

Expt. No. Subject: Chemical Engineering Thermodynamics - I

Code - AS-4073, (CH-2301)

Section A

Ans 1,

- (i) c, d, (iii) e, (iv) d, (v) b, (vi) c  
 (vii) d, (viii) d, (ix) c, (x) a

Section - B

Unit - I

Ans 2 (i) Thermodynamic Property: A thermodynamic property is characteristic of a system which is associated with energy and its transformation and which can be quantitatively evaluated.

\* Also put some properties like temp, press, etc.  
 \* Types of properties like extensive & intensive property give detailed above two properties with example, etc.

(ii) Thermodynamic Equilibrium:

point focus on what is equilibrium, types of equilibrium, with details,

(iii) Reversible and Irreversible process:

Point focus on: what is process, what is reversible & irreversible process? examples.

(iv) System and its type: A thermodynamic system

refers to a definite quantity of matter enclosed by a boundary on which we focus our attention for thermodynamic analysis.

Give details: open system, closed system, isolated system with example etc.

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Ans 3

The parameters a and b of the RK equation of state are given by

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c T_c^{1.2}} = \frac{0.42748 \times (8.314)^2 \times (569.4)^{2.5}}{2.497 \times 10^6 \times (1427.85)^{1.2}}$$

$$= 4.426 \text{ m}^6 \text{ Pa mol}^{-2}$$

$$b = \frac{0.08664 \times R T_c}{P_c} = \frac{0.08664 \times 8.314 \times 569.4}{2.497 \times 10^6} = 0.1643 \times 10^{-3} \text{ (m}^3/\text{mol)}$$

Let us use Cardan's method to determine  $y_0$  and  $y_1$

$$A = \frac{aP}{(RT)^2} = \frac{4.426 \times 0.215 \times 10^6}{(8.314 \times 1427.85)^2} = 0.0752$$

$$B = \frac{bP}{RT} = \frac{0.1643 \times 10^{-3} \times 0.215 \times 10^6}{8.314 \times 1427.85} = 9.9306 \times 10^{-3}$$

$$\alpha = -1$$

$$\beta = A - B - B^2 = 0.0752 - 9.9306 \times 10^{-3} - (9.9306 \times 10^{-3})^2 = 0.0652$$

$$\gamma = -AB = -0.0752 \times 9.9306 \times 10^{-3} = -7.4678 \times 10^{-4}$$

$$p = \beta - \frac{\alpha^2}{3} = 0.0652 - \frac{1}{3} = -0.2681$$

$$q = \frac{2\alpha\beta}{27} - \frac{\alpha\beta}{3} + \gamma = -\frac{2}{27} + \frac{0.0652}{3} - 7.4678 \times 10^{-4} = -0.0531$$

$$D = \frac{q^2}{4} + \frac{p^3}{27} = \frac{(0.0531)^2}{4} - \frac{(0.2681)^3}{27} = -8.8155 \times 10^{-4}$$

$$x = \left( -\frac{p^3}{27} \right)^{1/2} = \sqrt{\frac{(0.2681)^3}{27}} = 0.0267$$

$$\cos \theta = -\frac{q}{2} \left( -\frac{27}{p^3} \right)^{1/2} = \frac{0.0531}{2} \times \frac{1}{0.0267} = 0.9944 \quad \text{or } \theta = 6.07$$

$$z_1 = 2 \times 8^{1/3} \text{ mol} (0/3) - \frac{x}{3} = 2(0.0267)^{1/3} \text{ mol} (6.07)^{1/3}$$

$$= 0.9308$$

Similarly  $z_2 = 0.0163$

$$z_2 = 0.0528$$

$z = 0.9308$  corresponds to saturated vapor and

$z = 0.0163$  corresponds to saturated liquid.

