COURSE CODE: CHM 231

COURSE TITLE: BASIC PHYSICAL CHEMISTRY

CREDIT UNIT: 02

COURSE DURATION: TWO HOURS PER WEEK

COURSE DETAILS:

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COURSE CONTENT:

1. The kinetic theory of gases

   ➤ Postulates of kinetic theory
   ➤ Derivation of Ideal gas equation from the kinetic theory
   ➤ Deductions of gas laws from kinetic theory

1. Deviation from Ideal gas behavior

   ➤ Causes of deviation

   ➤ van der Waals equation

2.   The distribution of molecular velocities

➤ The most probable velocity, mean velocity and mean square velocity

➤ Mean free path, collision frequency and collision density

3.   Thermal energy and Heat capacity

4.   Internal modes of motions

➤ The equipartition principle

5.   Phase equilibria

➤ Phase rule, phase diagrams and triple points

READING LIST:

Atkins, P.W. *Physical chemistry*. Oxford University Press, sixth edition, 1999

1. Gross, J.M. and Wiseall, B. *Principle of physical chemistry*. MacDonald and Evans Handbook series, 1972

2. Alberty, R.A. and Sibley, R.J. *Physical Chemistry*. John Wiley & sons, Inc. 2nd edition, 1986

3. Griffiths, P.J.F. and Thomas, J.D.R. *Calculations in advanced physical chemistry*. Edward Arnold Inc. 3rd edition, 1978

4. Engel, T. and Ried, P. *Physical Chemistry*. Pearson Education Inc., 2006

5. Bahl, A and Bahl, B.S. *Essentials of physical chemistry,* S.Chand and Company Ltd. 2007

6. Brown, T.L., Lemay, H.E., Bursten, B.E and Murphy, C.J *Chemistry: The central science.* Pearson Education, 11th Edition 2009.

7. Sharma, K.K. and Sharma, L.K. *Physical chemistry.*

COURSE REQUIREMENTS:

Students are expected to have a minimum of 75% attendance in this course before they could be allowed to write the examination.

CHM 231; BASIC PHYSICAL CHEMISTRY II

SECTION A

CHEMICAL   THERMODYNAMICS

Thermodynamics: This is the study of energy changes in chemical and physical processes and of the laws and relationships which govern them. Some terms are commonly used:

(a) **System;** A system in thermodynamics is defined as collection of matter i.e that part of the universe under study. The rest of the universe of course being isolated.

(b) **Surrounding:** The rest of the universe not under study. A system could be isolated from its surrounding i.e it's completely insulated such that no heat flow exists between the system and its surrounding.

(c) **State of a system:** The state of a system is specified by determining all its properties such as pressure, volume etc.

(d) **Process:** A process is a change from one state A to another state B.

(e) **State function:** A state function is a property or function of properties which depends only on the state and not on path by which the state was reached, a differential dx of a function x (not necessarily a state function) is termed a perfect differential if it can be integrated between two states to give a value $X_{AB} = (A < x < B)$ dx which is independent of the path from A to B. If this holds, X must be a state function. Kinetic energy, Internal energy are state functions.

(f) **Intensive Properties.** Are those whose values are independent of the size of system taken i.e the properties will be the same whether small or great amount of the system is considered. E.g. temperature, pressure, density, refractive index ,etc.

(g) **Extensive properties:** are those whose values depend or are proportional to size of the system. Increase in size of the system obviously will increase this property , e.g, heat capacity, mass, volume, enthalpy, and entropy.
There are four basic laws of thermodynamics, all having many different formulations that can be shown to be equivalent. The zeroth law states that if two systems are each in thermal equilibrium with a third system, then they is in thermal equilibrium with each other.

First Law of thermodynamics

The first law states that for any process the difference of the heat Q supplied to the system and the work W done by the system equal the change in internal energy, U.
$\Delta U = Q-W$
A chemist is often faced with the task of determining whether a particular process will occur under specified conditions, and if it does occur

Measurement of Change in Internal Energy

From the first law $\Delta U = q - w$, when work done is zero then $\Delta U = q$. One way of making a system do work is to make it expand against external pressure. If however the process is performed in a rigid vessel (i.e. a vacuum) i.e. constant volume, then, no work is done and $q = \Delta U$. A process of making this happen can be done in a bomb calorimeter e.g. Figure (1 NOT SHOWN): Determination of heat of combustion in a bomb calorimeter.

In the bomb calorimeter combustion occurs at constant volume and as such heat changes is reflected in its internal energy $\Delta u = q_v$.

Pressure – Volume work

Consider a cylinder of cross-sectional area x, with a frictionless and weightless piston, let the pressure on the piston be P. Pressure = Force/ Unit area.

Total force acting on the piston = P_x, if as a result of expansion the piston moves a distance dl, therefore work is done (dw) by the gas on the surroundings which is equivalent to $dw = F.dl = Pxdl$. But $x.dl = dv$ (sectional area x length = volume) which is the increase in volume due to movement of the piston. Therefore, $dw = Pdv$.

The total work in the expansion of the gas from initial volume v_1 to the final volume v_2 is given by $W = (V_1 < x < V_2) \quad PdV$. Therefore, $\Delta u = q - Pdv$, this means:

At constant volume (i.e. where there is no change in volume) $dv = 0$, $w = 0$ and $\Delta U = q$, and as such any thermal change in the calorimeter at constant volume must be the change in the internal energy due to the chemical reaction or physical reaction.

When the opposing pressure is zero (i.e. free expansion) that is the gas expands against a zero external pressure, no work is done $\Delta U = q$.

Opposing pressure is constant i.e. when opposing pressure is constant.

Then, $\Delta U = q - Pdv$ or

$q = \Delta u + Pdv$

$\quad = U_2 - U_1 + P (v_2 - v_1)$

$U_2 = U_1 + Pv_2 - Pv_1$

$q = U_2 + PV_2 - (U_1 + Pv_1)$

Since u is a state function and Pv are properties of a state, therefore U + Pv represents a state function which is represent as H. Then H = U + Pv, therefore heat absorbed at constant pressure is called the enthalpy. $q_p = \Delta H$.

Opposing pressure variable

This can be calculated by putting P versus v and determine the area under the curve. In general w, will be positive if $V_2 > V_1$ i.e. work is done by the gas on its surrounding (this is what happens when a system expands, pushing back its surroundings. If $v_1 > v_2$ then w, is negative and a compression has taken place i.e. work is done by the surroundings on the gas.

Heat capacities

From the Bomb calorimeter, heat capacities are calculated. There can be two types,, C_v:- heat capacity at constant volume and C_p:- heat capacity at constant pressure.

$C_v = dq_v/dT$ and $C_p = dq_p/dT$, since $\Delta U = q_v$ and $q_p = \Delta H$, then $C_v = (du/dT)_v$ and $C_p = (dH/dT)_p$

Heat capacity of a system is the heat required to raise the temperature of the system by one degree if dq is a small amount of heat added to a system, the temperature of the system will rise by dT. Therefore the heat capacity is represented by $C = dq/dT$.

$C_v = (dU/dT)_v$, therefore C_v is the rate of change of internal energy with temperature at constant volume. While $C_p = (dH/dT)_p$, C_p at constant pressure is the rate of change of enthalpy with temperature at constant pressure.

Relationship between C_v and C_p (for an ideal gas)

$C_p - C_v = (dH/dT)_p - (dU/dT)_v$, but H = U + PV, therefore dH/dT = dU/dT + d(PV)/dT for one mole of ideal gas PV = RT

$C_p = C_v + R$, therefore the difference between the molar heat capacities for an ideal gas is R, the gas constant.

Internal Energy of an Ideal Gas (Joule Experiment)

When an ideal gas expands into a vacuum there is no gain or loss of heat.

Figure 2 (NOT SHOWN): Joule experiment.

