Boyle's Law

At constant temperature, the volume of a definite mass of gas is inversely proportional to the pressure i.e. At fixed temperature, the product of the pressure (P) and volume (V) of a given mass of gas is constant.

This can be written in the form of the equation:

$$V \propto \frac{1}{P} \quad \text{(At constant temp.)}$$

$$V = \frac{K}{P}$$

where, P = pressure, V = volume of a definite mass of gas at constant temp.

or $PV = K$ ..... (1)

where K = constant, its magnitude depends on temp. and mass of the gas and also upon its nature.

Boyle's law can be expressed in another manner:

$$P_1 V_1 = P_2 V_2 \quad .. (2)$$

V_1 = volume of a given mass of gas when the pressure is P_1

V_2 = " " = the same mass of gas when the pressure is changed to P_2 at the same temperature.

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Example :- A given mass of gas occupies a volume of 240 ml at pressure of 1.25 atm. By howmuch would the volume change if the pressure were altered to 0.75 atm. at the same temperature ??

If we plot the pressure as ordinates and the volume (at const. temp) as abscissae, we obtain Figure (1). The curve is rectangular hyperbola

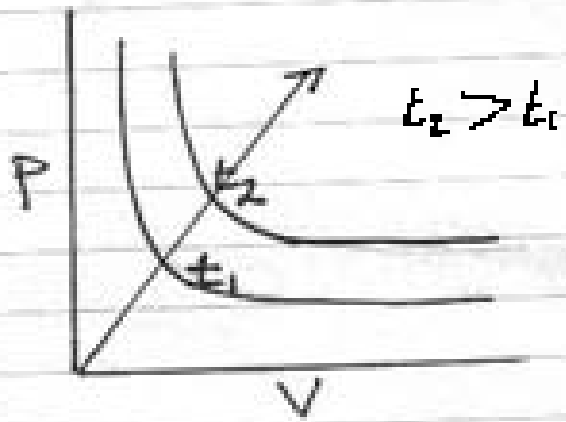

Figure (1) – Isotherm for ideal gas

The curve is described as Isotherm

Isotherm :- Variation of volume with pressure at constant temperature.

as shown in Fig (1), for each temp a different curve (hyperbola) is obtained

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Gay - Lussac's Law or Charles law

Charles Law

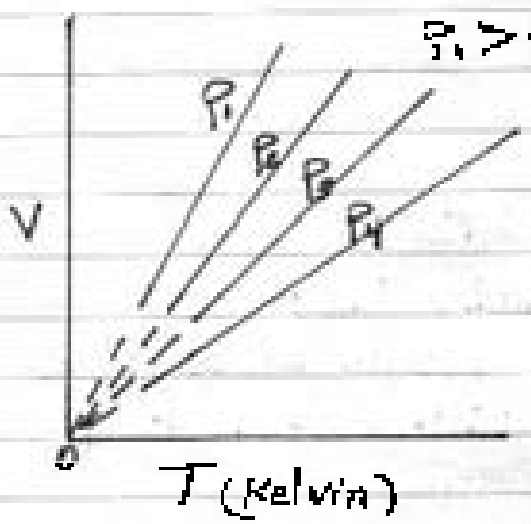
At constant pressure (P), the volume of a fixed mass of any gas increases by the same relative amount (or fraction) for any degree rise in temperature.

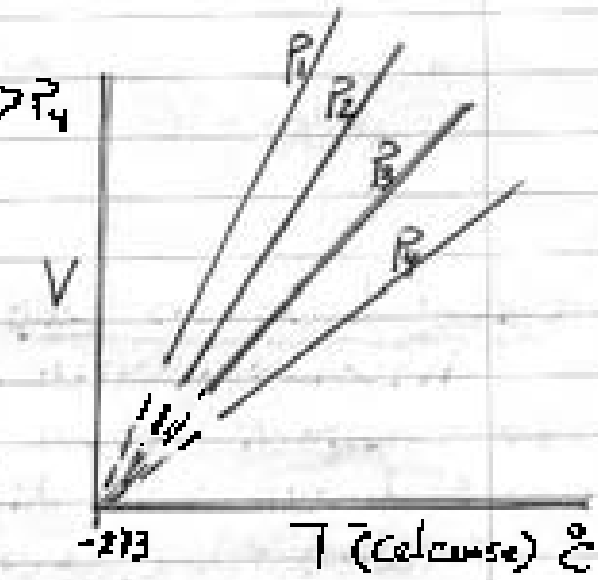
or The volume increases linearly with temperature

$$V \propto T \quad \text{(at constant P)}$$

$$V = K T \quad \cdots (3)$$

The linear variation of volume (V) with temperature is illustrated in Fig (2)





(2) Gay - Lussac's Law isobars for an ideal gas

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant.} \quad \text{(at const press)}$$

$$\frac{V_1}{V_2} = \frac{T_1}{T_2} \quad \left(\frac{V}{T} = \text{constant}\right)$$

Charles's Law

~~Any Lussac's law can be expressed as~~ :-

The volume of a given mass of a gas at a definite pressure is directly proportional to the absolute temp (T)

The straight lines in Fig (2) called 'isobars' (const. press) which extrapolates to zero volume at 0°C.

Example :- The volume of a given mass of gas is 300 ml at 15°C. At what temp. will the volume be 480 ml ?? Assuming const. pres.

Equation of State

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The expression which represents the relationship between the pressure (P), volume (V) and temperature (T) of a given mass of gas.

Suppose the gas has initially a volume V_1 at press. P_1 and temp. T_1. Then when the pressure is changed to P_2 and the temp to T_2, the volume will be V_2

Suppose the temp is maintained constant at T_1 while the press. is changed from P_1 to P_2 and the volume is changed from V_1 to V_1'

Then Boyles equation becomes :-

$$P_1 V_1 = P_2 V_1' \quad (\text{fixed temp } T_1)$$

$$\therefore V_1' = \frac{P_1 V_1}{P_2} \quad \text{---- (1)}$$

2- Now the pressure is kept constant at P_2 and the temp. is altered from T_1 to T_2, the volume will change from V_1' to V_2

Applying ~~Gay-Lussac~~ Charles equation at const. press :-

$$\frac{V_1'}{T_1} = \frac{V_2}{T_2} \quad \text{--- (2)}$$

Introducing the value of V_1' in equation (2)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{--- (3)}$$

Similar results can be obtained for the volume V_3 at press. P_3 and temp. T_3 :-

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \frac{P_3 V_3}{T_3} = \text{---} \quad \text{etc} \quad \text{..(4)}$$

In general $\boxed{\frac{PV}{T} = \text{Constant}}$ (for a given mass of gas)

For a definite mass of gas, any change of T and P will be accompanied by an adjustment of V, so that the quantity $\frac{PV}{T} = \text{const.}$ ... R

Very important on P(5).

Example: A given mass of a gas occupies a volume of 250 ml at 21 C° and a pressure of 1.40 atm. At what pressure will the volume be 300 ml when the temp. is raised to 49 C° ?

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Gay-Lussac's law:

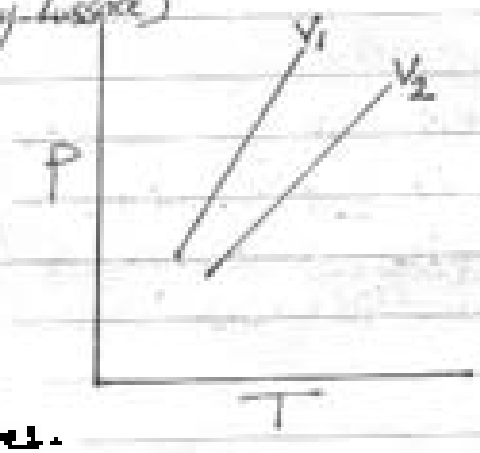
Dependence of pressure on Temperature

If the volume of a fixed mass of gas is maintained constant ($V =$ constant), then:

$$\frac{P}{T} = \text{constant}$$

or

The pressure of a given mass of gas at constant volume is directly proportional to the absolute temp. (Gay-Lussac)



Why the pressure depends on Temp ??

The explanation is that raising the temperature of a gas increases the average speed of its molecules. The molecules collide with the walls more frequently and do so with greater impact. Therefore they create a greater pressure on the walls of the container.

The variation of the volume or pressure of a fixed mass of gas as a function of temperature ($V, P \propto T$) forms the basis of the system of temp measurment (e.g in gas thermometers with He-gas).

Now, mercury "Hg" in glass thermometers are used. These are calibrated under ordinary atmospheric conditions at sea level (i.e) 760 mm at 0°C

The height of the column of Hg above the lower Hg surface represents the pressure (measured as force per unit area exerted by earth's atmosphere $\frac{F}{A}$).

Avogadro's Law :-

Equal volumes of gases at the same pressure and temperature contain the same number of molecules (i.e) at const. T & P (the volume is prop. to the no. of moles)
Then, 1 mole (1 gm molecular weight) of any substance at the same P & T always contains the same number of molecules.
Hence, for 1 mole of gas, $\frac{PV}{T}$ will be equal to universal constant (R) known as the gas constant

The ideal gas equation (The combined gas law)

According to Boyle's, Charles, Gay Lussac and Avogadro Laws, the general equation of state of any gas would be :-

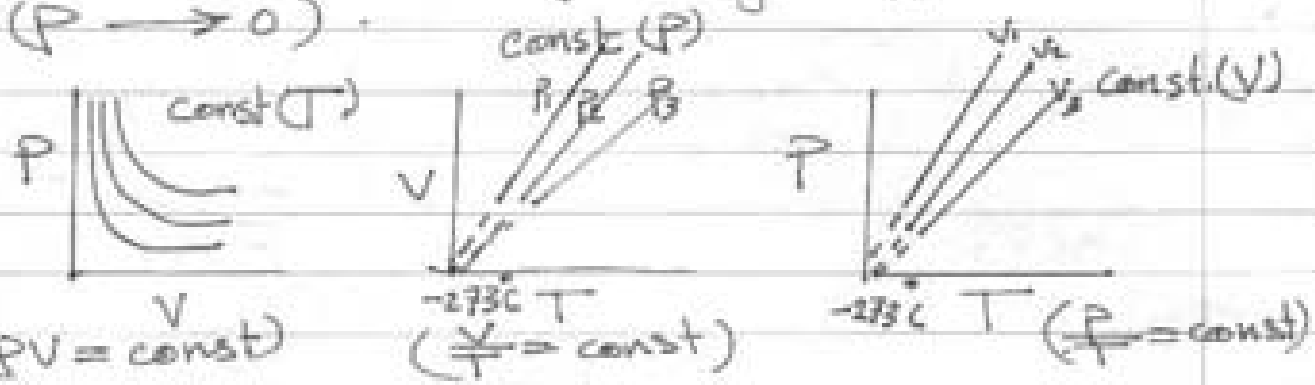
$$\frac{PV}{T} = \text{constant} = R \quad \ldots (1)$$

where, V = The volume occupied by 1 mole (Molar volume) at press. P and Temp. T
The volume of "n" moles should be n times as great as for 1 mole.

If V_n is the volume for 'n' moles, then :-

$$\boxed{PV_n = nRT} \text{ (Ideal gas equation)} \quad \text{----(2)}$$

This is called the perfect or ideal gas equation
The constant (R) is called the gas constant, it is the same for all gases.
The equation of state (2) is consistent with Boyles law (PV = constant) and charles, Gay Lussacs laws ($P, V \propto T$) and Avogadro's principle ($V \propto n$) when P, T are constants.
The Ideal or perfect gas is the gas to which the laws of Boyle and Gay Lussac are strictly applicable. Equation (2) is the approximate equation of state of any gas and becomes increasingly exact when the pressure of the gas approaches zero. ($P \longrightarrow 0$).



To correct for departure from ideal behavior :- measuring the volumes of gases at different pressures and constant temp. and extrapolating the data to zero pressure.
The volume of any gas should extrapolate to zero at $t = -273\,°C$ and therefore ($-273\,°C$) is a natural

zero of a temp scale (celcius). The thermodynamic temp. scale devised by Kelvin is (T=0)
$(T = C^{\circ} + 273)$
Also, 1 mole of an ideal gas at standard temp and press (S.T.P) defined as $T = 0^{\circ}C$ or 273 K and 1 atm (760 mm mercury) is 22.414 liters.

