}{c^3}\,d\nu \text{ — Ray-Leigh Jean equation}$$

The equation above implees that a spectral intensity increases as frequency increases, so, classical can't explain experimental behaviour. Then, Max planck proposed that $\bar{E}_{osc}$ is also a function of ν, i.e

$\bar{E}_{osc} \propto \nu$ $\qquad$ $\bar{E}_{osc} = nh\nu$ where h is planck constant (most important in physics)

Experimentally, colour of hot object shift with temperature, not all wavelenght are emitted equally ~~nort~~ and at any temperature the intensity of the emitted light approach zero as ν approach zero. The displacement of intensity ~~of~~ is ~~tha~~ ~~as~~ account for by Ray" displacement law, which state that the product of maximam wavelenght and temperature is constant, i.e $\qquad \lambda_{max}T = \text{constant}$

This law could not be explained by classical mechanics and also that the emissivity (emission power) is proportional to the fourth power of temperature, i.e

$E \propto T^4$ $\qquad$ $\varepsilon = \sigma T^4$ where σ is stefan's constant, given by $5.67 \times 10^{-8} W/K^4$

By the knowledge of thermodynamics and theorges of electromagnetism, Max discovered that,

$$\bar{E}_{osc} = \frac{h\nu}{e^{\frac{h\nu}{K_BT}} - 1} \qquad \text{at high temperature} \quad e^{h\nu/K_BT} - 1 = \frac{h\nu}{K_BT}$$

$$\rho(\nu,T)\,d\nu = \frac{8\pi\nu^2}{c^3} \times \frac{h\nu}{e^{\frac{h\nu}{K_BT}}-1}\,d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{K_BT}}-1}\,d\nu$$

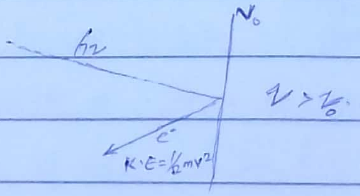
The approximated value of energy of oscillation is such that at high temperature $\frac{h\nu}{K_BT} << 1$ and at low temperature $\frac{h\nu}{K_BT} >> 1$. So, at high temperature, Ray-Leigh Jean equation is close ~~is~~ ~~close~~ to experiment result while at low temperature, it fails woefully.

PHOTO ELECTRON EMISSION

CHM 203

PHOTO ELECTRON EMISSION

When light is incident or irradiated ~~on a~~ on a metal ~~on a~~ ~~metal~~ plate at a frequency, electrons are ejected and this photo-electron effect, as shown below



Noting that intensity and energy are not same, e.g Sun ~~radiate~~ radiate ~~its~~ mass ~~energy~~ all time, making solar pane works, i.e intensity, even at night when energy is low. So, when classical light is incident as a plane wave over a whole metal plate and consequently light is absorbed by many electrons on the surface, hence; electrons are emitted for all light frequencies of the light is of sufficient intensity

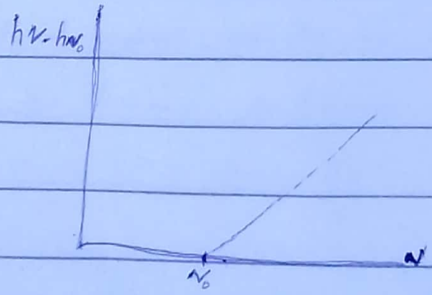
Kinetic energy per electron increase with light intensity, however experimentally, though number of electron inc with light intensity, kinectic energy of emitted electron is independent on intensity of light

No electron is emitted unless frequency is above a certain minimum called threshold ~~frequency~~ frequency

Electron are emitted even at low intensity as long as frequency is above threshold frequency.

The binding energy that bind electron to metal is called work function which depends on composition of metal, hence differs from metal to metal.

$$K.E = h\nu - \phi = h(\nu - \nu_0)$$



Since, it is not all energy leads to ejection of electron, hence energy is quantized