Two similar bulbs, one containing air under pressure and the other empty were connected by a wide tube with a control. The water was stirred and temperature noted. After thermal equilibrium the control was opened and temperature noted (No change in temperature). It was deduced that since the gas expands into a vacuum i.e. when the external pressure is zero, no work is done by the gas in its expansion i.e. w = 0, and as no change was recorded in the temperature, the q = 0. Therefore, it means that $\Delta u = q - w = 0$ and that there is no change in the internal energy of an

ideal gas as a result of free expansion. (The internal energy, U of an ideal gas is independent of volume at constant temperature)

$(dU/dv)_T = 0$, $(dU/dv)_T dv + (dU/dT)_v dT = 0$.

It can be calculated that the energy of the gas is a function of temperature only. The fact that $(dU/dv)_T = 0$ indicate that for ideal gases intermolecular force of attraction is zero, but for real gas $(dU/dv)_T$ is a small but positive quantity.

Effect of Pressure and Temperature on C_p and C_v

Since the internal energy du is independent of volume it is expected to be independent of pressure, $C_v = dU/dT$, indicating that heat capacity at constant volume of an ideal gas is independent of the volume or the pressure of the gas but a function of temperature. This is also similar for C_p, $C_p = dH/dT$.

Show that by differentiating the equation $H = U + Pv$ with respect to volume at constant temperature that $(dH/dv)_T = 0$.

Heat Capacity and Temperature Relationship

Both C_v and C_p increases with temperature. And the dependence on temperature is predicted from experimental measurements. Such relationship is $C_p = a + bT + cT^2 + dT^3$

Where a, b, c and d are constant determined from experimental values of heat capacities over a range of temperatures (temperature in K). Using this type of relationship, the amount of heat required to raise the temperature of a gas system from T_1 to T_2 at C_v and C_p is given by

$\Delta U = (T_2 < x < T_1) \quad C_v dT = (T_2 < x < T_1) \quad (a + bT + cT^2 + dT^3)dT$

$\Delta H = (T_2 < x < T_1) \quad C_p dT = (T_2 < x < T_1) \quad (a + bT + cT^2 + dT^3)dT$

Isothermal Process

Temperature is constant, and since U varies with temperature, it means that at constant temperature $\Delta U = $ constant, therefore for isothermal process $\Delta U = 0$ and q = w.

$q = (v_2 < x < v_1) \quad PdV$, $q = \Delta U + w$ and $\Delta U + \quad PdV$

The magnitude of q will vary with w from zero, for a free expansion (when exert pressure against which expansion occur is zero) to a maximum for reversible process. (In which exert pressure and internal pressure only differ by an infinitesimal amount).

$q = W = (v_2 < x < v_1) \quad Pdv$, for an ideal gas $PV = nRT$

$q = (V_2 < x < V_1) \quad (nRT/V)dV$,

$W_{max} = nRTln(V_2/V_1)$ or $2.303nRTlog(V_2/V_1)$,

but for an ideal gas at constant temperature the relationship $P_1V_1 = P_2V_2$ holds (boyles law), thus $P_1/P_2 = V_2/V_1$

$W_{max} = nRTln(P_1/P_2)$.

For real gases $\Delta u \neq 0$ under isothermal conditions because even when temperature is constant, internal energy will change due to change in volume or pressure. The same is true ΔH. Therefore for real gases expanding, W_{max} will be less than the volume above depending on the degree of non-ideality.

Example 1:- Calculate the maximum work obtainable by the isothermal reversible expansion of 2 mole of Nitrogen from 10 litres to 20 litres at 25^oC.

Solution:-

$W_{max} = nRTln(V_2/V_1)$

$\qquad = 2.303nRTlog(V_2/V_1)$

$\qquad = 2 \times 2.303 \times 8.314 \times 298 \times \log(20/10)$

$\qquad = 3.44kJmol^{-1}$

$\qquad = 0.821kcalmol^{-1}$

Tutorial: - An ideal gas undergoes a reversible isothermal expansion from an initial volume V_1 to a final volume $10V_1$ and thereby does 16.628 Joules of work. The initial pressure was $100Nm^{-2}$. (a) Calculate V1 (b) if there were 2 moles of gas. What must its temperature have been?

Adiabatic Process

An adiabatic process is one which there is no exchange of heat between the system and its surroundings i.e. $q = 0$. Work done is at the expense of the internal energy $\Delta U = -W$, this implies that if work is done on the system, the internal energy of the system will increase and Δu will decrease if work is done by the system. From the first law;

$\Delta U = -PdV$

$C_vdT = -PdV$, but for an ideal gas $P = RT/V$

$C_vdT = -R(dV/V)$

For a process that takes the gas from V_1 at T_1 to V_2 at T_2

$(T_1 < x < T_2) C_v \quad dT/T = -(V_1 < x < V_2) R \quad dV/V$

$(C_v/R)\ln(T_2/T_1) = -\ln(V_2/V_1)$, by rearranging

$\ln(T_2/T_1) = \ln(V_1/V_2)^{R/Cv}$

But we know that $C_p - C_v = R$,

therefore $\ln(T_2/T_1) = \ln(V_1/V_2)^{(Cp-Cv)/Cv}$

Let $C_p/C_v = $, this is the ratio of heat capacities at constant pressure and constant volume.

$\ln(T_2/T_1) = \ln(V_1/V_2)^{-1}$

Other equivalent relationships are: $T_2V_2^{-1} = T_1V_1^{-1}$ or $P_2V_2 = P_1V_1$

Or $T_2 P_2^{-1} = T_1 P_1^{-1}$

and $W = nR (T_2 - T_1) / (-1)$

The Joules Thompson Effect: Use in measuring quantitative deviation from ideal law.

Figure (3 'NOT SHOWN)

A gas from a high pressure region A is allowed to pass to a low pressure region C through a porous plug B. Temperature of the gas is then taken at C. The entire system is thermally insulated (i.e. an adiabatic process, $q = 0$).

Then $\Delta U = -PdV$, work done before gas is forced through is $-PdV$ and work done by expansion is PdV.

But $H = U = PdV$, therefore $H = -PdV + PdV$

$\Delta H = 0$, heat content of a system during its expansion through a porous plug remains constant.

Joule-Thompson Coefficient ($_{JT}$):- It is the rate of change of temperature with the pressure when a gas flows through a plug from a higher pressure to a low pressure

$_{JT} = (dT/dp)_H$

For an ideal gas $_{JT} = 0$. That is no change of temperature is observed in expanding through a porous plug. For real gases it is not zero but becomes smaller and approaches zero as conditions for ideality are approached. For most gases at normal temperature except for H_2 & He $_{JT}$ is positive, showing that expansion results in cooling. For H_2 and He at a very low temperature i.e. -80°C for H_2 is required before $_{JT}$, can be positive. This is responsible for the extremely great difficulty of obtaining liquid H_2 and liquid He.

Variation of Enthalpy with Temperature

Consider a reaction, Reactant → Products

$\Delta H = H_p - H_r$, differentiating both sides with respect to temperatures;

$(d\Delta H/dT)_p = (dH_{product}/dT)_p - (dH_{reactant}/dT)_p$

Therefore $(d\Delta H/dT)_p = C_{p(product)} - C_{p(reactant)}$.

Or $(d\Delta H/dT)_p = \Delta C_p$, Kirchoffs equation, where $\Delta C_p = \sum C_{p(product)} - \sum C_{p(reactant)}$.

For a small range of temperature $d(\Delta H) = \Delta C_p dT$, that is C_p can be taken as constant. If it is constant then $(\Delta H_1 < x < \Delta H_2)$ $d(\Delta H) = (T_1 < x < T_2)$ $\Delta C_p dT$

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

$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$. Where ΔH_2 is the heat of reaction at T_2 and ΔH_1 is that at T_1.

However if the temperature internal is very large then ΔC_p is not constant, and also a function of temperature. Note that generally heat capacities of gases vary with temperature as a function of power series of T.

$\Delta C_p = a + bT + cT^2 + dT^3$.

$\Delta H_2 = \Delta H_1 + (T_1 < x < T_2)$ $\Delta C_p dT$.