Example Using the perfect gas equation

In an industrial process, nitrogen is heated to 500 K in a vessel of constant volume. If it enters the vessel at a pressure of 100 atm and a temp. of 300 K. What pressur would it exert at the working temp. if it behaved as a perfect gas ?.

n	P	V	T
const.	100	Const.	300
const.	?	const.	500

Mixture of gases

Dalton's Law of Partial pressures.

The total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases.

The partial pressure of each gas in a mixture is defined as the pressure the gas would exert

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if it alone occupied the whole volume of the mixture at the same temperature.

A vessel of volume 'V' containing three gases, the amounts being n_1, n_2 and n_3 moles respectively

* Suppose the vessel is occupied exclusively by 'n_1' moles of the first gas, the pressure would be 'P_1'.
* If the vessel contained the 'n_2' moles of the second gas only, the pressure would be 'P_2'
* If the 'n_3' moles of the third gas are the sole occupants of the vessel, the pressure would be 'P_3'

All at a definite temperature (T = const.).

By the law of partial pressures :-

$$P = P_1 + P_2 + P_3 + \cdots etc \quad \text{---} (1)$$

P = Total pressure when the three gases are present in the vessel.

And so on for any mixture of gases.

When the gases separately occupy the vessel of volume (V), then equation of state for each gas is :-

$$P_1 V = n_1 RT \quad \text{---} \quad 2(a)$$
$$P_2 V = n_2 RT \quad \text{---} \quad 2(b)$$
$$P_3 V = n_3 RT \quad \text{---} \quad 2(c)$$

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$$(P_1 + P_2 + P_3 + \cdots) V = (n_1 + n_2 + n_3 + \cdots) R T \quad \ldots (3)$$

Substituting eq. (1) :-

$$PV = (n_1 + n_2 + n_3 + \cdots) RT = n RT \quad \ldots (4)$$

where, $n = n_1 + n_2 + n_3$ = Total number of moles in the gas mixture.

Dividing equation 2(a) by equation (4) :-

$$\frac{P_1 \cancel{V}}{P \cancel{V}} = \frac{n_1 \cancel{RT}}{n \cancel{RT}}$$

$$\frac{P_1}{P} = \frac{n_1}{n} \quad \ldots\ldots (5)$$

Similarly from equation 2(b) and (4) :-

$$\frac{P_2}{P} = \frac{n_2}{n}, \quad \frac{P_3}{P} = \frac{n_3}{n}, \ldots \text{etc}$$

The fractions $\frac{n_1}{n}, \frac{n_2}{n}, \ldots$ etc are called the <u>mole fractions</u> of the respective gases.

<u>The mole fraction</u> of a constituent of any mixture is the number of moles of that constituent divided by the total number of moles in the mixture

If $\frac{n_1}{n}, \frac{n_2}{n}, \ldots = x_1, x_2$ = mole fraction

then equation (5) may be written :-

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$$P_1 = X_1 P \quad , \quad P_2 = X_2 P \quad , \ldots \text{ etc}$$

By this Law, the partial pressure of any constituent of a mixture of ideal gases to be calculated from the total pressure at the same temperature, if the mole fraction is known

The sum of mole fractions equal to 1

$$X_1 + X_2 + X_3 + \cdots = 1$$

Example

Mixture of gases consists of 0.495 gm gas 'A' of molecular wt (M.wt = 66) and 0.182 gm gas 'B' of (M.wt = 45.5). The total pressure is 76.2 cm of mercury. Calculate the partial pressure of the two gases.

	wt(gm)	M.wt
A	0.495	66
B	0.182	45.5
Total pressure (P)	P = 76.2	

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Thermodynamics & Thermochemistry

Thermodynamics and Energy

The energy of a body is its capacity to do work (e.g.) the kinetic energy of the body in motion, potential energy due to position, heat energy as measured by the temperature, electrical energy, chemical energy or

The release of energy can be used to provide heat when a fuel burns in a furnace or to produce electrical work when a chemical reaction pumps electrons through a circuit

Thermodynamics is the study of the transformations of energy

In physical chemistry, the universe is divided into two parts :- The system and its surroundings. The system may be a reaction vessel, an engine, an electrochemical cell, a biological cell and so on. The surroundings are where we make our measurements.

The dynamic system is classified into 3 types :-

1- Open system
Matter can be transferred through the boundary between the system and its surroundings

2- Closed system
Matter cannot pass through the boundary

3- Isolated system
It is a closed system that neither mechanical nor thermal contact with its surroundings

Open system
Exchange matter and energy with the surrounding

Closed system
Exchange energy with its surroundings but cannot exchange matter

Isolated system
A closed system which has neither mechanical nor thermal contact with its surrounding

Both open and closed systems can exchange energy with their surroundings (e.g) a closed system can expand and thereby raise ~~the temperature~~ a weight in the surroundings and it may also transfer energy to them if they are at a lower temperature. An isolated system that has neither mechanical or thermal contact with its surroundings.

Energy dimensions = $\frac{\text{mass} \times \text{area (length)}^2}{(\text{time})^2}$

= erg, joul, calorie

1 joul = 10^7 erg

<u>Mechanical equivalent of heat</u>

when a definite amount of any form of energy e.g (mechanical, electrical) is converted into heat a perfectly definite number of calories of heat is always produced.

1 calorie = 4.18 joules

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Conservation of Energy

First Law of Thermodynamics

Although energy can be converted from one form to another, It CANNOT BE CREATED OR DESTROYED or الطاقة لا يمكن خلقها ولا تفنى

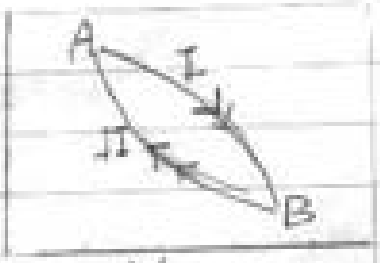
Whenever a quantity of one kind of energy is produced an exactly equivalent amount of other kinds must disappear. يعني لو حصلت طاقة لازم للنظام تبقى محسوبة

- The law can also be stated in the following form.
- The Total Energy of The System and its Surroundings Must Remain Constant Although it May be Changed From one form to Another

Thermodynamic properties

- The energy of a system depends upon its pressure 'P', volume 'V', temperature 'T', mass and composition. These four quantities are always related by an equation of state ($PV = nRT$). For a system of constant mass and composition only two of the quantities P, V, T need be given since the temperature is thereby determined.

Consider a system (gas, liquid or solid) represented by point 'A' in Fig (1)
If the conditions, volume (V) or pressure (P) are altered so that the system moves to B by path I and



Fig(1)-Energy change (Independent on path)

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as there brought back again to state (A) by different path II.

Then the total energy change in path I must be identical with that in path II. (a direct consequence of the first law of thermodynamics).

If the total energy change in path I is not identical to that in path II, then motion or work would be possible.

If the increase in energy involved in path I is greater than the decrease in returning by path II, then by carrying out the process A → B by path I and B → A by path II, the system could be brought back to its original state, but there would be a net gain of energy. In other words energy have been created without the disappearance of an equivalent amount of another kind.

The resultant energy in passing from the state 'A' to the state 'B' depends only on the initial and final conditions and is independent of the path followed in going from A → B

If, E_A = Energy in the state 'A'

E_B = " " " 'B'

Then, the change in energy in passing from A to B is

$$\Delta E_I = E_B - E_A \quad \text{(} \Delta E \text{ is independent of the path)} \quad \ldots (1)$$

E = Internal energy of the system

$\Delta E_{II} = E_A - E_B$

$\therefore \Delta E_{II} = -\Delta E_I$

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Let us assume that $\Delta E_2 > \Delta E_1$. This means that energy must have been created in going around the cycle by two different paths. This is in contradiction to the first law of thermodynamics, hence

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$$\Delta E_2 = -\Delta E_1$$

$$\Delta E_{A \to A} = \Delta E_1 - \Delta E_2 = 0$$

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The properties of a system may be distinguished as being either Extensive or Intensive.

Extensive property :- depends upon the amount of the substance present in the system. If the quantity of material in the system is changed the extensive property is changed in a proportional manner. Volum 'V' and mass 'm' are examples of extensive properties, heat capacity, Internal Energy, Entropy

Intensive property :- A specific characteristic of the system and is independent of the amount of material concerned, e.g. Temp., density, surface tension, refractive index, viscosity, chem. potential. All these properties are characteristic of the substance and are independent of its amount

Work, Heat and Energy

Work (w) is done when an object is moved against an opposing force. Example of doing work is :-

- The expansion of a gas that pushes out a piston and raises a weight.
- A chemical reaction that drives an electric current through a resistance also does work because the same current could be driven through a motor and used to raise a weight.

When a system changes from one state to another, it may perform some kind of external work such as :- mechanical work as expansion, electrical work etc.

The Energy of the system is its capacity to do work e.g. by compressing a gas or winding a spring the capacity to do work is increased so the energy of the system is increased.

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When the system does work (e.g when the piston moves out or the spring unwinds) its energy is reduced because it can do less work than before.

The energy of the system (its capacity to do work) may be changed by means other than work itself. When the energy of a system changes as a result of a temperature difference between it and its surroundings, we say that the energy has been transferred as heat. e.g. when a heater is immersed in a beaker of water (the system), the capacity of the system to do work increases because hot water can be used to do more work than cold water.

Work is represented by the symbol (w).

- w is positive if work is done by the system (e.g. expansion of a gas)
- w is negative if work is done on the system (e.g. compression of a gas)

The system may absorb or evolve heat

The quantity of heat is represented by (q)

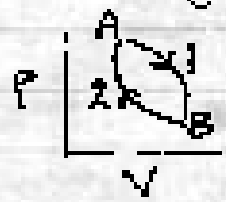
- q is positive if the system absorbs heat
- q = negative = heat is evolved by the system.

According to the first law of thermodynamics, the total system and surroundings must remain unaltered as the system changes from A → B (Fig. 1)

Then the change in the internal energy (ΔE)

$\Delta E = q - w$ (Mathematical Statement of the 1st Law)

The change in internal energy of the system (ΔE) must exactly equivalent to the energy absorbed in the form of heat (q) from the surroundings minus the energy lost to the surroundings in the form of external work (w)



$\Delta E_1 = E_B - E_A$

$\Delta E_2 = E_A - E_B$

$\Delta E_{A \to A} = \Delta E_1 + \Delta E_2 = 0$

$\Delta E_1 = -\Delta E_2$

For an infinitisimal process, the 1st Law is written as:

$dE = dq - dw$

dE = small change in the internal energy

dq = " " amount of heat absorbed

dw = " " " " external work done by the system.

<u>Pressure-Volum work</u> (e.g) Expansion work

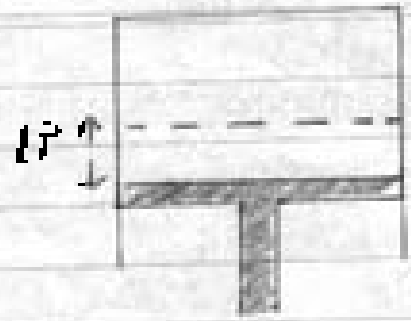
The work arising from a change in volume and pressure. The work done by a gas as it expands and drives back the atmosphere, examples.

Chemical reactions resulting in the generation or consumption of gases (thermal decomposition of calcium carbonate or the combustion of octane)

In order to find the pressure volume work involved in the expansion of a gas against external force, consider a cylinder of cross sectional area A fitted with a frictionless and weightless piston.

Let, pressure on the piston = P

Since pressure is force per unit area, the total force acting on the piston is :-



$$F = P.A \quad \ldots (1)$$

As a result of expansion, suppose the piston moves through a distance "dl". The small amount of work done by the gas on the surroundings

$$dW = F\,dl \quad \ldots (2)$$

substitute (1) into (2)

$$dW = PA\,dl \quad \ldots (3)$$

But $A\,dl = dV$ = increase in volume due to the movement of the piston.