$$V_g = zRT = \frac{0.9308 \times 8.314 \times 427.85}{0.215 \times 10^6}$$

$$= 15.3999 \times 10^{-3} \text{ m}^3/\text{mol.}$$

$$\therefore V_f = \frac{0.0163 \times 8.314 \times 427.85}{0.215 \times 10^6} = 0.2697 \times 10^{-3} \text{ m}^3/\text{mol.}$$

$$\therefore V_g = 15.3999 \times 10^{-3} \text{ m}^3/\text{mol.}$$

$$V_f = 0.2697 \times 10^{-3} \text{ m}^3/\text{mol.} \quad \left. \vphantom{V_g} \right\} \text{Answer.}$$

→

Unit - II

Solution 4

Given data : 60 liter of ideal gas  
at 290K and 1 bar

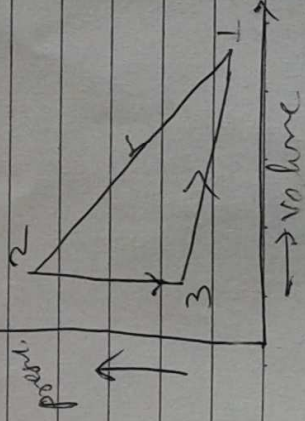
$$\gamma = \frac{C_p}{C_v} = \frac{14.25}{10.15} = 1.404$$

Characteristic gas constant

$$R = C_p - C_v = 14.25 - 10.15$$

$$= 4.10 \text{ kJ/kg K}$$

$$V_1 = 60 \text{ liters} = 0.060 \text{ m}^3.$$



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Considering adiabatic process 1-2,

$$V_2 = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} V_1 = \left(\frac{1}{10}\right)^{\frac{1}{1.404}} \times 0.060 = 0.01164 \text{ m}^3$$

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} = 290 \times \left(\frac{10}{1}\right)^{\frac{1.404-1}{1.404}} = 562.47 \text{ K}$$

Considering isothermal process 3-1,

$$P_3 = P_1 \frac{V_1}{V_3} = \frac{1 \times 0.06}{0.01164} = 5.155 \text{ bar. } \left\{ \therefore V_2 = V_3 \right\}$$

$$(b) \text{ Mass of gas } m = \frac{P_1 V_1}{R T_1} = \frac{1 \times 10^5 \times 0.06}{4100 \times 290} = 5.046 \times 10^{-3} \text{ kg.}$$

Change in internal energy during constant volume process 2-3

$$\begin{aligned} U_3 - U_2 &= m (v (T_3 - T_2)) \\ &= 5.046 \times 10^{-3} \times 10.15 (290 - 562.47) \\ &= -13.85 \text{ kJ.} \end{aligned}$$

During constant volume cooling process, temperature and hence internal energy is reduced. This decrease in internal energy equals the heat flow to surroundings since the work done is zero.

$$\begin{aligned} (c) \quad W_{1-2} &= \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} = \frac{m R (T_1 - T_2)}{\gamma - 1} \\ &= \frac{5.046 \times 10^{-3} \times 4100 (290 - 562.46)}{1.404 - 1} \\ &= -13952 \text{ Nm (or J)} \end{aligned}$$

$$\begin{aligned}
 W_{2-3} &= 0 \quad (\text{as volume remains constant}) \\
 W_{3-1} &= P_3 V_3 \ln \frac{V_1}{V_3} = P_1 V_1 \ln \frac{P_2}{P_1} \\
 &= 1 \times 10^5 \times 0.06 \ln \frac{5.155}{1} = 9840 \text{ J}
 \end{aligned}$$

$$\text{Net work done } W_{1-2} + W_{2-3} + W_{3-1}$$

$$= -13.952 + 0 + 9.84 = -4.112 \text{ kJ.}$$

Negative sign means that work has done on the system.

For a cyclic process  $\oint \delta Q = \oint \delta W$

$$\therefore \text{Heat transfer during complete cycle} = -4.112 \text{ kJ.}$$

Negative heat transfer implies that heat has been lost from the system.