$\Delta H_2 = \Delta H_1 + (T_1 < x < T_2)$ $(a + bT + cT^2 + dT^3)dT$

Tutorial: - The standard heat of formation for NH_3 is -11.02kcalmol^{-1} at 298k. Heat capacities at this temperature for N_2, H_2 and NH_3 are 6.96, 6.89 and 8.38calmol^{-1}; determine $\Delta H^o{}_{298k}$ and ΔH_{773k} for the reaction.

Questions

Explain the terms:-

1. System, surroundings, state of system, change of system.
2. What do you understand by the term internal energy and enthalpy of a system? How are they related?
3. Two litres of N_2 at 0^oC and 5 atm pressure are expanded isothermally against a constant pressure of 1 atm until the pressure of the gas is also 1 atm, assuming ideal behaviour. What are the values of W, Δu, ΔH and q?
4. One mole of an ideal gas is allowed to expand reversibly against a confining pressure that is at all-time infinitesimally less than the gas pressure of 0.1 atm, the temperature being

kept constant at 0^oC. (a) How much work is done by the gas (b) What is the change in u and H. (c) How much heat is absorbed?

Second Law of Thermodynamics

A chemist is often faced with the task of determining whether a particular process will occur under specified conditions, and if it does occur, it is important to estimate its extent. This is the essence of the second law of thermodynamics.

Many natural processes are known to occur spontaneously in one direction only. (1) For example a gas expands to occupy all the space made available to it. No gas is ever known to collect its molecule together leaving or vacating some available space and congregating in only a section of the space. (2) Heat flows spontaneously from a hot body when place in contact with cold body. (3) A mixture of hydrogen and water in ratio 1:2 by volume explodes when exposed to sunlight forming water. All these processes and their un-natural reverse processes satisfy the 1st law which predicts energetic of change but not direction of change.

General experience such as these show that systems tend to make from a non-equilibrium state to the one of equilibrium and once in this state they remains unchanged unless disturbed by some external agent. This means that the path to equilibrium is normally thermodynamically irreversible. Example one is not at equilibrium because of difference in pressure, and example two because of temperature difference while example three is a chemical change. What then determines the direction of change?

The second law predicts the criterion of chemical change and the direction of change, 1st law predicts energetic of change, but not the direction of change. There is a quantity called entropy, which is a function of the state of the system. In a reversible process the entropy of the universe remains constant. Therefore, **second law of thermodynamics states that spontaneous reaction occurs in the direction of increasing entropy**.

Entropy a state functions

That entropy is a state function can be proved from the axiom called the inequality clausius. This states that for all thermodynamic cycles $dq/dT \leq 0$, the equality holds for a reversible cycle while the inequality holds for the irreversible cycle. Let a system undergo a reversible process from state 1 to 2 along path A and let the cycle be completed along path B, which is also reversible.

$dq/T = 0 = (1A < x < 2A)$ $dq/T + (2B < x < 1B)$ dq/T .... (1)

Now consider another reversible cycle which has the same initial path A but is completed along path C (which is also reversible) thus

dq/T = 0 = (1A < x < 2A)   dq/T + (2C < x < 1C)   dq/T .... (2)

Substituting eqn (2) from (1); (2B < x < 1B)   dq/T = (2C < x < 1C)   dq/T

Therefore   dq/T is the same for all reversible paths between states 1 and 2 and is independent of the reversible path between state 1 and 2; dq/T is a state function and thus property is called entropy and denoted by S thus, dS = $(dq/T)_{rev}$ and (1 < x < 2)   dS = (1 < x < 2) $(dq/T)_{rev}$.

Therefore, $S_2 - S_1 = \Delta S$ = (1 < x < 2) $(dq/T)_{rev}$.

Note that the definition involves only the heat released or absorbed in a reversible path only. When the path is irreversible the heat absorbed or released is not usable in calculation of ΔS.

Therefore, $(dq/T)_{rev} \neq (dq/T)_{irr}$, dq/T depends on path, but ΔS does not.

How the second law does predicts the direction of change

Note that a spontaneous change is irreversible and 2nd law state that during this process, the entropy of the universe increases. To predict whether a change is spontaneous or not ΔS is completed for system and its surroundings which contribute the universe during the change. If ΔS is +ve, process is spontaneous, if ΔS is zero or −ve, no spontaneous change will occur and the process is already in equilibrium.

Entropy changes for some simple processes

Phase changes at constant T and P

$\Delta S_{trans} = \Delta H_{trans}/T_{trans}$

Solid → Liquid, Solid → Vapour, Liquid → Vapour and Solid I → Solid II

Reversible Isothermal volume change

Isothermal (i.e. T constant) $\Delta u = 0$, from first law q = W = P_{ext} dV =   PdV =   (nRT/V)dV = $nRTln(V_2/V_1) = q_{rev}$.

But $\Delta S = q_{rev}/T = (nRT/T)ln(V_2/V_1) = nRln(V_2/V_1)$.

Note that for expansion $V_2 > V_1$ and ΔS is positive. Thus the expansion of a gas to fill all available space is spontaneous.

Irreversible Isothermal volume change

ΔS is a state function independent of path, hence ΔS is the same as for reversible path between the two states, $\Delta S = nRln(V_2/V_1)$.

Mixing of two gaseous samples (even if both are at constant T & P)

$\Delta S = n_1 R \ln[(V_1 + V_2)/V_1] + n_2 R \ln[(V_1 + V_2)/V_2]$

Therefore, even if $V_1 = V_2$, ΔS must increase i.e. mixing is a spontaneous process.

Reversible Adiabatic & Irreversible Adiabatic change $dq_{rev} = 0$, therefore $\Delta S = 0$.

Entropy change on heating or cooling a substance at constant volume process

$\Delta S = (T_1 < x < T_2) \quad C_v dT/T$. Also at constant pressure $\Delta S = (T_1 < x < T_2) \quad C_p dT/T$. The investigation of this expression depends on whether C_v & C_p are temperature dependent or are completely constant and independent of temperature in the range considered.

Entropy change for an Ideal gas

Simultaneous heating and expansion of a gas initial $T_1 V_1$ and final $T_2 V_2$, this can be seen as 2 reversible steps, $q_{rev} = \Delta u + W$ and $q_{rev} = C_v dT + PdV$.

Step 1: Heat at constant volume V_1 from T_1 to T_2, $\Delta S_1 = (T_1 < x < T_2) \quad C_v dT/T$.

Step 2: Expand gas Isothermally at T_2 from V_1 to V_2,

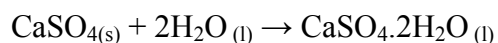$\Delta S_2 = (V_1 < x < V_2) \quad RdV/V = (V_1 < x < V_2)(1/T) \quad (RT/V)dV$

Therefore, $\Delta S_{total} = \Delta S_1 + \Delta S_2 = (T_1 < x < T_2) \quad (C_v/T)\, dT + (V_1 < x < V_2) \quad (R/V)\, dV$

$= (T_1 < x < T_2) \quad (C_v/T)\, dT + R\ln(V_2/V_1)$.

Similarly, $\Delta S_{total} = (T_1 < x < T_2) \quad (C_v/T)\, dT - R\ln(P_2/P_1)$

For a process occurring at constant volume $\Delta S = C_v \ln(T_2/T_1)$

Application of 2nd law to some simple types of chemical reaction

$A \rightarrow B$, Ice $\rightarrow$ Liquid water

$CaSO_{4(s)} + 2H_2O_{(l)} \rightarrow CaSO_4.2H_2O_{(l)}$

In this way we deliberately avoid complications due to gaseous expansion. If we assume reactions occur in calorimeter at pressure P immersed in a heavily lagged thermo flask maintained at temperature T. Then let the entropy change accompanying 1 mole of $A \rightarrow 1$ mole of B be ΔS. If x mole of A has reacted, then entropy change of reaction is $x\Delta S$. Entropy change of both is $-x\Delta H/T$, where ΔH is the enthalpy change accompanying the transformation of 1 mole of $A \rightarrow 1$ mole of B. Therefore, $\Delta S_{(total\ for\ isolated\ system\ or\ universe)} = x\Delta S - x\Delta H/T = x(\Delta S - \Delta H/T) = -x/T(\Delta H - T\Delta S)$.