Therefore,

$$dW = P\,dV \quad \ldots (4)$$

The total work in the expansion of the gas from initial volume V_1 to the final volume V_2 is then obtained by integrating equation (4) between the limits V_1 and V_2 :-

$$W = \int_{V_1}^{V_2} P\,dV \quad \ldots (5)$$

If this is the only type of work done by the system, then substitution of equation (5) in the first law expression gives :-

$$\Delta E = q - \int_{V_1}^{V_2} P\,dV \quad \ldots (6)$$

Equations (5) and (6) are perfectly general and can be utilized to calculate W, q and ΔE in any expansion and compression of the system.

Special cases

(a) Constant volume

When there is no change in volume, $dV = 0$ and equation (6) takes the form :-

$$\Delta E = q$$

(i.e) Any thermal change occuring in the calorimeter at constant volume must be the change in the internal energy due to the chemical reaction or physical transformation.

(b) Opposing pressure Zero

When the gas expands against a zero external pressure, no work is done and hence again ..

$$\Delta E = q$$

This type of expansion is called free expansion

(c) Opposing pressure constant

When P is constant, equation (5) becomes :-

$$W = P(V_2 - V_1)$$

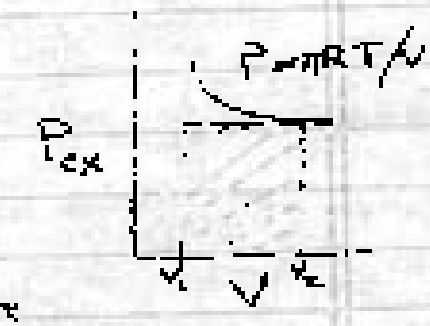
and equation (6) becomes :-

$$\Delta E = q - P(V_2 - V_1)$$

(d) Opposing pressure variable

If 'P' is variable, it must be known as a funct volume. So equation (5) can be integrated and

or the integration is carried out graphically by plotting P versus V and determining the area under the curve. When W is known, it can be substituted into equation (6) to determine ΔE or q



In all calculations of W involving gas expansion it must be kept in mind that when a volume change occurs the amount of work done by the gas on the surroundings depends on the pressure that the surroundings exert on the system rather than the pressure within the system itself.

Note that the pressure in equation (5) is always the quantity

W will be positive if $V_2 > V_1$ (expansion)

A positive value of W means that work is done by the gas on the surroundings. This is what happens when a system expands pushing back the surroundings

On the other hand if $V_2 < V_1$, then we have a compression W is negative and work is done by the surroundings on the gas.

<u>Conclusion</u>

In any expansion, the system does work

In a compression, work is done on the system.

Reversible Processes

Reversible processes are processes that may be reversed at any moment by changing an independent variable by an infinitesimal amount. A process is said to be reversible when the properties of the system at every instant remain uniform during the process. It can be described as a succession of states each of which is a state of equilibrium. Reversible process is an extremely slow process and would

If the gas is compressed, the final volume is smaller ($V_2 < V_1$) and W_{rev} is positive ($W > 0$). That means the work is done on the gas (eng)

Example :- How much work we get from the expansion of 1 mole a perfect gas by a factor of (10) at 273 K ?

Solution :- $W_{rev} = -RT \ln 10 = -5229\ J.mole^{-1}$

When $V_2 < V_1$ -- compression -- $W > 0$ work is +ve
work is done on the gas

When $V_2 > V_1$ -- expansion -- $W < 0$ work is -ve
work is done by the gas

Example

Calculate the maximum work in ergs for the expansion of 1 mole of an ideal gas from a volume of 10 liters to 20 liters exactly at 25°C.

Since for a perfect gas at constant temperature

$P_1 V_1 = P_2 V_2$ (at constant temp.)

so :-

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

substituting in equation (8), the maximum work in isothermal expansion can also be written as :-

$$W_{rev} = -nRT \ln \frac{P_1}{P_2} \quad \text{---- (9)}$$

[illegible]

[illegible] 303 kJ g[illegible]

[illegible] erg · mol[illegible]

require an infinite time.
In Irreversible process the change is produced rapidly and the system does not have change to achieve equilibrium
Reversible processes are of great importance because they yield the maximum amount of work obtained from a given net change.
In Irreversible processes, less work is obtained than would be required to return the system to its initial state. (e.g)
Reversible expansion when P_{ex} equal to P at each stage of expansion

$$W_{rev} = -\int_{V_1}^{V_2} P\,dV = \text{Total work of expansion} \quad \text{---(7)}$$

<u>Conclusion</u>:- Only if the expansion is carried out reversibly at const temperature can sufficient energy be obtained to reverse the process compressing the gas to its original conditions.

<u>Reversible Isothermal Expansion of a Real gas</u>
The system in thermal contact with its surroundings

$$PV = nRT \quad \text{(Equation of state)}$$

The pressure at each stage of expansion is expressed as:-

$$P = nRT/V$$

where P, V are pressure and volume at each step of expansion
T = constant (Isothermal expansion)
n, R have constant values
Substituting P in equation (7) we obtain:-

$$W_{rev} = -nRT\int_{V_1}^{V_2}\frac{dV}{V} = -nRT\ln\frac{V_2}{V_1} \quad \text{---(8)}$$

#SARTSH

Heat Capacity

The heat capacity of a system is defined as the heat required to raise the temperature of the system by one degree.

$$C = \frac{dq}{dT} \quad \ldots (1)$$

dq = the heat absorbed when the temperature is raised by (dT) degree

The heat capacity at constant volume and pressure is given by :-

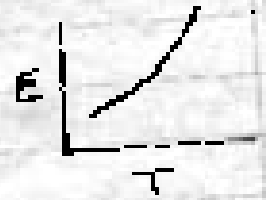
$$C_v = \frac{dq_v}{dT} \quad \text{(at const. volume)} \quad \ldots (2)$$

$$C_p = \frac{dq_p}{dT} \quad \text{(at const. pressure)} \quad \ldots (3)$$

The internal energy (E) of a substance increases when the temp. is raised. This increase depends on the conditions under which the heating takes place

The heat absorbed at constant volume is equal to the increase in internal energy under the same conditions

$$dE_v = dq_v$$



Equation (2) may be written as

$$C_v = \left(\frac{dE}{dT}\right)_v \quad \text{(const. volume)}$$

The internal energy is a function of T and V. For an ideal gas, E is independent of the volume. Therefore

$$C_v \text{ (ideal gas)} = \frac{dE}{dT}$$

The heat capacity is <u>extensive property</u>, (e.g) 100 gm of water has 100 times the heat capacity of 1 gm of water and therefore requires 100 times the heat to bring about

same rise in temperature

<u>Molar heat capacity</u> (at constant volume), C_{vm} is :- the heat capacity per mole of material and is an <u>intensive property</u>. All molar quantities are intensive.

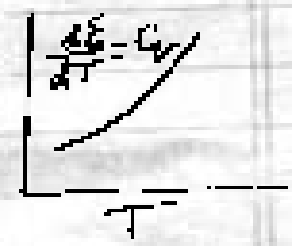
<u>Specific heat capacity</u> of a substance is :- The heat capacity of a sample divided by the mass, usually in grams (e.g.) the specific heat capacity of water at room temp (25°C) is close to ($4\ J.K^{-1}.g^{-1}$)

The heat capacity can be used to relate a change in the internal energy (E) to a change in temperature (T) at constant-volume system.

$$dE = C_v\, dT \quad \text{at constant volume}$$

(i.e) the infinitesimal change in temp varies about an infinitesimal change in internal energy and the constant proportionality is the heat capacity at constant volume (C_v).

$$\Delta E = C_v\, \Delta T \text{ (at const. volume)}$$



This relation provides a simple way of measuring the heat capacity of a sample, example :-
A measured quantity of heat is supplied to the sample (e.g. electrical) and the resulting increase in temperature is monitored. The ratio of the heat supplied to the temperature rise is the heat capacity of the sample.

A large heat capacity means that for a given quantity of heat, there will be only a small increase in temperature (i.e. the sample has a large capacity for heat, and

An infinite heat capacity means that there will be no increase in temperature however much heat is supplied

example :- At a phase transition (such as boiling point of water) the temperature of water does not rise as heat is supplied that means the energy is use to drive endothermic phase transition (to vaporize the water) rather than to increase its temperature. So at the temperature of phase transition, the heat capacity of a sample is infinite (∞)

Example :- Most systems expand when heated at constant pressure. such systems do work on the surroundings and some of the energy supplied to them as heat escapes back to the surroundings. As a result the temperature of the system rises less than when the heating occurs at constant volume.

A smaller increase in temperature means a larger heat capacity $C = \frac{dE}{dT}$. So we conclude that :-

At constant pressure, the heat capacity of a system is larger than the heat capacity at constant volume.

for a perfect gas $(PV = nRT)$

At const press. $P\left(\frac{dV}{dT}\right)_P = nR$

The relations between the heat capacities of a perfect gas

$$C_P - C_V = nR$$

∴ The heat capacities of a perfect gas at const press. and const volume differ from each other by a constant amount equal to the gas constant (R)

Enthalpy

The change in internal energy is not equal to the heat supplied when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work, so (dE) is less than (dq) ($dE = dq - W$). In this case, the heat supplied at constant pressure is equal to the change in another thermodynamic property of the system called the "Enthalpy".

As constant-pressure processes are more common in chemistry than constant-volume processes because most operations are carried out in open vessels, and if only pressure-volume work is done and the pressure is constant, the work done on the system will be :-

$$W = P\Delta V \quad \ldots\ldots (1)$$

$$E = q - W$$

$$\therefore E = q - P\Delta V \quad \ldots\ldots (2)$$

$$E_2 - E_1 = q - P(V_2 - V_1) \quad \ldots\ldots (3)$$

V_1 = Initial volume $\qquad E_1$ = Initial internal energy

V_2 = Final " $\qquad E_2$ = Final " "

So that the heat absorbed in equation (3) is given by :-

$$q = E_2 - E_1 + PV_2 - PV_1 \quad \ldots\ldots (4)$$

$$q = (E_2 + PV_2) - (E_1 + PV_1)$$

The heat absorbed is equal to the difference of two quantities that are functions of the state of the system

$$\text{let} \quad H = E + PV = \text{Enthalpy.}$$

E, P, V are state functions, then the enthalpy "H" is a state function

The change in enthalpy (ΔH) between any pair of initial and final states is independent of the path between them

$$H_2 - H_1 = \Delta H = q_p$$

At constant pressure, the change in enthalpy is equal to the heat supplied to the system (if the only work done is the pressure - volume work)

<u>example</u> :- to calculate ΔE and ΔH in a constant volume calorimeter, the evolution of heat (q) is the measure of the decrease in internal energy ΔE ($q = \Delta E$).

In a constant pressure calorimeter, the evolution of heat (q) is a measure of the decrease in enthalpy (ΔH)

$$\boxed{(q = \Delta H)}$$

<u>proof</u> of the example.

When pressure-volume work is the only kind of work

$$H = E + PV \quad \ldots\ldots (1)$$

For a general infinitesimal change in the state of the system E changes to $E + dE$, P changes to $P + dP$ and V changes to $V + dV$, so H changes from $(E + PV)$ to :-

$$H + dH = (E + dE) + (P + dP) \times (V + dV)$$

$$H + dH = E + dE + PV + PdV + VdP + dPdV \quad \ldots (2)$$

The term ($dPdV$) is the product of two infinitesimal small quantities and can be neglected and as

$H = E + PV$ then equation (2) become :-

$$\cancel{H} + dH = \cancel{H} + dE + PdV + VdP \quad \ldots (3)$$

$$dH = dE + PdV + VdP \quad \ldots (4)$$

we know that :- $dE = dq + dw \quad \ldots (5)$

Substituting equation (5) into equation (4), we get :-

$$dH = dq + dw + PdV + VdP \quad \text{--- (6)}$$

If the system is in mechanical equilibrium with its surroundings at a pressure P and does only expansion work, then :-

$$dw = -PdV \quad \text{--- (7)}$$

Substitute (7) into (6) we get :-

$$dH = dq - PdV + PdV + VdP$$

$$dH = dq + VdP \quad \text{--- (8)}$$

When the heating occurs at constant pressure then

$dP = 0$ (no change on pressure)

$$\boxed{dH = dq}$$ at constant pressure

[At constant pressure, the change in enthalpy is equal to the heat supplied to the system]

Adiabatic Processes

An adiabatic process is one in which there is no change of heat between the system and its surroundings (i.e) the system is thermally isolated from its environment.