Solution 5 (a) Kelvin Planck statement: it is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.  
A. elaborate with example

Clausius statement: it is impossible to devise a cyclically operating device, the sole effect of which is to transfer energy in the form of heat from a low temp. body to high temp. body.

A elaborate with example.

Equivalence: At first sight, Kelvin-Planck's and Clausius statement may appear to be unconnected, but it can be shown that they are virtually two parallel statements of the second law and it can be shown that the violation of one statement implies the violation of the second, and vice-versa.

(a) Explain the figure.

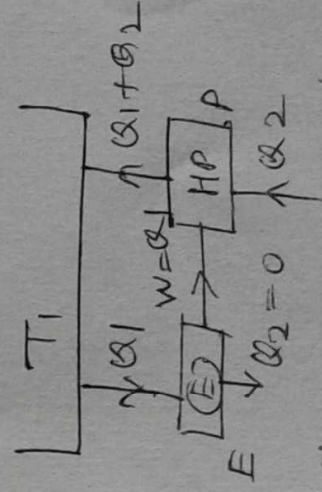
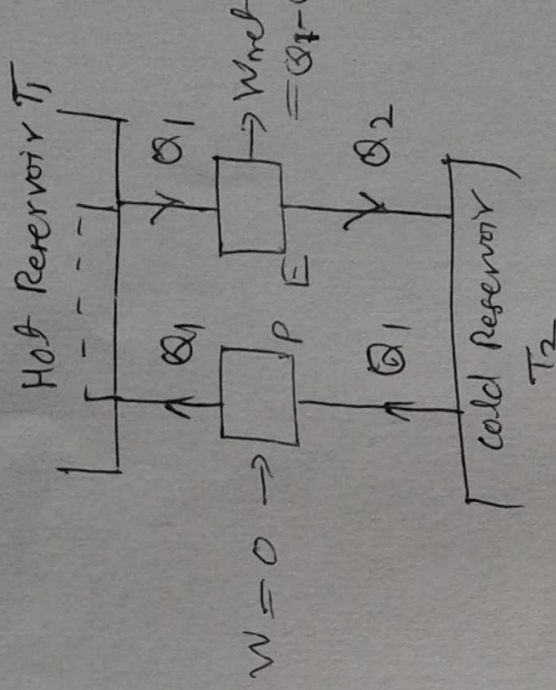
Let assume a cyclic heat

engine  $E$  operating between the same thermal energy reservoirs, producing  $W_{net}$  in one cycle. The state of working of heat engine is such that it draws an amount of

heat  $Q_1$  from hot reservoir eqn is

that discharged by the heat pump. Then the hot reservoir may be eliminated and the heat  $Q_1$  discharged by the heat pump is fed to the heat engine. So we see that the heat pump  $P$  and the heat engine  $E$  acting together constitute a heat engine operating in cycle and producing net work while exchanging heat only with one body at a single fixed temp. This ~~not~~ violates the Kelvin-Planck statement.

(b) elaborate same as above.



Solution 5 (b.)

Let us now consider a system undergoing a reversible cycle. The given cycle can be subdivided into a large number of Carnot cycles. This can be done by drawing several reversible adiabatic lines on the original cycle and by joining the two adjacent adiabatic lines by isothermal lines as explained above.