$\Delta S_{total} = -x/T[(H_2 - H_1) - T(S_2 - S_1)] = -x/T[(H_2 - TS_2) - (H_1 - TS_1)]$

Since H, S and T are properties of the state of system, the quantity H - $T\Delta S$ is also a state property which is denoted by ΔG that is the Gibbs free energy.

Therefore, $\Delta S_{total} = -x/T(\Delta H - T\Delta S) = -x/T(G_2 - G_1) = -x/T(\Delta G)$. For the process to be spontaneous in this isolated the system $\Delta S > 0$ i.e. +ve since x is the number, than ΔG must be negative.

Thus for spontaneous process $\Delta G = \Delta H - T\Delta S$ must be –ve. If ΔG is zero, $\Delta S_{total} = 0$ then the system must be in thermodynamic equilibrium. If ΔG is +ve, then ΔS_{total} is –ve, then the change under consideration cannot be spontaneous i.e. it will not occur naturally.

Molecular Interpretation of Entropy

Entropy is a measure of the disorder or change in a system. High orderliness means low entropy, e.g. as in crystal and solids. Whereas low orderliness indicates high entropy e.g. as in a gas, Hence entropy increases with volume increases or with temperature increases. For example melting i.e. change from solid to liquid usually involves little entropy increase, whereas evaporation i.e. change from liquid to gas involves high entropy change.

Example:- 14g of Nitrogen gas at 10^oC and a pressure of 1 atm are heated to 14^oC. Calculate the entropy change when the process takes place at constant pressure. Take the heat capacity of Nitrogen in the relevant temperature range to be given by

$C_p = 26.98 + 5.90 \times 10^{-3}T – 3.40 \times 10^{-7}T^2$ $Jmol^{-1}k^{-1}$. Answer = $5.473Jk^{-1}$.
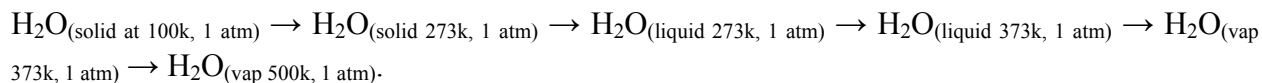
Calculate the heat of formation (ΔH) for 1 mole of ammonia gas at 120^oC. You are given that the standard heat of formation for ammonia $\Delta H^o_f(NH_3) = 46.18kJmol^{-1}$.

The following data are provided for the reaction, $CO_{(s)} + \frac{1}{2}O_{2 (g)} \rightarrow CO_{2 (g)}$. Standard enthalpies of formation $CO_2 = -393.4kJmol^{-1}$, $CO = -110.5kJmol^{-1}$, $O_2 = -121.5kJmol^{-1}k^{-1}$. Standard entropy of formation $CO_2 = 213.6Jmol^{-1}k^{-1}$, $CO = 197.9Jmol^{-1}k^{-1}$ and $O_2 = 205.0Jmol^{-1}k^{-1}$. Calculate the free energy change for this reaction at 25^oC and 1 atm.

Calculate the change in entropy ΔS when one mole of water at 100k is heated at constant, pressure of 1 atm to 500k. You may assume the normal freezing point and boiling point of water to be 273k and 373k. Latent heat of vaporization is $40.28kJmol^{-1}$, latent heat fusion is $6.00kJmol^{-1}$, molar heat capacities in units of $Jmol^{-1}k^{-1}$

Solid, $C_p = 2.092 + 0.125T$, liquid, $C_p = 75.29$ and Vapour, $C_p = 30.315 + 9.621 \times 10^{-3}T + 1.184 \times 10^{-6}T^2$.

First identify the various steps,

$H_2O_{(solid\ at\ 100k,\ 1\ atm)} \rightarrow H_2O_{(solid\ 273k,\ 1\ atm)} \rightarrow H_2O_{(liquid\ 273k,\ 1\ atm)} \rightarrow H_2O_{(liquid\ 373k,\ 1\ atm)} \rightarrow H_2O_{(vap\ 373k,\ 1\ atm)} \rightarrow H_2O_{(vap\ 500k,\ 1\ atm)}$.

$\Delta S = (100 < x < 273)$ C_p $(dT/T) = (100 < x < 273)$ $[(2.092 + 0.125T)/T]dT =$ $(2.092/T + 0.125)dT = 2.092\ln(273/100) + 0.125(273 - 100) = 23.726.$

$\Delta S = \Delta H_{fussion}/T_{fussion} = (6.003 \times 10^3)/273 = 21.989.$

$\Delta S = (100 < x < 273)$ C_p $(dT/T) = (273 < x < 373)$ $(75.3/T)dT = 75.3\ln(373/273) = 23.486$

$\Delta S = \Delta H_{vap}/T_{vap} = (40.282 \times 10^3)/373 = 107.99$

$\Delta S = (373 < x < 500)$ C_p $(dT/T) = (373 < x < 500)$ $[(30.315 + 9.621 \times 10^{-3}T + 1.184 \times 10^{-6}T^2)/T]dT$

$\Delta S = (373 < x < 500)$ $[(30.35/T) + 9.621 \times 10^{-3} + 1.184 \times 10^{-6}T]dT$

$= 30.35\ln(T_2/T_1) + 9.621 \times 10^{-3}(T_2 - T_1) + (1.184 \times 10^{-6}/2)[T_2^2 - T_1^2]$

$= 8.893 + 1.222 + 0.0654 = 10.192$

$\Delta S_{total} = 23.726 + 21.989 + 23.486 + 107.995 + 10.192 = 187.388 Jmol^{-1}.$

Gibbs free energy and Total Energy

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

ΔH can be regarded as total energy absorbed or evolved. ΔS has to do with ordering of the system. Therefore $T\Delta S$ can be regarded as energy involved in organizing or ordering the system. The balance $\Delta H - T\Delta S$ denoted by ΔG is called the free energy which is the energy available to do work by the system. The implication of this is that the total energy of the system is partially tied down with organizing the component of the system, while the rest is energy freely available to do useful work.

Relationship between ΔG and the Equilibrium constant k

From $H = u + PV$, $G = H - TS$, then $G = u - TS + PV$.

$dG = dH - TdS - SdT$. ($G = H - TS$), but $dH = du + PdV + VdP$ (from $H = u + PdV$)

$TdS = du + PdV$ at equilibrium, therefore $dG = du + PdV + VdP - du - PdV - SdT$

$= -SdT + VdP$

At constant temperature $dT = 0$, $(dG/dP)_T = V$ or $dG = VdP$. For 1 mole of a perfect gas,

PV = RT, V = RT/P and dG = (RT/P)dP

$(G_1 < x < G_2)$ dG = $(P_1 < x < P_2)$ RT   dP/P

$G_2 - G_1 = RTln(P_2/P_1)$, where (P_2/P_1) = K, but (P_1/P_2) = -k

$\Delta G = -RTlnk$.

Relating the eqn $\Delta G = \Delta H - T\Delta S = -RTlnk$.

$\Delta H - T\Delta S = -RTlnk$, $k = e^{-\Delta G/RT}$

$lnk = -\Delta H/RT + \Delta S/R$.

Therefore if one knows the value of the equilibrium constant at a number of different temperature. Then a plot of lnk vs. 1/T gives a straight line slope of $\Delta H/R$ from which ΔH can be found. Also it can be obtained by calculation of only 2 mole of k are known.