Since no heat enters or leaves the system, then ($q = 0$) and work is done at the expense of the internal energy of the gas and the temperature drops.

Thus if work is done on the system, the internal energy of the system (E) will increase. Conversely if work is done by the system, the internal energy of the system decreases and consequently the temperature of the system drops

From the First Law, we have $dE = q - w$

For adiabatic process, $q = 0$

$$\therefore dE = -w = -PdV \quad \text{--- (1)}$$

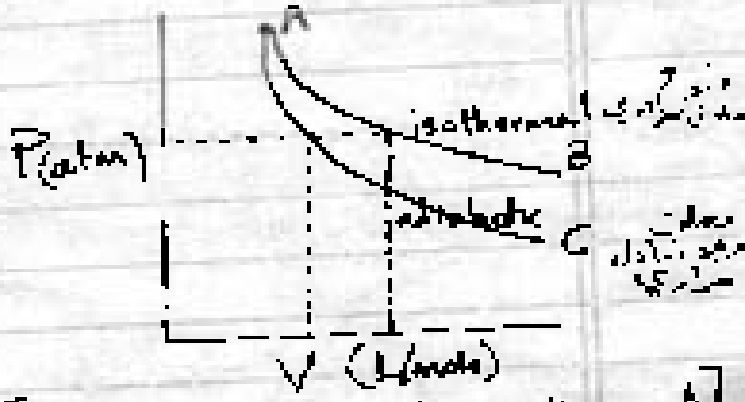
since, $dE = CdT \quad \text{--- (2)}$

Isothermal process

In isothermal process the temperature is maintained constant during the entire operation and PV = constant. For the same initial pressure and volume (P_1, V_1), isothermal expansion results in a larger final pressure than the final pressure for adiabatic expansion ($P_{2,isothermal} > P_{2,adiabatic}$).

- The reason for this lies in the fact that:- adiabatic expansion is accompanied by a fall in temperature which will diminish the volume, but in isothermal process the temperature is constant.

When a gas expands adiabatically to a larger volume and lower pressure, the volume is smaller than it would be after an isothermal expansion to the same pressure.



[Plots of P & V for isothermal and adiabatic expansions]

The work done by the isothermal reversible expansion of the gas represented by the area under AB is larger than the work done by the reversible adiabatic expansion represented by the area under AC. The energy for doing the additional work in the isothermal expansion is provided by the heat absorbed from the constant temperature reservoir. The energy for doing work in the adiabatic expansion comes from the cooling of the gas itself.

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proof of the example.

when pressure - volume work is the only kind of work

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$$\boxed{dH = dq} \quad \text{at constant pressure}$$

[At constant pressure, the change in enthalpy is equal to the heat supplied to the system]

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For adiabatic process, $q = 0$

$$\therefore \quad dE = -w = -PdV \quad ---- (1)$$

since, $dE = CdT \quad ---- (2)$

Ex Determine the work of isothermal reversible expansion of 3 moles of water vapor from 0.5×10^5 to 0.2×10^5 Pa at 330 K

Water vapor obeys the law of ideal gaseous state

$$W = nRT \ln \frac{V_f}{V_i}$$
$$= nRT \ln \frac{P_i}{P_f}$$
$$W = 3 \times 8.314 \times 330 \times \ln \frac{0.5\times10^5}{0.2\times10^5}$$
$$= 7.542 \times 10^3 \text{ J}$$

Ex How much work is done in the adiabatic expansion for the expansion of 3 mole of perfect gas from 22.4 L to a volume of 44.8 L at

$$W = \int C_v dT = R \ln \frac{V_f}{V_i}$$
$$= 3 \times 8.314 \times \ln \frac{22.4}{44.8}$$

Substituting eq (2) into (1)

$$C\,dT = -P\,dV \quad \ldots (3)$$

For an ideal gas, $PV = nRT$

For 1 mole, $P = \frac{RT}{V}$

Substituting the value of P into eq (3)

$$C\,dT = -\frac{RT}{V}\,dV$$

$$C\frac{dT}{T} = -R\frac{dV}{V} \quad \ldots (4)$$

assuming that C is independent on temp.

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R\int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_v \ln\frac{T_2}{T_1} = R \ln\frac{V_1}{V_2} \quad \ldots (5)$$

Equation (5) is an approximate equation for reversible adiabatic expansion.

In adiabatic expansion if $T_2 < T_1$, Temp will fall

" " Compression $T_2 > T_1$, " " rise

Reversible work in adiabatic expansion

$$\Delta E = W - q$$

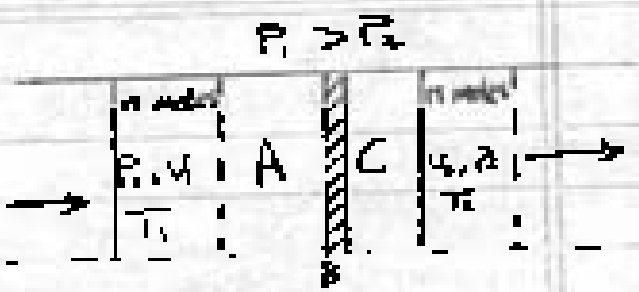
For adiabatic expansion, $q = 0$

$$\Delta E = W$$

$$\Delta E = C_v \Delta T$$

$$\therefore \boxed{\Delta E = W = \int_{T_1}^{T_2} C_v\,dT = C_v \ln\frac{T_2}{T_1}} = R \ln\frac{V_1}{V_2}$$

Joule – Thomson effect



A gas from a high pressure region (A) is allowed to pass to a low pressure region (C) through a throttle (B) which consists of a porous plug.
The gas emerging at (C) attains an equilibrium and its temperature can be measured directly. The entire system is thermally isolated so that the process is an adiabatic one ($q = 0$).
Let P_1, V_1, T_1 be the pressure, volume and Temperature of the gas befor it expands and P_2, V_2, T_2 be the final pressure, volume and the temperature of the gas.
The work done on the gas before it is forced through the porous plug will be ($W = P_1V_1$) and the work done by the gas in expansion will be ($W = P_2V_2$) and hence the net work done by the system :-

$$W = P_2V_2 - P_1V_1$$

Since the process is being carried out adiabatically, then $q = 0$ and therefore applying the first law :-

$$\Delta E = E_2 - E_1 = \overset{-W}{W} = -(P_2V_2 - P_1V_1)$$

$$E_2 - E_1 = P_1V_1 - P_2V_2$$

$$E_2 + P_2V_2 = E_1 + P_1V_1$$

Since, $H = E + PV$

$\therefore$ $H_2 = H_1$ or

$\Delta H = 0$ (for adiabatic process (proof))

(The heat content of a system during its expansion remains constant

Isothermal process

In isothermal process the temperature is maintained constant during the entire operation and PV = constant.
For the same initial pressure and volume (P_1, V_1), isothermal expansion results in a larger final pressure than the final pressure for adiabatic expansion ($P_{2\,isothermal} > P_{2\,adiabatic}$).
The reason for this lies in the fact that :-
adiabatic expansion is accompanied by a fall in temperature which will diminish the volume, but in isothermal process the temperature is constant.
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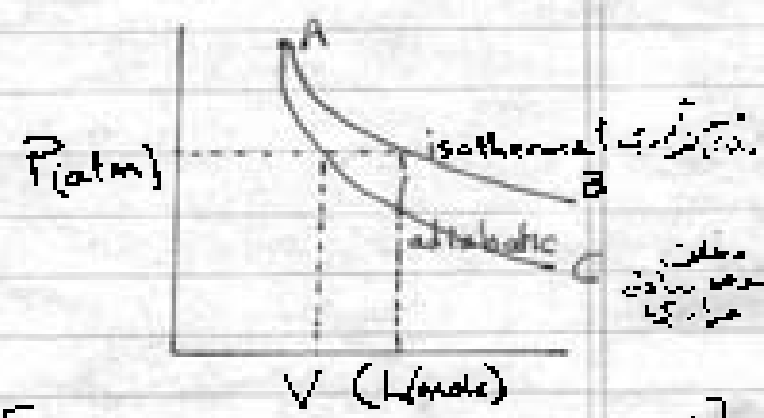

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Thermochemistry

[illegible] subject that deals [illegible] by chemical react[ion] [illegible] accompanying chemical [illegible]
[illegible] of thermochemistry are based [illegible] [ther]modynamic or the [illegible]

[illegible]

[Reac]tants ⟶ Products

[illegible]

[illegible]

[illegible]

Standard state for the heat [illegible]

The value of enthalpy (H) and [illegible] will depend on the temperature and pressure [illegible] The temp. of 25°C (298 K) and [illegible] are generally used as standard conditions [illegible] (pure solids, liquids and ideal gases).

If the reactants and products are in the standard state (25°C and 1 atm.), the heat transferred [illegible] standard heat for that reaction referred as :- ΔE°, ΔH° standards i.e. the initial and final substances are in their standard states.

More recently, the standard state is defined at pressure of 1 atm. at any specified temperature. The standard state at a specified temperature is its pure form at 1 atm.

examples :- [illegible] standard state [illegible] pure ethanol (C_2H_5OH) at 25°C (298 K) [illegible]

Pure liquid [illegible] 1 atm.

The standard [illegible]

pure iron ([illegible]) [illegible]

The [illegible] standard [illegible]

[illegible]

Heat of [illegible]

The standard [illegible] energy (ΔH°) [illegible]

process is the difference between the enthalpy of the products in their standard states and the enthalpy of the reactants in their standard states.

<u>Example (2)</u> for a standard enthalpy change [illegible]

The standard enthalpy of vaporization (ΔH_{vap}) is the enthalpy change per mole of pure liquid that vaporizes to gas at 1 atm [illegible]

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H^\circ_{vap}(373\ K) = +40.66\ kJ/mol$$

The standard enthalpy (ΔH°) may be reported for any temperature. However, the conventional temp. for reporting thermodynamic data is (25°C or 298 K). All thermodynamic data will refer to this conventional temp. unless otherwise mentioned.

<u>Example</u>: The reaction between solid carbon (graphite) and gaseous oxygen to yield carbon dioxide gas at 25°C (chemical change)

$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^\circ_{298} = -94.05\ kcal$$

This means that when 1 mole (12 gms) of solid carbon and 1 mole (32 gms) of gaseous oxygen react completely at 25°C to yield 1 mole (44 gms) of gaseous carbon dioxide at constant pressure (1 atm). There is a decrease in enthalpy, since ΔH is negative of 94.05 kcal. The negative value of ΔH means that the enthalpy of the products is less than that of the reactants at the specified temp. In other words, the reaction at a given temp. is associated with an evolution of heat.

ΔH is -ve, the reaction is exothermic.

The standard heats of formation of chemical compounds are listed in index tables.

[illegible] of carbon

[illegible]

The [illegible] formed from its elements in their standard [illegible] stable forms at ordinary temp. and [illegible]

In the reaction between carbon (C) and [illegible] Carbon dioxide (CO_2), the standard heat [illegible] to form carbon dioxide (CO_2) is 94.05 [illegible] is the stable form of carbon and hence [illegible] state of the element.

example

The thermodynamic [illegible] hydrogen iodide is [illegible]

[illegible] $\longrightarrow$ 2 [illegible] $\Delta H^{\circ}_{f(298)}$ [illegible] 2 [illegible] of HI are formed, the heat of formation [illegible]

[illegible] simplicity in calculation, the [illegible] be calculated by assuming the [illegible] standard states to be zero and [illegible] heat of formation.

[illegible] formation of hydrogen [illegible]

[illegible] $I_{2(g)}$ — 2 [illegible] ΔH°_{f} [illegible]

[illegible] + $H_{2(g)}$ — [illegible]

[illegible] is formed [illegible] in enthalpy [illegible] H_2 and I_2 [illegible]

Example: Calculate the enthalpy of the reaction

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

	ΔH_f° (kcal)
$CO_2(g)$	[illegible]
$O_2(g)$	[illegible]
$H_2O(l)$	[illegible]

Example:

[illegible]

Heat of combustion

It is the enthalpy change accompanying the complete combustion of 1 mole of a compound.