We know that for a Carnot cycle,  $\frac{Q_2}{T_2} = \frac{T_2}{T_1}$

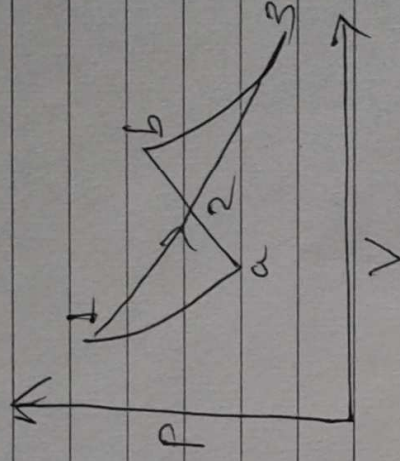
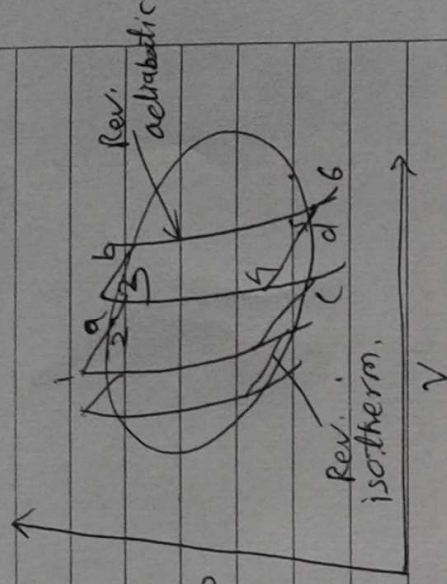
$$\text{or } \frac{-Q_2}{Q_1} = \frac{T_2}{T_1}$$

$$\text{or } \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \sum \frac{Q}{T} = 0$$

where we have used the sign convention for heat interaction. For a cycle consisting of a large number of infinitesimal Carnot cycles, we can write,

$$\oint \frac{dQ}{T} = 0. \quad (\text{for a reversible cycle}), \quad 5.23,$$

Suppose the given cycle is irreversible. If this cycle is replaced by a large number of infinitesimal cycles, some of them are reversible and some are irreversible. We know that the efficiency of an irreversible engine



That is  $\eta_1 < \eta_2$  or

$$\frac{|Q_1'| - |Q_2||}{|Q_1'|} < \frac{|Q_1| - |Q_2|}{|Q_1|} \quad \text{or} \quad \frac{|Q_2|}{|Q_1|} > \frac{|Q_2|}{|Q_1|} = \frac{T_2}{T_1}$$

$$\text{or} \quad \frac{|Q_2'|}{T_2} > \frac{|Q_1'|}{T_1} \quad \text{--- (1)}$$

where the primed quantities refer to the heat into an irreversible engine. If we adopt the sign convention for heat interaction, Eqn. (1) can be written as,

$$-\frac{Q_2'}{T_2} > \frac{Q_1'}{T_1}$$

$$\frac{Q_1'}{T_1} + \frac{Q_2'}{T_2} = \sum \frac{Q_i'}{T_i} < 0$$

for the infinitesimal irreversible cycles we get.

$$\oint \frac{dQ}{T} < 0.$$

If the given original cycle is replaced by a large number of infinitesimal cycles out of which some are irreversible, we get.

$$\oint \frac{dQ}{T} < 0 \quad (\text{for an irreversible cycle})$$

and can be generalised and state

$$\left[ \oint \frac{dQ}{T} \leq 0 \right] \quad \left| \begin{array}{l} \text{Note } \oint = \text{for reversible cycle.} \\ < \text{for irreversible cycle.} \end{array} \right.$$

Above Clausius inequality.



## Solution 6: Statistical thermodynamics or Statistical Mechanism.

Statistical mechanism or statistical thermodynamics is a branch of physics that applies probability theory, which contains mathematical tools for dealing with large populations, to the study of the thermodynamic behavior of systems composed of a large number of particles.

What it provides? Statistical mechanism provides a framework for relating the microscopic properties of individual atoms and molecules to the macroscopic bulk properties of material that can be observed in everyday life.

\* Statistical mechanism provides a molecular-level interpretation of macroscopic thermodynamic quantities such as work, heat, free energy, and entropy.

\* It enables the thermodynamic property of bulk material to be related to the spectroscopic data of individual molecules.

\* Statistical thermodynamics is a function of the distribution of the system on its micro states.

What it does?

The essential problem in statistical thermodynamics is to calculate the distribution of a given amount of energy  $E$  over  $N$  identical systems.