$\Delta H^o = (2.303RT_2T_1)/(T_2 - T_1)log(k_1/k_2)$

$ln(k_1/k_2) = -\Delta H/R[(T_2 - T_1)/(T_1T_2)]$

- The vapour pressure of H_2O above mixtures of $CuCl_2.H_2O$ and $CuCl_2.2H_2O$ is given in the following tables:

t^oC	17.9	39.8	60.0	80.0
P atm	0.0049	0.0247	1.20	0.332

Using a graphical procedure calculate (a) the standard enthalpy ΔH^o of the reaction

Third Law of Thermodynamics

This law states that the entropy of a pure perfectly crystalline substance is zero at the absolute zero of temperature. If a crystal is imperfectly by a way of being a mixture of two or more substance, or having lattice vacancies or defects, then entropy at absolute zero will be greater than zero, although it can be small.

The third law establishes for us a reference zero of entropy. Therefore it is possible to obtained absolute values of entropy for any substance at any temperature T. The third law is of considerable importance in that it permits the calculation of absolute values of entropy of pure substances from thermal data alone. Consider a process involving the transformation of a solid from the absolute zero of temperature to some temperature T below its melting point.

Solid $_{(0ok, p)}$ = Solid $_{(T,p)}$

The entropy change for such a process is given by $(S_o < x < S_T)$ dS = $(0 < x < T)$ $(C_p/T)dT$

$S_T - S_o = (0 < x < T) \ (C_p/T)dT$ where S_T is the entropy at temperature T and S_o is the entropy at 0k. Since by the third law $S_o = 0$ at T = 0k one has $S_T = (0 < x < T) \ (C_p/T)dT$

$= (0 < x < T) \ (C_p dlnT$

$\Delta S = (0 < x < T) \ (C_p ln (T_2/T_1)$.

The integral above is positive since entropy can only increase with temperature. S_T known as the absolute entropy of a substance or the third law. Third law can also be utilized to determine absolute entropies of substances that are liquid or gaseous at ordinary temperatures. This is possible because the total absolute entropy of a substance in a particular state at a given temperature is the sum of all the entropy changes the substance has to undergo in order to reach the particular state from the crystalline solid at 0k. Thus to obtain the entropy of a gas above the boiling point of the substance we have (a) the entropy change of heating the crystalline solid from T = 0 to T = T_f $C_{psolid}(dT/T)$. (b) The entropy change on fusion $\Delta H_f/T_f$. (c) the entropy change due to heating the liquid from the fusion T_f temperature to boiling temperature T_b, $C_{pliq}(dT/T)$ (d) the entropy change due to vaporization $\Delta H_{vap}/T_{vap}$ (e) the entropy change due to heating of the gas from T_b to the desired temperature T, $C_{pg}(dT/T)$. Hence,

$\Delta S_{Total} = \ Cp^s dlnT + \Delta H_{fus}/T_{fs} + \ Cp^l dlnT + \Delta H_{vap}/T_{vap} + \ Cp^g dlnT)$.

The expression above is general for the evaluation of the absolute entropy for all the phases, solid, liquid, gaseous. For a solid, only the first two terms in the equation are relevant. If however, the substance is a liquid at temperature T, then use the first four terms and replace the upper limit of the fourth expression with T, When the substance is gaseouse , all terms must be used.

Debye Theory of heat capacity of crystals (or Debye third power law for heat capacities of solids at low temperatures)

This law is ;

$C_p^s = a \ T^3$ .... (1)

where a is a constant The contribution to solid, s, from the curve below the lowest experimental temperature, T' is obtained from ;

$S(T') = (0 < x < T) \quad aT^2 dT = \ 1/3aT'^3 = 1/3Cp^s(T')$. .... (2)

This means that the correction term is one-third the measured heat capacity at the lowest experimental temperature, T' provided that this temperature is within the range for which equation (1) is valid.

$\Delta S_{Total} = \ Cp^s dlnT + \Delta H_{fus}/T_{fs} + \ Cp^l dlnT + \Delta H_{vap}/T_{vap} + \ Cp^g dlnT)$.

Calculate the entropy change in ΔS when one mole of water at 100k is heated at constant pressure of 1 atm to 500k. (Given that normal freezing point & boiling point of water to be 273k and 373k, Heat of vaporization is 40.28kJmol^{-1} latent heat of fusion 6.00kJmol^{-1}). Molar heat capacities in unit of Jmol^{-1}k^{-1}, Solid C_p = 2.092 + 0.125T, liquid C_p = 75.29, gas C_p = 30.352 + 9.621 x 10^{-3} + 1.184 x 10^{-6}T^2.

Absolute entropies may be used to calculate the entropy changes accompanying chemical reactions. The standard entropy change for a general chemical reaction is

ΔS^o = $\sum_{ini}S^o$(product) + $\sum_{ini}S_i^o$(reaction). Where n_i is the number of moles of component i in a balanced eqn and S_i is the standard molar entropy for component i. Thus in order to determine the entropy change required for the reaction at 25°C.

$S_{(S, \text{ rhombic})}$ + 3/2O$_{2\,(g)}$ → SO$_{3\,(g)}$
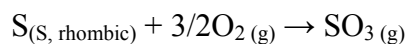
$\Delta S_{(\text{reaction})}$ = S^o(SO$_3$) − [S^o$_{(S, \text{ rhombic})}$ + 3/2S^o(O$_{2(g)}$)]

Since the molar entropies of SO$_{3\,(g)}$, S$_{(\text{rhombic, S})}$ and O$_{2(g)}$ are 61.24, -7.62 and -49.0 respectively.

ΔS^o $_{(\text{reaction})}$ = -61.24 − [-7.62 + 3/2(-49.0)] = 19.9

SECTION B

Kinetic theory of gases

### Postulates of kinetic theory

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

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

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

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

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

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

7. There is <mark>no effect of gravity</mark> on the motion of the molecules of a gas.

Derivation of Ideal gas equation from the kinetic theory

Consider a cubic container of a gas of each side 'a' containing N number of molecules. The velocity u of the gas can be resolved into 3 component velocities u_x, u_y and u_z.
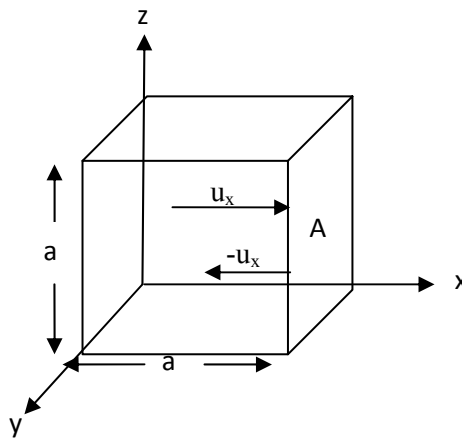
The magnitude of u is given by the Pythagoras' theorem as

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

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

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

The time between successive collisions is given by $\Delta t = \dfrac{2a}{U_x}$

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

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

∴ Change in momentum, $\Delta mU_x = 2mU_x$ (3)

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

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

Area of surface A=a² and pressure, $P = \dfrac{Force}{Area}$ (5)

The pressure exerted by the molecule on surface A is P₁,

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

Let V represent the volume of the cubic box, then V=a³

∴ $P_1 = \dfrac{mU_x^2}{V}$

So,

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

Since the collisions of molecule 1 with surface A are perfectly elastic, the velocity U_x and mass of each molecule are constant. i.e. $P_1 =$ constant

Total pressure on surface A will be given by

$P = P_1 + P_2 + P_3........+ P_N$

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

Recall that

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

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

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

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

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

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

For each molecule,

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

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

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

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

Adding up:

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

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

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

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

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

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

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

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

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

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

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

Deductions of gas laws from kinetic theory

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

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

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

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

Multiply both sides by 2/3

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

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

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

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

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

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

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

$$P_1 V_1 = \frac{1}{3} N_1 m_1 \bar{U}_1^{\,2} \text{ ------- For gas 1} \qquad\qquad (18a)$$

$$P_2 V_2 = \frac{1}{3} N_2 m_2 \bar{U}_2^{\,2} \text{ ------- For gas 2} \qquad\qquad (18b)$$

But P and V for the 2 gases are the same

$$\therefore \qquad P_1 V_1 = P_2 V_2$$

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

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

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

Thus, the equation 19 is reduced to $N_1 = N_2$ which authenticate the law.