Organic compounds [illegible]

[illegible]

[illegible]

The values of ΔH_f° for a [illegible] compound are tabulated [illegible] in each case.

[illegible] heat of combustion of benzene [illegible] = 781.0

[illegible] methane [illegible] 8 Kcal.

[illegible]

[illegible] compound equal to [illegible] by heat supplied

Example

[illegible] of liquid [illegible] [illegible] the [illegible] [illegible] boiling [illegible] [illegible]

[illegible]

Thermochemical Laws

The Laws of thermochemistry are based on the principle of conservation of energy, and hence on the first law of thermodynamics

The First Law of thermochemistry was given by Lavoisier and Laplace in 1780, stated that :-

The quantity of heat which must be supplied to decompose compound into its elements is equal to the heat evolved when the compound is formed from its elements.

Thus, if the reverse of a chemical reaction is written, the sign of (ΔH) is changed but its magnitude remains same.

$$\Delta H (A \rightarrow B) = -\Delta H (B \rightarrow A)$$

Example the heat evolved when water is formed from hydrogen and oxygen is exactly equal to the heat absorbed when water decomposes into hydrogen and oxygen

[illegible]

[illegible]

[illegible]

[illegible]

The second Law of thermochemistry discovered by Hess in 1840
The overall heat change in a chemical reaction carried out either at constant pressure or at constant volume is the same irrespective of the fact whether the reaction proceed in one or several steps (The Law of constant heat summation)
This is a direct consequence of the first law of thermodynamics according to which ΔE and ΔH are equal to the heats of reaction at constant volume and constant pressure respectively and are dependent only on the initial and final states of system.
(Constant volume, $q = \Delta E$) ; (Constant pressure, $q = \Delta H$)

[illegible] (The law of constant heat summation).
[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

$NH_{3(aq)}(2M)$ [illegible]

$HCl_{aq}(2M)$ [illegible]

$NH_{3(aq)} + HCl_{(aq)}(2M) \longrightarrow$ [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

Heat of Solution

[illegible]

[illegible] $HCl_{(g)}$ [illegible]

When a substance is dissolved in a large excess of a solvent, the heat of reaction is the heat of solution at infinite dilution.

[illegible] $HCl_{(g)}$ [illegible]

The heat evolved in the dilution of solution from one concentration to another concentration is called the integral heat of dilution.

[illegible] H_2SO_4 [illegible]

[illegible] aq [illegible]

Heat of neutralization

When aqueous [illegible] of acids [illegible] heat is evolved.

The heat of neutralization of the acid [illegible] in enthalpy when one gram equivalent of [illegible] neutralized by one gram equivalent of a base [illegible] solution

The heat of neutralization of one strong acid by one strong base is practically the same as the heat of neutralization

[illegible]

The neutralization of HCl by NaOH can be represented as

[illegible]

Hence every neutralization reaction involves the combination of H^+ and OH^- ions to form neutralized water.

The heat of neutralization of a strong acid by a strong base is independent because a strong acid or a strong base is completely ionized. The heat of neutralization of a strong acid by a strong base also takes place.

Example :- The neutralization of acetic acid by sodium hydroxide solution

CH_3COOH [illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

Hence the heat of neutralization of a weak acid or a weak base can be determined from the heat of neutrali

Example :-

The heat of neutralization of hydrocyanic acid (HCN) by sodium hydroxid (NaOH) is −29 kcal/gm equivalent at 25°C

Calculate the heat of neutralization at 100°C ?

HCN + NaOH ⟶ NaCN + H_2O + 29 kcal

Variation of heat of reaction with temperature

The enthalpy of the general reaction :-

Reactants ⟶ Products

is given by :-

$\Delta H = H_{products} - H_{reactants}$

Differentiating both sides of the equation with respect to temperature we get :-

$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_{products}}{dT}\right)_P - \left(\frac{dH_{reactants}}{dT}\right)_P$$

The heat capacity at constant pressure is :-

$$C_P = \left(\frac{dH}{dT}\right)_P$$

Therefore :-

$$\left(\frac{d\Delta H}{dT}\right)_P = C_{P\,products} - C_{P\,reactants}$$

or $$\left(\frac{d\Delta H}{dT}\right)_P = \Delta C_P$$

Similarly, at constant volume:

$$\left(\frac{\partial \Delta U}{\partial T}\right)_V = \Delta C_V$$

$$\Delta U_2 - \Delta U_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\boxed{\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)}$$

[illegible] = liquid

Exercise

The Standard heat of formation of liquid water is 68.3 kcal at 25°C. Calculate the value at [illegible]. The molar heat capacities at constant pressure in the given temperature range are :-

[illegible] ΔC_p, $H_{2g} = 6.84$, $O_{2(g)} = 6.77$, [illegible]

[illegible] units of $\Delta C_p = \text{Cal} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$

Solution

ΔH_f [illegible] at [illegible] $= -68.3$ kcal

[illegible] $\Delta H_{[illegible]} = -[illegible]$ kcal

[illegible] $= -[illegible]$ kcal

[illegible] $= [illegible] \times 10^{[illegible]}$ kcal

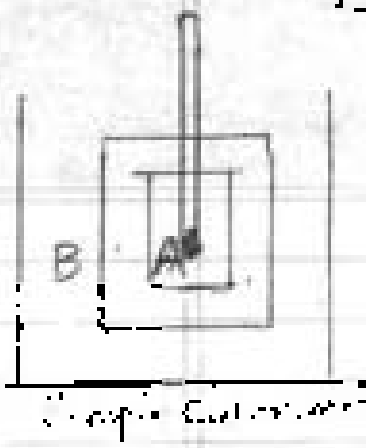
[illegible]

[illegible]

$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$

$\Delta H_2 = -68.3 + [illegible] \times 10^{-3} \times [illegible]$

$\Delta H_2 = -[illegible]$ kcal



Calorimetric Measurements

The calorimeter is used to measure the heat changes involved in chemical reactions by carrying out the process (chemical reaction) in a container (vessel 'A') containing a definite amount of water 'B'. If heat is liberated in the reaction, the temp. of the water rises, and if heat is absorbed, the temp. falls.

The heat change of the reaction equals the product of the rise or fall of temp. and the heat capacity of the water can be measured.

$$\Delta H = C \cdot \Delta T$$

Bond Energy:

The bond energy is defined as:- The average amount of energy (per mole) required to break a particular bond in a molecule, producing free atoms or radicals.

Thus, the C-H bond energy is ~~of~~ the amount required to dissociate 1 mole of methane (CH_4) into gaseous carbon and hydrogen atoms

$$(CH_4)\ H-\overset{H}{\underset{H}{C}}-H \longrightarrow C + 4H$$

For diatomic molecules like H_2, Cl_2, O_2 or polyatomic like NH_3 this energy is called 'bond dissociation energy'.

In polyatomic molecules, the energy required to break a given bond is dependent on the nature of the molecule or more specifically on the compound in question. For example, the energy required to break C-H bond in alkanes is not the same as the energy needed to break the same bond in alkenes. Therefore, the bond energy for polyatomic compounds is the average amount of energy required to break

Example

[illegible]

[illegible]

$\Delta H_{298} = [\ \ + 2(\ \ )] - [\ \ ] = [-179.9\ \ ]$
$= -205\ \ kJ/mol$

Heat of combustion:-

The enthalpy change accompanying the complete combustion of 1 mole of a compound

Organic compounds can be burnt in oxygen [illegible] and water as the sole products. (C_xH_yO [illegible])

ΔH_c° is referred to the standard heat [illegible] substances are in their standard states.

* The values for a number of familiar [illegible] found in index tables. The combustion products [illegible] and liquid H_2O in each case (e.g.

(2)

(3)

$+3O_2$

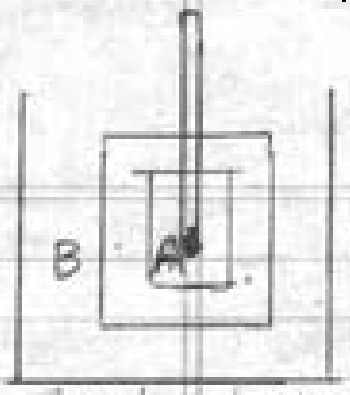
reactant

-3270

$x = -66.36$

ΔH_f° for liquid ethanol $= -66.36$

$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow C_2H_5OH_{(l)}$ $\Delta H_f = -66.36$ kcal



Simple Calorime

Calorimetry Measurement

The calorimeter is used to measure the heat changes involved in chemical reactions by carrying out the process (chemical reaction) in a suitable vessel immersed in a definite amount of water 'B'. If heat is liberated in the reaction, the temp. of the water rises, but if heat is absorbed the temp. falls.

The heat change of the reaction equals the product of the rise or fall of temp. and the heat capacity of the water (can be measured.

$\Delta H = m c \Delta T$

Bond Energy

The bond energy is defined as :- The average amount of energy (per mole) required to break a particular bond in a molecule, producing free atoms or radicals.

Thus the C-H bond energy is the amount required to dissociate 1 mole of methane (CH_4) into gaseous Carbon and hydrogen atoms

[illegible] molecules [illegible] a molecule [illegible] Mean average is called 'Mean Bond Energy'

In polyatomic molecules, the energy required to break a given bond may be different in different molecules and so the given compound is considered. For example, the energy required to break C-H bond in alcohol is not the same as the energy required to break the bond in aldehyde.

Therefore the bond energies tabulated are compared to the mean average amount of energy required to break

a particular bond in a mole of the compound
[illegible] the average bond in water vapour?

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

Example:

[illegible]

[illegible] $\longrightarrow$ [illegible]

	ΔH_f (Kcal)
$CH_{4(g)}$	[illegible]
$CO_{2(g)}$	[illegible]
$H_2O_{(l)}$	[illegible]

$\Delta H_{rxn} = [\ldots] - [-17.8]$ Kcal

$= -213.8$ Kcal

Heat of combustion:

The enthalpy change accompanying the complete combustion of 1 mole of a compound

Organic compounds can be burnt in oxygen [illegible] and water as the sole products. ($C_xH_yO_z$ [illegible])

ΔH_c° is referred to the standard heat of combustion [illegible] the substances are in their standard states.

- The values for a number of familiar compounds are found in index tables. The combustion products are [illegible] and liquid H_2O in each case (e.g.).

The second Law of Thermodynamics

Introduction

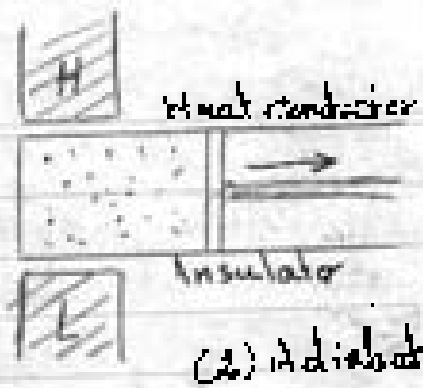
Some things happen naturally and some things don't (e.g.) :-
(a) Water runs downhill (b) A gas expands to fill the available volume
(c) The electricity tends to flow from a point of higher potential to one of low. (d) A chemical reaction runs from one direction rather than another (If aqueous solution of NaCl + $AgNO_3$ are mixed, AgCl is formed spontaneously).
This is the spontaneous direction of change that does not require work to be done to bring it about

<u>Question</u> Can we make water flow by itself upwards? Confine a gas to a smaller volume? Can we force some machine to go in reverse?
<u>Answer</u> Non of these processes happens spontaneously; each one must be brought about by doing work (Non-spontaneous processes).
<u>All naturally occurring processes always tend to change spontaneously in a direction which will lead to equilibrium.</u>
The second law of thermodynamics summarizes these two processes
- It is impossible for a cyclic process to take heat from a cold reservoir and convert it into work without at the same time transferring heat from a hot to a cold reservoir.