Fundamental:

in statistical thermodynamic entropy is represented

$$\text{by } S = k_B \ln \Omega$$

where  $k_B$  is Boltzmann's constant  $1.380 \times 10^{-23} \text{ J/K}$

and  $\Omega$  is the number of microstates.

This equation is valid only if each microstate is equally probable.

Boltzmann distribution:

if the system is large the Boltzmann distribution could be used

$$n_i \propto \exp\left(-\frac{U_i}{k_B T}\right)$$

where  $n_i$  stands for the number of particles occupying level  $i$  or the number of feasible microstates corresponding to microstate  $i$ ,  $U_i$  stands for the energy of  $i$ ,  $T$  stand for temperature and  $k_B$  Boltzmann constant.

if  $N_i$  is the total No of particles or states, the distribution of probability denotice follows:

$$P_i \equiv \frac{n_i}{N} = \frac{\exp\left(-\frac{U_i}{k_B T}\right)}{\sum_j \exp\left(-\frac{U_j}{k_B T}\right)}$$

where some of the denominators is over all levels.

Microstates: In statistical mechanics, a microstate is a specific configuration of a thermodynamic system that the system may occupy with a certain probability in the course of its thermal fluctuation.

Fundamental Postulate:

Given an isolated system in equilibrium, it is found with equal probability in each of its accessible microstates.

## Application of statistical thermodynamics:

Form

physics, statistical thermodynamics/mechanics provide such a bridge by teaching us how to conceive of a thermodynamic system as an assembly of units. More specifically, it demonstrates how the thermodynamic parameters of a system, such as temperature and pressure, are ~~interpre~~ interpretable in terms of the parameters descriptive of such constituent atoms and molecules.

Applications it also ~~include~~ include include in clude, application to the physical systems such as solids, liquids and gases, applications to chemical and biological systems (colloids, interfaces, complex fluids, polymers and biopolymers, cell physics), and other interdisciplinary applications to for instance biological, economical and sociological systems.

in biological like (olfaction mechanism).

Solution 2 (a) Kirchhoff equation: An expression for the variation of the heat to the heat of reaction with temperature can be derived in a simple manner.

If  $H_A$  is the total heat content of the reactants and  $H_B$  is that of the products, at the same temp and pres.

$$\text{Then } \Delta H = H_B - H_A$$

at const. pres. Differentiate both side with temperature.

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = \left( \frac{\partial H_B}{\partial T} \right)_P - \left( \frac{\partial H_A}{\partial T} \right)_P$$

According to equation (12.6), it is equal to  $C_p$ , and hence

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = (C_p)_B - (C_p)_A \quad \text{where } (C_p)_B \text{ \& } (C_p)_A \text{ are heat capacities.}$$

The right hand side of equation is the increase in the heat capacity of the system accompanying the chemical reaction, and so it may be represented by  $\Delta C_p$  thus (12.6) takes the form.

$$\left[ \frac{\partial(\Delta H)}{\partial T} \right]_P = \Delta C_p$$

equation

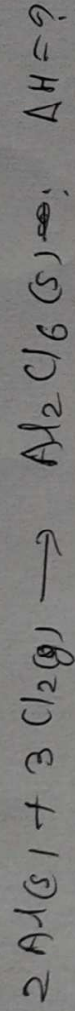
The cubic is a Kirchhoff eqn.

The rate of variation of the heat of reaction with temperature, at constant pressure, is thus equal to the increase in the heat capacity accompanying the reaction.