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

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

Hence, $\dfrac{r_1}{r_2} = \dfrac{\sqrt{d_2}}{\sqrt{d_1}}$ $\qquad\qquad$ (22)

Applying the kinetic theory, $PV = \dfrac{Nm\overline{U}^2}{3} = nRT$ $\qquad\qquad$ (23)

$$\overline{U} = \sqrt{\dfrac{3nRT}{Nm}} \qquad\qquad (24)$$

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

$$\therefore \quad \overline{U}_1 = \sqrt{\dfrac{3RT}{M_1}} \quad \text{and} \quad \overline{U}_2 = \sqrt{\dfrac{3RT}{M_2}} \qquad\qquad (25)$$

$$\therefore \quad \dfrac{\overline{U}_1}{\overline{U}_2} = \sqrt{\dfrac{M_2}{M_1}}$$

$$\Rightarrow \dfrac{r_1}{r_2} = \sqrt{\dfrac{d_2}{d_1}} = \dfrac{\overline{U}_1}{\overline{U}_2} = \sqrt{\dfrac{M_2}{M_1}} \qquad\qquad (26)$$

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

$$P_1 = \dfrac{1}{3}\dfrac{N_1 m_1 \overline{U}_1^2}{V} \qquad\qquad (27a)$$

Under similar condition, N_2 molecules of gas 2 exerted

pressure P_2, $P_2 = \dfrac{1}{3}\dfrac{N_2 m_2 \bar{U}_2^{\,2}}{V}$ (27b)

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

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

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

$\Rightarrow$ $P = P_1 + P_2 + P_3$ (28b)

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

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

Deviation from ideal gas behavior

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

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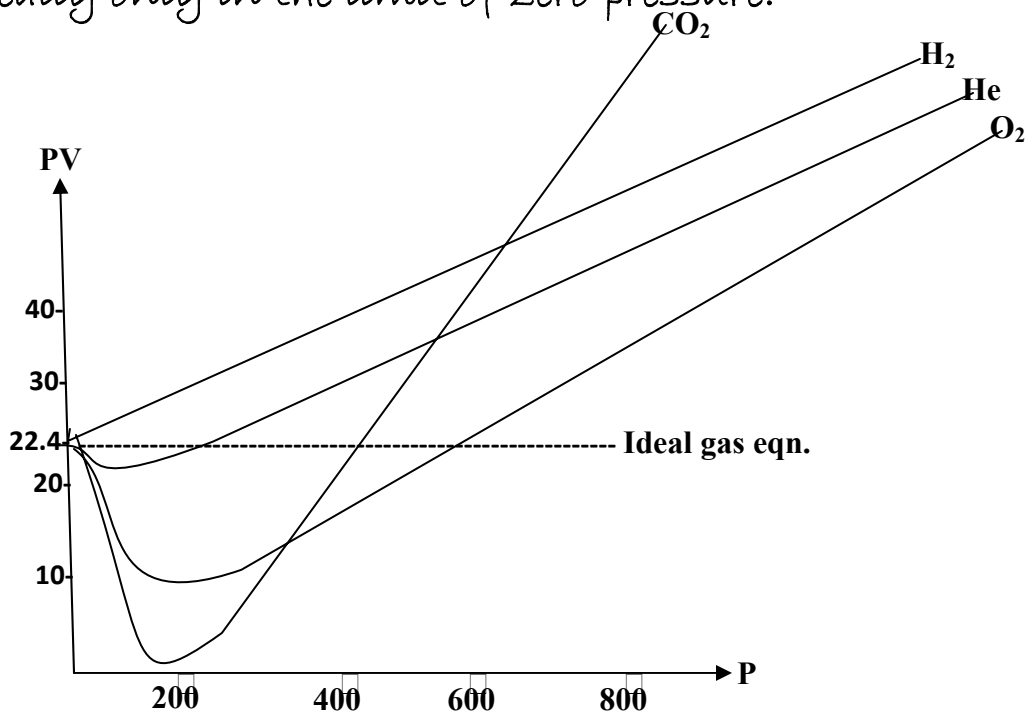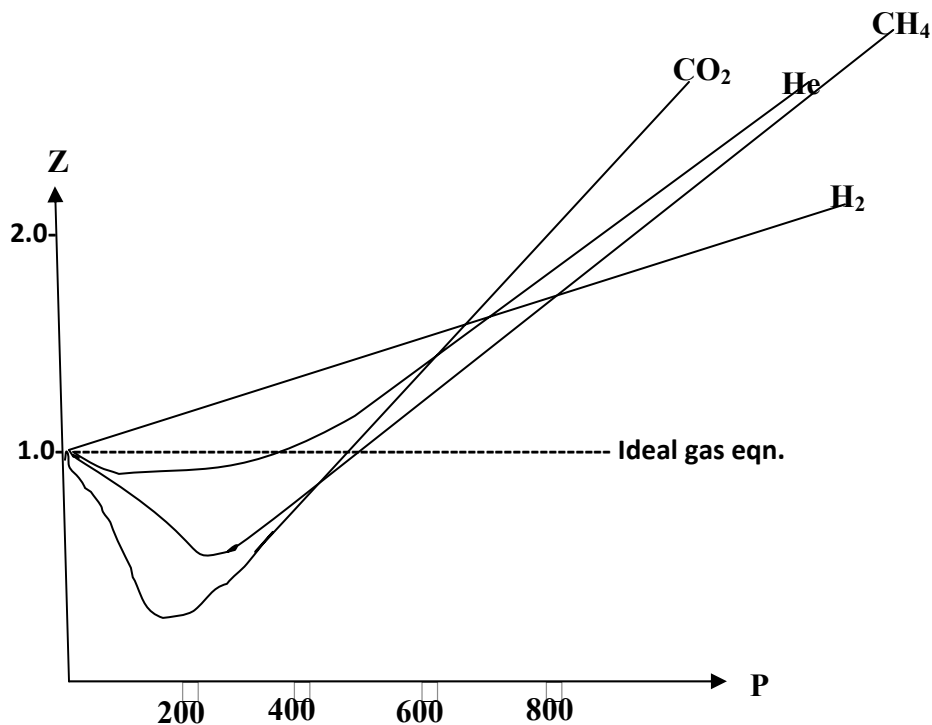

From the diagram,

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

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

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

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

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

For real gases, Z is a function of both temperature and pressure and its value varies. The amount by which the actual factor differs from unity gives a measure of deviation from ideality for the gas.