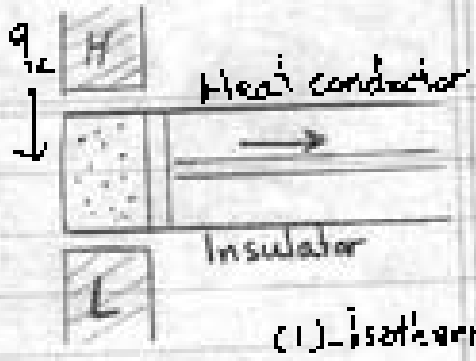
<u>or</u> It is impossible to construct a machine which is able to convey heat by a cyclic process from one reservoir at a lower temperature to another at higher temperature unless work is done on the machine by some outside agency.

The carnot cycle

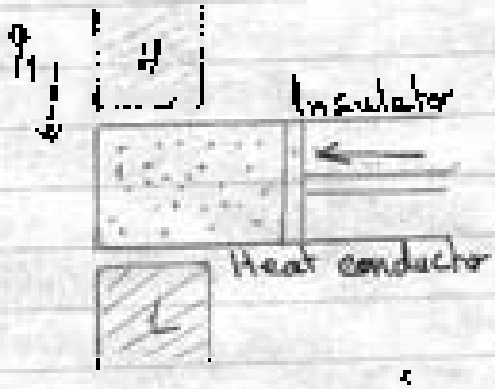
Carnot considered a hypothetical engine which converts heat into work by a cyclic process.
<u>Note</u> :- The cycle is a process in which a system returns to its original state after a succession of steps.



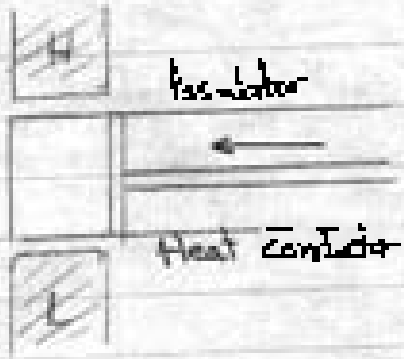
(2) Adiabatic expansion



(1) Isothermal expansion



(3) Isothermal compression



(4) Adiabatic compression

- The engine consists of a cylinder fitted with a weightless and frictionless piston and containing a given weight of a working substance. Two heat reservoirs at constant temperature T_2 (upper) and T_1 (Lower) respectively are also available.
- The Carnot cycle consists of four steps:-

1. Isothermal expansion
According to the first law :-
$$\Delta E_1 = q_2 - W_1$$

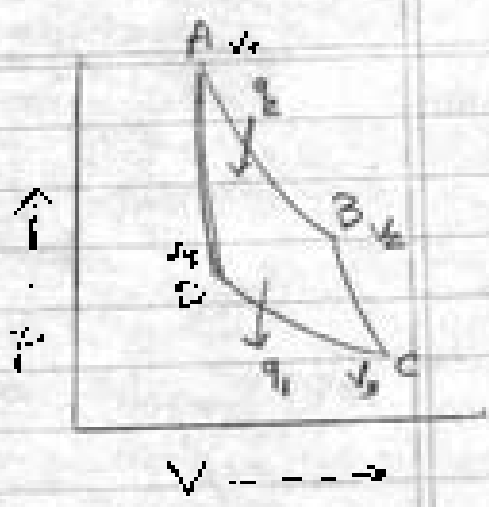
2. Adiabatic expansion
Since no heat is transferred, $q = 0$
According to the first law :-
$$\Delta E_2 = -W_2$$

3- Isothermal compression.

$$\Delta E_3 = -q_1 - W_3$$

4- Adiabatic compression.

$$\Delta E_4 = -W_4$$



A → B	Isothermal reversible expansion	
B → C	Adiabatic = =	
C → D	Isothermal =	Compression
D → A	Adiabatic =	=

As a result of these four stages, the system has returned to its original state.

The total change in energy for the complete cycle is :-

$$\Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 + \Delta E_4 \quad \ldots (1)$$
$$= (q_2 - W_1) - W_2 - (q_1 + W_3) - W_4$$
$$= q_2 - q_1 - (W_1 + W_2 + W_3 + W_4)$$

$$\Delta E = q_2 - q_1 - W_m \quad \ldots (2)$$

Where, W_m = net work in the complete cycle.
Since the sum of internal energy for the cyclic process is zero, then :-

net work $W_m = q_2 - q_1$ ... (3)

Only a portion of the heat taken in from the hot reservoir can be converted into work.
The efficiency of a machine is the fraction of heat absorbed at the higher temperature by the engine that it can convert into work.

$$\varepsilon = \frac{W_m}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

where, ε = efficiency of the carnot cycle.
ε is always less than unity ($\varepsilon < 1$) as $q_1 < q_2$

No engine can be constructed which completely convert all the heat energy supplied to it into work. Also ε is determined only by q_2 and q_1 and is independent on the nature of the working substance.

Entropy

In order for the reaction to be reversed, the heat involved in the original reaction would need to be completely converted into electrical energy without leaving changes in other parts of the system, therefore :-
All natural processes (processes occuring without external aid) are thermodynamically irreversible in character (spontaneous)
A characteristic of spontaneous process is that they are accompanied by an increase in the disorder of the system.
The entropy can be regarded as a measure of the disorder or random arrangement of the molecules of a system. examples :-
Fusion and evaporation are both associated with an increase of entropy of the substance concerned as there is a decrease of order in each instance.

In the solid state, the atoms, ions or molecules are arranged in a regular manner in the crystal lattice. Upon melting, most of the order is destroyed and evaporation results in a further increase of disorder.

* Increase of a temperature of a gas at constant pressure and increase of volume at constant temperatures are both processes for which the entropy of the gas is increased. In each case molecular disorder is increased.
* Lowering the temperature of a solid results in a decrease of entropy as the molecules or atoms become more and more ordered in their space lattices. At the absolute zero of temperature when the order is probably perfect, the entropy of most pure solids is actually zero.

Entropy is the function of spontaneity. It is a state function i.e. it depends only on the state of a substance or system and not on its previous history.

The increase of entropy (dS) in the course of the infinitesimal change is equal to (dq) the heat absorbed when the change is carried out in a reversible manner divided by the absolute temperature

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

The increase of entropy for a finite change in a system between initial state and final state can be expressed as:-

$$\Delta S = S_2 - S_1 = \int_{T_1}^{T_2} \frac{dq}{T}$$

S_1 = Actual entropy value in the initial state
S_2 = " " " " " final state

The value of ΔS depends only on the initial and final states of the system and not on the nature of the path.

Entropy change in a reversible process

The total entropy change of the system in a reversible process (e.g. in a Carnot cycle) must be zero since the system has returned exactly to its original thermodynamic state.

$$\Delta S = \oint \frac{dq_{rev}}{T} = 0$$

To calculate the entropy changes of systems and surroundings for a reversible isothermal process :-

Entropy change of the system is :-

$$\Delta S_{system} = \frac{q}{T}$$

At the same time the heat lost by the surroundings $= -q$

hence, the entropy change of surroundings is :-

$$\Delta S_{surroundings} = -\frac{q}{T}$$

The total change of entropy during expansion is then :-

$$\Delta S_{expansion} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= \frac{q}{T} - \frac{q}{T} = 0$$

and the total entropy change during compression is :-

$$\Delta S_{compression} = \Delta S_{system} + \Delta S_{surroundings}$$

$$= -\frac{q}{T} + \frac{q}{T} = 0$$

The total entropy change for the complete cycle is :-

$$\Delta S_{Total} = \Delta S_{expansion} + \Delta S_{compression} = 0$$

Conclusions

In a reversible isothermal process the entropy change of the system and surroundings is always zero.

or The total entropy change for a reversible isothermal cycle is zero i.e (at the end of the cycle the system has the same entropy as it had in the initial stage.

Entropy change in an irreversible process

Irreversible processes are those which have a natural tendency to occur. These processes are spontaneous. The driving force that causes reactions to occur spontaneously is the lack of balance in these processes

The work done by irreversible expansion is less than the work done in a reversible compression. The heat absorbed for irreversible expansion will also be less than heat absorbed for reversible expansion.

$$q_{irreversible} < q_{reversible}$$

$$W_{irrev.} < W_{rev.}$$

Since ΔS is a function of state (i.e) it depends on initial and final states irrespective of how the process is carried out. Entropy change for the system consisting of an ideal gas which is allowed to expand spontaneously from V_1 to V_2 means that the entropy has increased by an amount

given by the equation :- $\Delta S = R \ln \frac{V_2}{V_1}$.

For any irreversible cyclic process, the increase in entropy is due to the conversion of work into heat. Since the working substance has returned to its original state, it suffers no change of any kind. But the surroundings lost heat equal to q in the irreversible expansion and gained heat in the reversible compression. The net heat gained by the reservoir is :- $(q_{rev} - q)$

where q = heat lost, q_{rev} = heat gained

$$\Delta S = \left(\frac{q_{rev}}{T} - \frac{q}{T} \right)$$

Since $q_{rev} < q$, $\Delta S > 0$

and the net work on the cycle $= W - W_m = < 0$

where :-

W = work done by the working substance (gas)

W_m = " performed on the gas by surroundings

A negative value of the net work means that work is done on the working substance resulting in the liberation of heat which is taken by surroundings, thus causing entropy increase in surroundings. ($\Delta S = 0$ for reversible process & $\Delta S > 0$ for irrev.)

Since all natural processes are spontaneous and irreversible, they must occur in an increase of entropy and therefor :-

The entropy of the universe is continually increasing

<u>According to first law of thermodynamics</u> :-

The energy of the universe is constant

<u>According to 2nd law</u>

The entropy of the universe is continually increasing and tends to a maximum

Entropy changes for an ideal gas

Exercise Calculate the entropy change of a sample of perfect gas when it expands reversibly from volume 'V_1' to volume 'V_2'

Solution:- The heat absorbed "q" during reversible isothermal expansion of a perfect gas is to be calculated from the first law equation

$$\Delta U = q + w \qquad \ldots (1)$$

Since $\Delta U = 0$

$$q = -w \qquad \ldots (2)$$

Because the temperature T is constant

$$\Delta S = \frac{q_{rev}}{T} \qquad \ldots (3) \quad (\text{from } (2))$$

From the equation of state, $pV = nRT$

$$p = \frac{nRT}{V} \qquad \ldots (4)$$

The work of reversible expansion of an ideal gas from V_1 to V_2 at constant temperature is

$$w = -\int p\,dV \qquad \ldots (5)$$

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \qquad \ldots (6)$$

From eq (2)

$$q = -w$$

$$q = nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = \frac{q}{T} = nR \ln \frac{V_2}{V_1} \qquad \ldots (7)$$

Exercise Calculate the change in entropy when the volume of a perfect gas is doubled at constant temp

Entropy and change of state

The entropy of a system is determined by the freedom possessed by the molecules in the system. It can be regarded as a measure of the disorder or random arrangement of the molecules of a system. Melting and evaporation are both accompanied by an increase of entropy as the molecules move from a more ordered state to a less ordered state.

In the solid state, the atoms or molecules are arranged in a regular manner in the crystal lattice. Upon melting most of the order is discharged and vaporization results in a further increase of disorder.

Increase of temperature of a gas at constant V and increase of volume at constant T are both processes for which the entropy of the gas increases, because in each case the number of microstates is increased.

Increasing the temperature of a solid or liquid increases the entropy because the molecules move more rapidly in their equilibrium positions, and so the number of microstates is increased.

The entropy of a perfect crystal at absolute zero is zero.

The entropy of most substances is always positive.