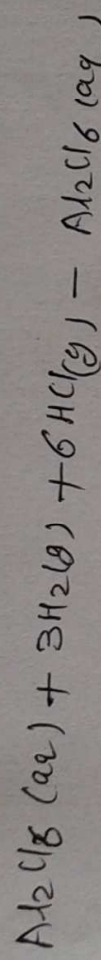
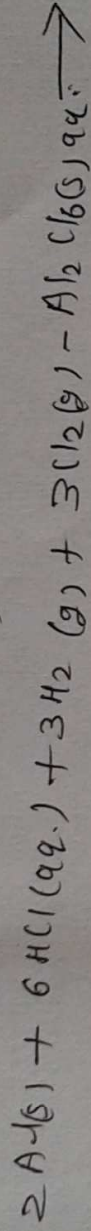
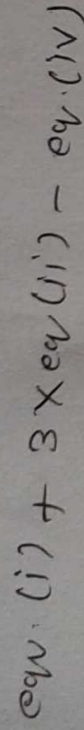
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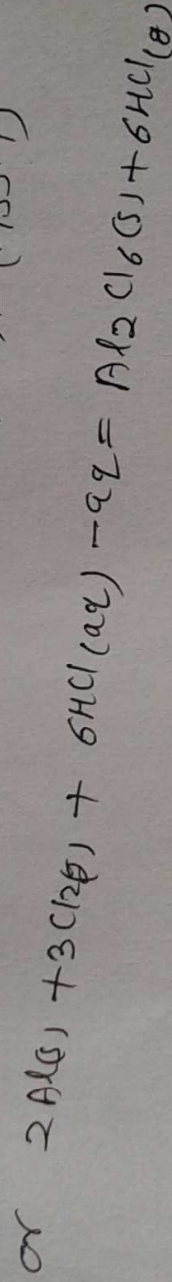
Solution 8(b) We have to calculate the  $\Delta H$  of the equation.



In given eq. (iii) does not contain any specie of eqv.  
Apply the arrangement of equations

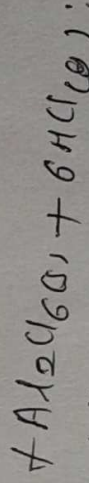
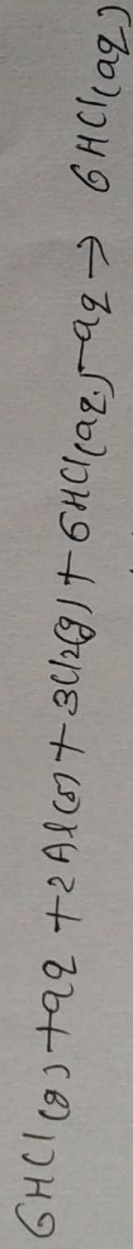


$$\Delta H = -244 + 3 \times (-44) - (-153.7)$$

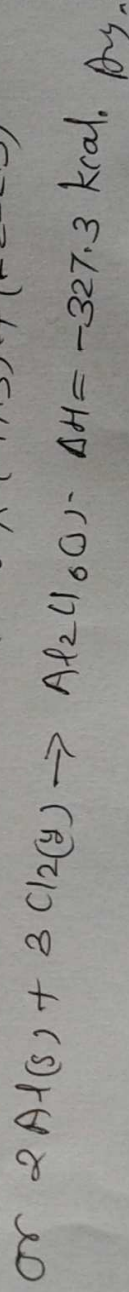


Now multiplying the eq. (ii) by 6 and adding it to the eqv.  
just above.

$$\Delta H = -222.3 \text{ kcal.}$$



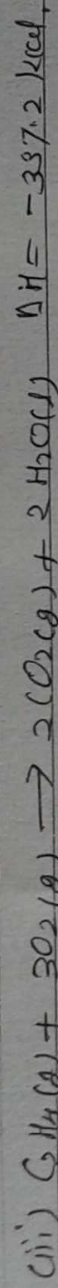
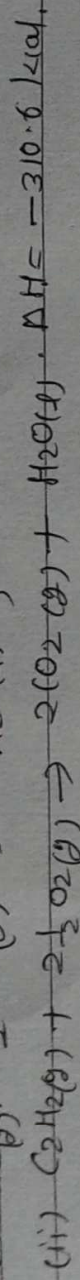
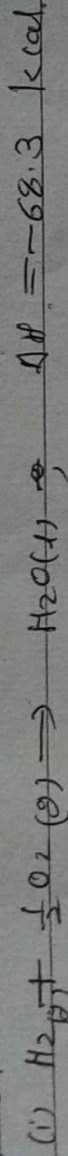
$$\Delta H = 6 \times (-17.5) + (-222.3)$$