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

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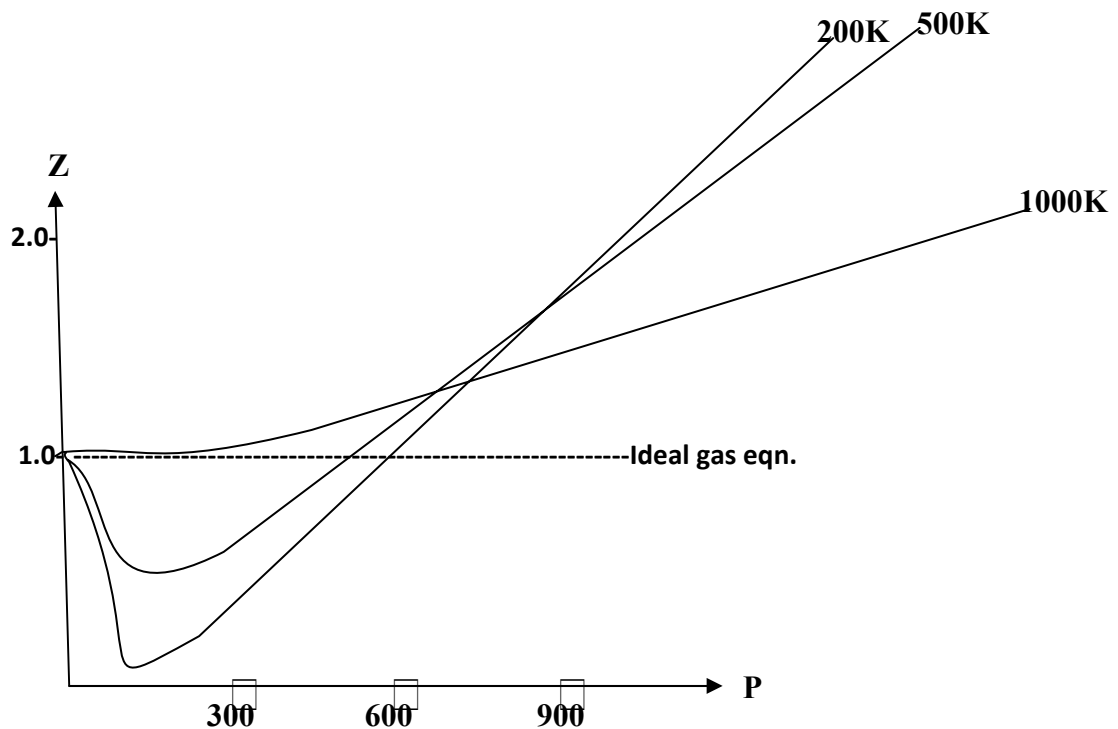
From the graph above, an increase in temperature causes the minimum to become smaller and at the same time, the position of the minimum moves toward lower pressure.

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

<u>Causes of deviation</u>

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

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

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

The van de Waal's equation

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

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

But for n mole, the equation becomes

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

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

Van der Waal and critical phenomenon

Critical temperature, T_c: critical temperature of a gas is that temperature above which it cannot be liquefied no matter how great the pressure the pressure applied. It is given by the expression

$$T_c = \frac{8a}{27 Rb}$$

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

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

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

$$V_c = 3b$$

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

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

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

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

N.B: Numerical problems related to these concepts shall be treated during the lecture hours.

The distribution of molecular velocities

While deriving the equation for pressure from the kinetic theory of gases, it was assumed that all molecules are moving with the same speed, i.e having the root mean square velocity ($\bar{u}^2$). However, in practice, all the molecules cannot move with the same speed because they are frequently colliding with each other and walls of container leading to the interchange of momentum by the molecules. For example, consider two

molecules with a given velocity moving in the same direction and collided. During collision, it is possible that one molecule may completely transfer its momentum to the other thereby causing the latter molecule to move off with increased velocity and the former may stop completely and vice versa.

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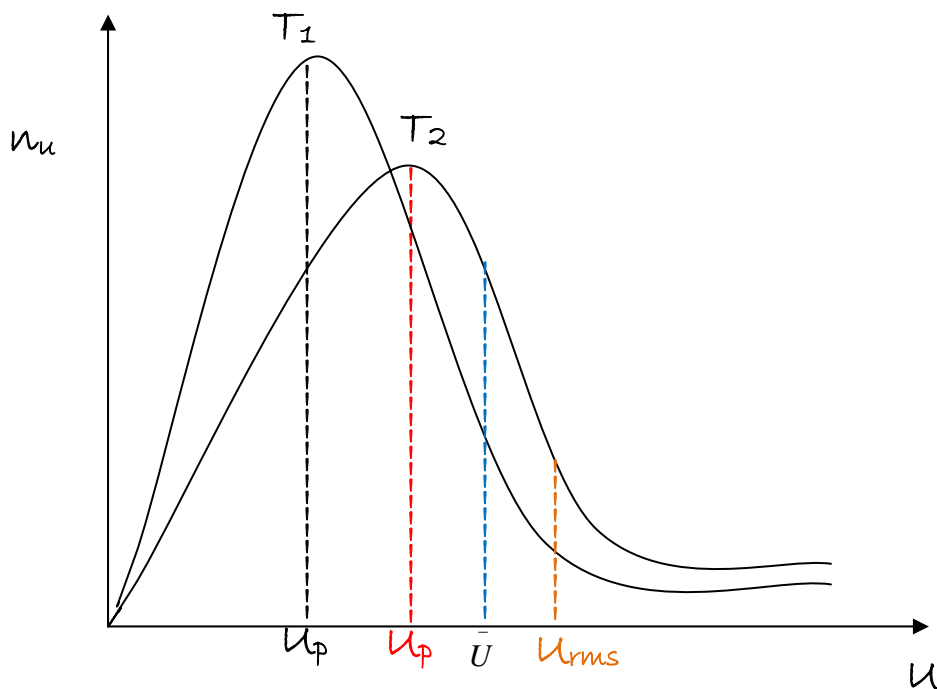
Total area under the curve = total number of molecules in the collection, i.e. total number of molecules having all velocities.

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

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

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

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

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

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

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

Therefore, the mean square velocity is given by

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

Hence, the root means square velocity, U_{rms} is given by

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

Relating the root mean square to the molar mass

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

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

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

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

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

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

Ratio of different velocities is

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

<mark>N.B: Numerical problems related to these concepts shall be treated during the lecture hours.</mark>

Collision properties

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

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

   $$\lambda = \frac{3\eta}{mnu_{rms}} = \frac{3\eta}{du_{rms}}$$ where λ is the mean free path, n is the number of molecules per m³, m is the mass and d is the density

   (b) In term of molecular diameter, δ

   $$\lambda = \frac{1}{\sqrt{2}\pi\delta^2\bar{n}}$$

where $\overline{n}$ is the average number of molecules per cubic

centimeter and it is expressed as $\overline{n} = \dfrac{P}{RT} N_A$.

2. Collision frequency, z: it is the number of molecular collisions taking place per second per unit volume of the gas. It is denoted by z and given by the relation

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

Where $<\overline{u}>$ is the average velocity and it is given as

$$<\overline{u}> = \sqrt{\dfrac{8RT}{\pi M}}$$

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

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

N.B: Numerical problems related to these concepts shall be treated during the lecture hours.

THERMAL ENERGY AND HEAT ENERGY

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

Since $N = nN_A$,

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

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

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

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

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

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

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

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

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

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

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

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

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

$$\therefore \qquad E = nRT$$

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

The heat capacity at constant volume (C_v) is given by

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

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

But R=8.314JK⁻¹mol⁻¹

$$\bar{C}_v = \frac{3}{2} nR = 12.47 \text{ Jmol⁻¹}$$

Comment: The fact that heat capacity can be predicted is the justification that for the equation $nRT = \dfrac{1}{3}Nm\bar{U}^{2}$

Internal Modes of Motions

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

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

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

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

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

For a linear molecules containing A atoms

Total D.O.F = 3A

Translation D.O.F = 3

Rotational = 2

Vibrational= (3A-5)

For non-linear molecules containing A atoms

Total D.O.F = 3A

Translation D.O.F = 3

Rotational = 3

Vibrational= (3A-6)

The equipartition principle

The principle of equipartition of energy states as follow:

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

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

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

➢ For monoatomic gas: $\bar{C_v} = 3 \bullet \frac{1}{2} R$

➢ For linear molecules :

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

➢ For non- linear molecules:

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

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

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Translational   rotational   Vibrational
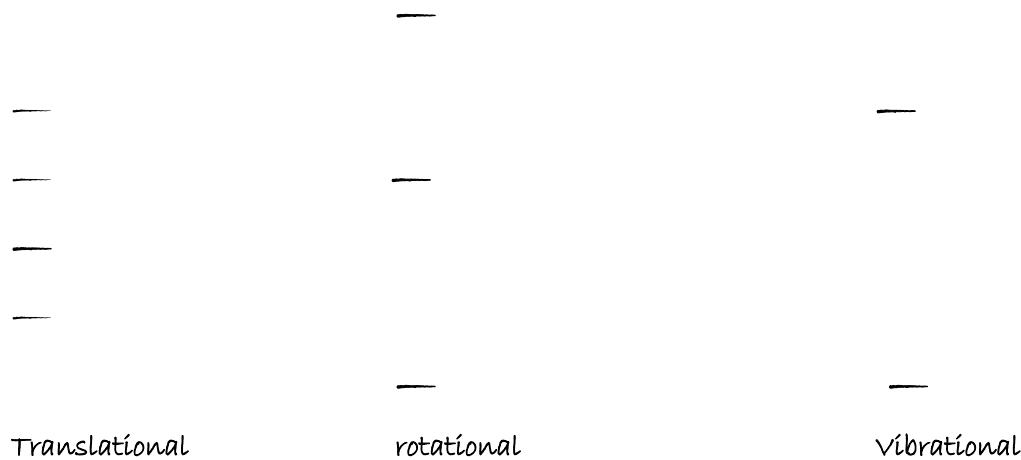
PHASE EQUILIBRIA

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

Phase rule

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

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

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

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

Under normal conditions, water constitutes a three-phase equilibria system (i.e. ice, water and water vapour). However,

at a very high pressure, six different crystalline forms of ice exist, each of which constitutes a separate phase, since each is clearly separated from the other by a definite boundary.