The values of boiling points, molar heat of vaporization and entropy change per mole of some liquids are listed in the following table:-

Many liquids have the value of [illegible] which means that the increase in molecular [illegible]

[illegible] nearly the same [illegible] type

Liquid	Boiling point (°C)	Molar heat of vaporization	Entropy change per mole
[illegible]	[illegible]	9[illegible]	[illegible]
[illegible]	[illegible]	9522	[illegible]
Methanol	[illegible]	852	[illegible]
Ethylene glycol	[illegible]	5700	[illegible]
[illegible]	[illegible]	7322	[illegible]
[illegible]	[illegible]	65[illegible]	[illegible]
[illegible]	[illegible]	56[illegible]	[illegible]
[illegible]	[illegible]	6500	[illegible]
[illegible]	[illegible]	6960	[illegible]

The corresponding equations for the change in enthalpy during change in state (fusion, vaporization and sublimation) are given as :-

$$\Delta H_{fus} = \frac{\Delta H_{fus}}{T_m}, \quad \Delta H_{vap} = \frac{\Delta H_{vap}}{T_b}$$

$$\Delta H_{sub} = \frac{\Delta H_{sub}}{T_m}$$

ΔH_{fus}, ΔH_{vap} and ΔH_{sub} are molar heat of fusion, vaporization and sublimation respectively, and T_m, T_b are the melting and boiling points respectively.

The Third Law of thermodynamics

(The determination of entropies of substances)

When a system goes from an ordered state to a disordered state, the entropy is increased. The converse is also true.

A perfectly ordered crystal at the absolute zero of temperature would then have a zero entropy value, since the atoms in a crystal are perfectly ordered and confined to one position only.

The entropy of a pure perfect crystalline substance is zero at the absolute zero of temperature

The importance of this law lies that it permits the calculation of absolute value of entropy of pure substances from thermal data alone.

Example

Consider a process involving the transformation of a solid from the absolute zero of temp. to a temp. T where it melts point

The entropy change for such a process is given by:

$$\Delta S = S_T - S_0 = \int_0^T C_p \, dT = \int_0^S dS$$

S_T = entropy at temp T ; S_0 = entropy at $T = 0$

Since by the third law $S_0 = 0$

$$S_T = \int_0^T C_p \, dT$$

[illegible]

Absolute entropies may be used to calculate the entropy change accompanying chemical reactions. The standard entropy change for a general chemical reaction is the difference between the molar entropies of the pure products and the pure reactants in their standard states at the specified temp.

[illegible]

Example

[illegible] the entropy [illegible] (molar entropies for [illegible]

[illegible]

solution

[illegible] Σ [illegible]

Note: The 3rd law of Thermodynamics [illegible] to a ~~specific~~ special class of substances [illegible] perfectly crystalline substances and not to all [illegible]

Free energy functions

Consider a system in contact with a reservoir at temperature T in which an irreversible isothermal process occurs and the only work done is the PV work for the irreversible process. The entropy change of the system is

$$dS \geq \frac{q}{T} \quad \ldots \quad (1)$$

q - quantity of heat exchanged with a reservoir.

$$\therefore \; T\,dS \geq q$$

$$\therefore \; q - T\,dS \leq 0 \quad \ldots \quad (2)$$

Since work done is only PV work, from the first law

$$dU = q - w \qquad q = dU + P\,dV$$

$$q = dU + P\,dV \quad \ldots \quad (3)$$

substituting (3) into eq (2)

$$dU + P\,dV - T\,dS \leq 0 \quad \ldots \quad (4)$$

Equation (4) is applied for a spontaneous change and the only work done is the PV work.

If the volume and entropy of the system are held constant, equation (4) becomes

$$(dE)_{V,S} < 0 \quad \ldots \quad (5)$$

<u>For any irreversible process in a system of constant volume and does not change its entropy, the internal energy decreases</u>

1- The volume and internal energy of a system may be taken constant by isolating the system. Equation (5) becomes

$$-(T\,dS)_{E,V} < 0$$

multiply by (-1) and divide by T.

$$(dS)_{E,V} > 0 \qquad \ldots (6)$$

∴ The entropy must increase in such irreversible process. <u>In systems of constant energy and constant volume such as isolated system, the equilibrium position is in the direction of highest entropy</u>

2- System volume is not isolated, there are entropy changes in the surroundings, and if the volume is constant during the irreversible process, eqn (1) becomes.

$$(dE - T\,dS)_V < 0 \qquad \ldots (7)$$

$$d(E - TS)_{T,V} < 0 \qquad \ldots (8)$$

The quantity $(E - TS)$ is referred to the <u>Helmholtz free energy</u> represented by A

$$A = E - TS \qquad \ldots (9)$$

differentiation at const. temp.

$$dA = dE - T\,dS \qquad \ldots (10)$$

For a spontaneous process, equation (8) becomes

$$(dA)_{T,V} < 0 \qquad \ldots (11)$$

<u>In an irreversible process at constant temp. and volume the Helmholtz free energy A decreases</u>

4. For a system at constant "T" and "V", the P-V work term will be zero, i.e. system does no other work

$$\therefore \quad dA = 0 \qquad \ldots (13)$$

The condition of equilibrium for a system that can do no work is then :- $dA = 0$

5. The physical processes and chemical reactions which are of interest are usually carried out in the laboratory at constant "T" and "P". For such processes, equation (4) can be written as :-

$$d(E + PV - TS)_{T,P} < 0 \qquad \ldots (14a)$$

The quantity $(E + PV - TS)$ is referred to as the <u>Gibbs free energy</u> represented by "G"

$$\therefore \quad G = E + PV - TS \qquad \ldots (14)$$

$$G = H - TS \qquad \ldots (14)$$

and for infinitesimal change under isothermal conditions

$$\boxed{dG = dH - T\,dS} \qquad \ldots (15)$$

For a change at constant "P" and constant "T" and where only mechanical work is done, the free energy is equal to the enthalpy change minus the product of absolute temperature and the entropy change.

Equation (14a) can be written as :-

$$(dG)_{T,P} < 0 \qquad \ldots (16)$$

For <u>reversible</u> processes at <u>constant T, P</u> in which only <u>P-V work is done</u>, the <u>Gibbs free energy decreases</u>

Irreversible process	Reversible process
$(dS)_{E,V} > 0$	$(dS)_{E,V} = 0$
$(dE)_{S,V} < 0$	$(dE)_{S,V} = 0$
$(dA)_{T,V} < 0$	$(dA)_{T,V} = 0$
$(dG)_{T,P} < 0$	$(dG)_{T,P} = 0$

Maxwell Relations

From the 2nd law of thermodynamics :-

$$dS = \frac{q}{T} \quad \ldots (1)$$

From the 1st law :-

$$dE = q - PdV \quad \ldots (2)$$

Combining equations (1) & (2) :-

$$\boxed{dE = TdS - PdV} \quad \ldots (3)$$

The differentials for H, G, A may also be obtained

$$H = E + PV$$

$$dH = dE + PdV + VdP \quad \ldots (4)$$

substituting dE from equation (3) :-

$$dH = TdS - \cancel{PdV} + \cancel{PdV} + VdP$$

$$\therefore \boxed{dH = TdS + VdP} \quad \ldots (5)$$

$$A = E - TS$$

$$dA = dE - TdS - SdT \quad \ldots (6)$$

substitute (3) in (6) :-

$$dA = \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$\boxed{dA = -SdT - PdV} \quad \ldots (7)$$

$$G = H - TS$$

$$dG = dH - TdS - SdT \quad \ldots (8)$$

substitute (4) in (8) :-

$$dG = dE + PdV + VdP - TdS - SdT \quad \ldots (9)$$

substitute (3) in (9)

$$dG = TdS - \cancel{PdV} + \cancel{PdV} + VdP - \cancel{TdS} - SdT$$

$$\boxed{dG = -SdT + VdP} \quad \ldots (10)$$

The four fundamental equation of thermodynamics are :-

$$\boxed{\begin{aligned} dE &= TdS - PdV \quad \ldots (I) \\ dH &= TdS + VdP \quad \ldots (II) \\ dA &= -SdT - PdV \quad \ldots (III) \\ dG &= -SdT + VdP \quad \ldots (IV) \end{aligned}}$$

At constant P, $dP = 0$ in equation (IV)

$$\therefore \quad dG = -SdT$$

$$\left(\frac{dG}{dT}\right) = -S \quad \ldots (11)$$

and at const. T

$$dG = VdP$$

$$\left(\frac{dG}{dP}\right)_T = V \quad \ldots (12)$$

For an ideal gas :- $PV = nRT$

for 1 mole of an ideal gas :- $V = \frac{RT}{P}$

substituting V in equation (1) :-

$$\left(\frac{dG}{dP}\right)_T = \frac{RT}{P}$$

$$\Delta G = G_2 - G_1 = RT\int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1}$$

Exercise

Calculate the change in molar Gibbs energy of a perfect gas when the pressure is increased isothermally from 1.0 bar to 2.0 bar

At constant P, $S = -\left(\frac{dG}{dT}\right)_P$

$$\Delta S = S_2 - S_1 = -R \ln \frac{P_2}{P_1}$$

$$\therefore \boxed{S_2 = S_1 - R \ln \frac{P_2}{P_1}}$$

Exercise :-

The standard entropy of O_2 at 298 K is 205.03 $J \cdot K^{-1} \cdot mol^{-1}$. What is the entropy at 0.1 atmosphere?

Phase Equilibria

The relationship between variables in equilibrium between phases of one component (e.g. liquid and vapor, solid and vapor, solid and liquid ...etc can be obtained from a thermodynamic relationship :-

Consider a liquid in equilibrium with its vapor at temperature 'T' and pressure P. At equilibrium, let the temp. be changed to T+dT and pressure to P+dP.

For liquids :-

$$(dG)_l = V\,dP - S\,dT \quad \text{--- (1)}$$

For vapors of the liquids :-

$$(dG)_v = v\,dP - S\,dT \quad \text{--- (2)}$$

When two phases are in equilibrium :-

$$(dG)_l = (dG)_v \quad \text{--- (3)}$$

$$\therefore \quad V_{(l)}\,dP - S_{(l)}\,dT = V_{(v)}\,dP - S_{(v)}\,dT \quad \text{--- (4)}$$

$$\therefore \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad \text{--- (5)}$$

ΔS, ΔV = changes in entropy and volume respectively

Again at equilibrium :- $\Delta G = 0$

$$(\Delta G)_v = (\Delta H)_v - T\Delta S = 0 \quad \text{--- (6)}$$

$$\therefore \quad \Delta S = \frac{\Delta H_v}{T} \quad \text{--- (7)}$$

Substituting ΔS in equ. (5) :-

$$\frac{dP}{dT} = \frac{\Delta H_m}{T\,\Delta V_m} = \frac{\Delta H_v}{T(V_v - V_l)} \quad \text{--- (8)}$$

$$\text{or} \quad \frac{dP}{dT} = \frac{\Delta H}{T(V_g - V_s)} \quad \text{--- (9)}$$

$$\text{and} \quad \frac{dP}{dT} = \frac{\Delta H}{T(V_g - V_l)} \quad \text{--- (10)}$$

In vaporization and sublimation equilibria in which one of the two phases is gaseous, equations (9) and (10) can be put in a more convenient form :-

$$(\Delta V)_{vap} = V_g - V_l$$

Since $V_{(g)} >>> V_{(l)}$

$\therefore$ $V_{(l)}$ can be neglected

$$\Delta V = V_{(g)} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H_v \times P}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H_v}{R} \times \frac{dT}{T^2}$$

$$\int \frac{dP}{P} = \frac{\Delta H_v}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \boxed{\frac{\Delta H_v}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$ Clausius-Claperon equation

Exercise

The boiling point of ether is 35.5 °C at 760 mm pressure. At what temp. will it boil at a pressure of 750 mm ?

The latent heat of vaporization of ether = 88.4 cal/gm and Mol. wt = 74.

Chemical Potential

The chemical potential can be regarded as a force which drives the chemical systems to equilibrium. It shows how the Gibbs free energy of a system changes as a substance is added to it.

The chemical potential of a substance i is equal to the rate of change in Gibbs free energy of the system with the number of moles (n_i) of the component when the number of moles of all other components are held constant

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P} \quad \ldots (1)$$

For a pure substance the Gibbs free energy is

$$G_T = n \times G_m$$

where G_m = molar Gibbs free energy

equation (1) becomes:

$$\mu_i = \left(\frac{\partial (n G_m)}{\partial n}\right)_{T,P} = G_m$$

∴ the chemical potential is the same as the molar Gibbs free energy.

Special case: The chemical potential of a perfect gas at pressure P can be written as: $\mu_G = RT \ln P_G$

or $\mu = \mu_\theta + RT \ln P_G$

where μ_θ = standard chemical potential

For real gases the chemical potential can be expressed in terms of relatively fugacities instead.

$$\mu = \mu_\theta + RT \ln f$$

Chemical Equilibrium

Reversible Processes

$$A + B \rightleftharpoons C + D$$

A stage of "chemical equilibrium" is reached when the rate of the forward reaction becomes equal to the rate of the backward reaction. In this stage, the composition of the reactants and products get fixed. Thus chemical equilibrium is dynamic in nature.

$$H_2 + I_2 \rightleftharpoons 2HI$$

At 425°C, the composition of the equilibrium mixture is found to be :- 12% H_2, 12% I_2 and 76% HI

If the reaction is started with HI at the same temp (425°C), we shall find that the same composition prevails for the equilibrium mixture.

The law of mass action

At constant temperature, the rate of change of substance reacts is directly proportional to its active mass.

The velocity of a chemical reaction is proportional to the product of the 'active masses' of the reactants.

The term 'active mass' is a thermodynamic quantity and is given by :-

$a = C f$ where

a = active mass, C = molar concentration

f = activity coefficient, $f = 1$

For reactions involving gases and solutions, C may be substituted for the active mass, $C = a$

For the general reversible reaction

$$A + B \rightleftharpoons C + D$$

According to the law of mass action,

The rate of the forward reaction R_f is given by :-

$$R_f = K_f C_A C_B$$

K_f = proportionality constant for the forward reaction

The rate of the reverse reaction R_r is given by :-

$$R_r = K_r C_C C_D$$

K_r = proportionality constant for the reverse reaction

C_A, C_B, C_C, C_D = concentrations of A, B, C and D respectively at

At equilibrium, the two rates must be equal :-

$$R_f = R_r$$

$$K_f C_A C_B = K_r C_C C_D$$

$$\boxed{\frac{C_C C_D}{C_A C_B} = \frac{K_f}{K_r} = K_c}$$

K_c = equilibrium constant

The equilibrium condition is expressed in terms of concentration units, i.e., moles per litre of the various species

For a process involving more than a single molecule of each of the reactants and products, then :-

The rate is proportional to the concentration of the given substance raised to the power equal to the number of molecules of the substance participating

$$a A + b B \cdots \rightleftharpoons C + d D \cdots$$

The rate rates are given by :-

$$R_f = k_1 C_A^a \cdot C_B^b$$

$$R_r = k_2 C_C^c \cdot C_D^d$$

$$R_f = R_r \quad \text{at equilibrium}$$

$$\therefore \boxed{\frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} = \frac{k_1}{k_2} = K_c}$$

$$K_{\text{association}} = \frac{1}{K_{\text{dissociation}}}$$

Equilibrium constants expressed in different units :-

For reactions involving gases, the concentration of any gas at any given temperature can be expressed in terms of its partial pressure of the reactants and products.

For the general gaseous reaction :-

$$aA + bB + \dots \rightleftharpoons cC + dD + \dots$$

If P_A, P_B, P_C and P_D are the partial pressures of the various gaseous species at equilibrium, then :-

$$K_P = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

K_P = equilibrium constant in terms of partial pressure and is constant at a given temp.

Le-Chatelier's Principle :-

If a change occurs in one of the variables such as T, P or concentration under which a system is in equilibrium, the system will adjust itself so as to counteract the effect of that change.

Application of the law of mass action

Homogeneous gaseous equilibria :-

Examples are :-

$H_2 + I_2 \rightleftharpoons 2HI$

$N_2 + O_2 \rightleftharpoons 2NO$

For hydrogen-iodide equilibrium :- (in terms of conc.)

$H_2 + I_2 \rightleftharpoons 2HI$

Let a = no. of moles of H_2

b = " " " " I_2

x = " " " " HI

V = volume of the system

Initial molar concentration :- $C_{H_2} = \frac{a}{V}$, $C_{I_2} = \frac{b}{V}$, $C_{HI} = 0$

Equilibrium molar conc. $C_{H_2} = \frac{a-x}{V}$, $C_{I_2} = \frac{b-x}{V}$, $C_{HI} = \frac{2x}{V}$

From the law of mass action

$$K_c = \frac{(C_{HI})^2}{C_{H_2} C_{I_2}} = \frac{(2x/V)^2}{(a-x)(b-x)}$$

$$\therefore K_c = \frac{4x^2}{(a-x)(b-x)}$$

b. Equilibrium constant in terms of pressure

Initial number of moles :- (a) (b) (0)

$H_2 + I_2 \rightleftharpoons 2HI$

~~Total~~ no. of gaseous moles at equilibrium $(a-x)$, $(b-x)$ $(2x)$

Total no. of gaseous moles at equilibrium $= a-x+b-x-2$
$= (a+b)$

At equilibrium, total pressure = P

From Dalton's law, partial pressure $= xP$, x = mole fra

$$P_{H_2} = \frac{a-x}{a+b} P \quad , \quad P_{I_2} = \frac{b-x}{a+b} P \quad , \quad P_{HI} = \frac{2x}{a+b} P$$

$$K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}} = \frac{\left(2x/(a+b)\right)^2 P^2}{\left(\frac{a-x}{a+b}\right) P \cdot \left(\frac{b-x}{a+b}\right) P}$$

$$\therefore \boxed{K_p = \frac{4x^2}{(a-x)(b-x)}}$$

$\therefore K_p = K_c$, that is ...

Equilibrium constant remains unchanged by change of volume and pressure.

Exercise (1)

15 gm. molecules of H_2 on reaction with 5.2 gm. molecules of I_2 vapors at 444°C produced 10 gm. molecules of HI. Determine the equilibrium constant of the reaction.

Exercise (2)

A mixture containing 25 moles of H_2 and 15 moles of I_2 was heated in a sealed tube at equilibrium at 250°C, when 30.5 moles of HI was obtained. Calculate the equilibrium constant of the reaction.

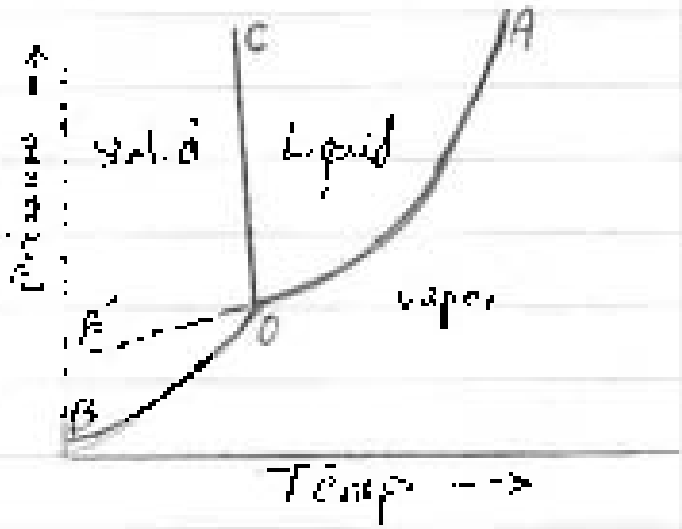
Exercise

A mixture of 1.25 gm. moles of H_2 and 2 gm. moles of I_2 was heated at 444°C until equilibrium was attained. How many moles of HI were there present? (K = 45.9)

Phase Equilibria

The phase diagram

The condition of equilibrium between various forms or phases of a substance is illustrated by a diagram called "phase diagram"



– Phase equilibrium diagram –

* OA and OB represent the variation of vapor pressure with temp.
* OC shows the dependence of the melting point on pressure

It may be said that two phases (a) liquid & vapor along OA (b) Solid and vapor along OB and (c) Solid and liquid along OC are in equilibrium at temperatures and pressures represented by each of the curves in the diagram.

The three phases (Solid, liquid & vapor) are in equilibrium at the triple point "O" where the three curves meet. There is only one point at which the three phases can occur.

In the areas between the curves there can be one phase, either solid or liquid or vapor

(a) In the region between OA and OC only liquid exist

(b) Region to the left of OB and OC represents T & P at which solid only exist

(c) Only vapor exist below OB and OC.

The phase rule

A phase is any homogeneous and physically distinct part of a system which is separated from the other parts of the system by definite bounding surfaces (e.g). Ice & water and vapor are three phases

A component is the smallest number of chemical constituents by means of which the composition of every phase can be expressed (e.g) The water system consist of one component and three phases (ice, water and vapor)

Degree of freedom or Variance

Number of variable factors such as temp, press and conc. which need to be fixed in order that the condition of a system at equilibrium is defined.

Systems with one, two, three, etc degrees of freedom are said to be Univariant, bivariant, trivariant, etc

Phase rule

The number of degrees of freedom (F) of the system is related to the number of components (C) and phases (P) present at equilibrium by the equation :-

$$F = C - P + 2$$

For a one component system, $C = 1$, $F = 3 - P$ or $F + P = 3$. The sum of the degrees of freedom and the number of phases should be 3 if the system is equilibrium

- For a system consisting of one phase only, $P = 1$
  $F = 2$, thus two degrees of freedom (bivariant)
  e.g. solid, liquid or vapor (area under the curve).
  i.e. Temp. and press are required to specify any point in a region of the diagram.
- For a system with two phases in equilibrium, $P = 2$
  $F = 1$ $(i.e. 3 - 2 = 1)$ (univariant).
- When three phases $(P = 3)$ can coexist at the triple point 'O', the system will then have no degree of freedom $(F = 3 - 3 = 0)$ (invariant)

<u>Solutions</u> A mixture of two or more chemically non-reacting substances whose relative amounts can vary within certain bounds.

(a) Homogeneous mixtures — particles of molecular size (1.5 Å)
(b) Heterogeneous mixtures — " " " (> 200 Å)
(c) Colloidal solutions — (< 200 Å)

- Types of solutions (Examples of binary system types)

	Solute	Solvent	Example
1-	gas	gas	Any mixture of gases (Dalton)
2-	"	liquid	Ammonia in water
3	"	solid	Hydrogen in Pd.
4-	liquid	gas	Vaporization of liquid into
5-	"	liquid	water in alcohol.
6-	"	solid	liquid benzene in solid benz
7-	solid	gas	Sublimation of a solid into g
8-	"	liquid	Sugar in water
9-	"	solid	Pd in Ag, Cu, Ni

Composition of solutions

Composition is the relative amount of each component in a solution.

For a binary solution of two components A & B where B is the solute and A is the solvent

(a) percentage weight, $w/w\ (\%) = \frac{w_B}{w_A + w_B} \times 100$

(b) Weight Ratio $\frac{w_B}{w_A}$.

(c) percentage volume of B $= \frac{V_B}{V} \times 100$

(d) Molarity (number of moles of solute in 1 litre solution)

$M_B = \frac{n_B}{V}$.

(e) Normality (number of equivalents of solute in 1 litre solution)

(f) Mole fraction (number of moles of one component to the number of moles of all components).

$$X_B = \frac{n_B}{n_A + n_B}$$

$$X_A + X_B = 1$$

$$X_B = \frac{w_B / M_B}{w_A / M_A + w_B / M_B}$$

M_A, M_B are Mole of A & B.

Exercise.

Calculate the percentage w/w (w/w %) of each component of a solution which contains 90.0 gm NaCl, 200.0 gm CH_3OH and 1000.0 gm H_2O.

Exercise:

Determine the molarity of a solution containing 2.5 grams $AgNO_3$ (M.W. = 169.87) per liter of solution in water.

Solution: Molarity = number of moles of $AgNO_3$ / liter

number of moles, $n_{AgNO_3} = \frac{2.5}{169.87} = 0.014$ mole

$$\text{Molarity} = \frac{0.014}{1 \text{ liter}} = 0.014 \text{ mole/liter}$$

Solutions of gases in liquids

The solution of a gas in a liquid is an example of a two-component system ($C = 2$), and since there are two phases ($P = 2$). According to the phase rule:

$$F = C - P + 2 = 2 - 2 + 2 = 2$$

Thus the system is bivariant.

If the temp is kept constant, both the pressure of the gas and composition of solution (solubility of the gas) are the variables. If the composition is kept constant, the pressure and Temp. are the variables