<u>Component</u>: The number of components in a system is the minimum number of independent chemical constituents necessary to describe the composition of each phase present either directly or in the form of a chemical equation.

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

Consider this equation

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

Phase 1   phase 2   phase 3
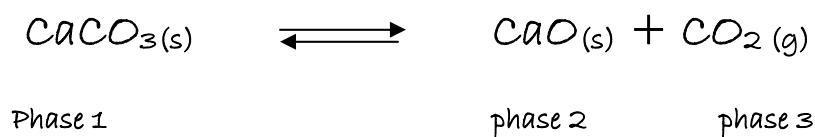
The equation involves 3 phases but only 2 components. To specify the composition of the gas phase, specie CO_2 is needed. Also, to specify the composition of solid phase, either $CaCO_3$ or CaO is needed.

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

<u>Degree of Freedom</u>: is the number of independent intensive variables (e.g. temperature, pressure, concentration, density etc) which must be fixed in order to completely define the system at equilibrium. For instance, in a single-component, single-phase system (i.e. C=1, P=1), the pressure and temperature may be changed independently without changing the number of phases. So, F=2 (a bi-variant system i.e. a system with 2 degree of freedom)

APPLICATION OF THE PHASE RULE TO WATER

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

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

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

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

i.e. two-phases in equilibrium have 1 degree of freedom implying that only one of the two variables (temperature or pressure) needs to be specified in order to define the system.

(iii)   Three-phase regions: is a region where 3 phases are present in equilibrium. $F=1-3+2=0$

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

Phase Diagram

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

Phase diagram of water
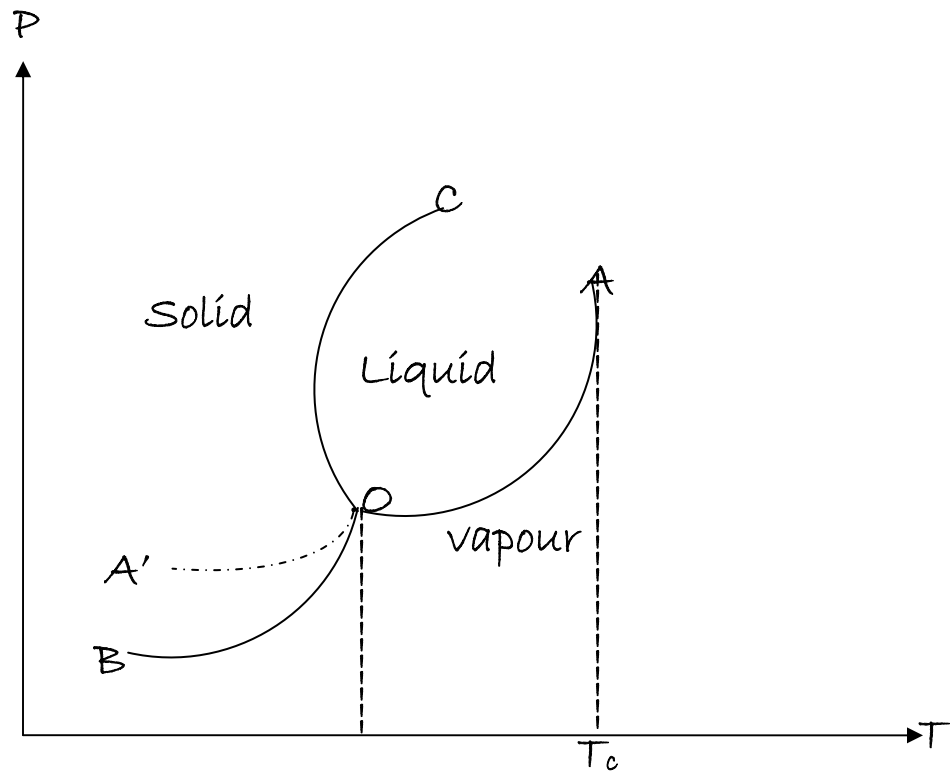
OA- equilibrium between liquid-vapour

OB- equilibrium between solid-vapour

OC- equilibrium between solid-liquid

OA and OB represent the variation of the vapour pressure of solid and liquid with temperature. OA continues to the critical

temperature T_c (where liquid and vapour becomes indistinguishable) and OB continues down to zero Kelvin.

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

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

Phase diagram of Sulphur
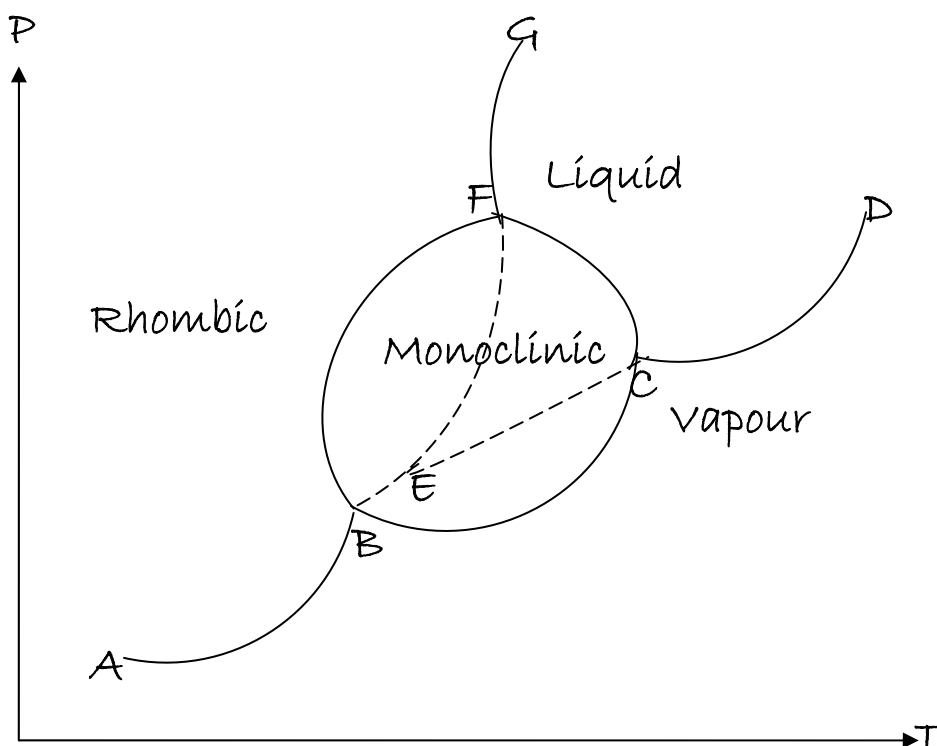
There are 4 triple points, they are:

F- Triple point for Rhombic-Monoclinic-Liquid sulphur

B- Triple point for Rhombic-Monoclinic-Vapour sulphur

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

C- Triple point for Monoclinic-Liquid- Vapour sulphur

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

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