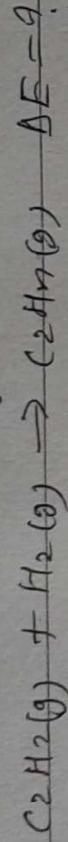
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Solution g(a) ~~write~~ it contains some part of solution 8(a).

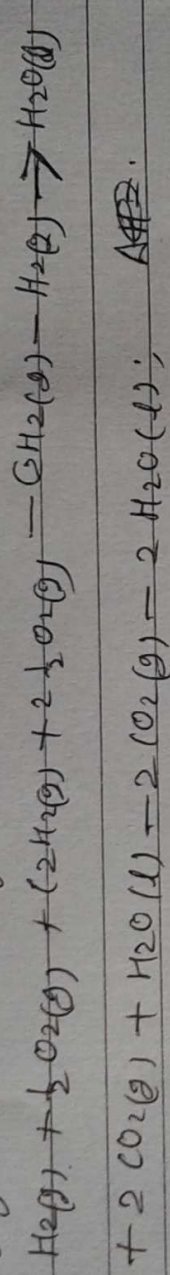
(b). Given that



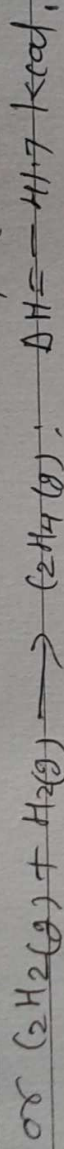
We have to calculate  $\Delta E$  for the equation



Arranging the above eqn.



$$\Delta H = -68.3 + (-310.6) - (-337.2)$$



$\Delta H$  is the heat of reaction at constant pressure and to calculate heat at const. volume, we determine  $\Delta E$  by using the equation,

$$\Delta H = \Delta E - \Delta n_g RT$$

where  $\Delta n_g = \text{mole of gaseous product} - \text{mole of gaseous react.}$

$$= 1 - 2 = -1$$

$$R = 0.002 \text{ kcal/K/mole}, \quad T = 273 + 25 = 298 \text{ K}$$

Thus we have

$$\Delta E = -41.7 - (-1 \times 0.002 \times 298)$$

$$= -41.104 \text{ kcal. } \underline{\underline{\text{Ans.}}}$$

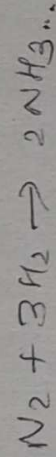
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Solution 10(a) Le Chatelier's principle states that any disturbance in a homogeneous system induces spontaneous processes in a direction to annul the inhomogeneity so as to restore the system to a new state of equilibrium.

Or  
States that a system at equilibrium when subjected to a disturbance responds in a way that tends to minimise the effect of that disturbance.

The equilibrium in the gas-phase reaction  $A \rightleftharpoons 2B$ , when pressure is applied to this system, it responds in such a way as to minimise the effect of the increase in pressure. This is achieved by decreasing the reaction  $A \leftarrow 2B$ . Thus, increase in pressure decreases the number of B molecules and increases the number of A molecules.

Similarly for Ammonia reaction,



Solution (b) Basis 1 mole  $N_2$ , 3 mole  $H_2$ ,

let  $\epsilon$  be the extent of reaction.

Then the number of moles of various species at equilibrium are calculated using  $n_i = n_{i0} + \nu_i \epsilon$

moles of  $N_2$ ,  $H_2$  and  $NH_3$  are  $1 - \epsilon$ ,  $3 - 3\epsilon$ , and  $2\epsilon$ .

Total moles at eq. =  $4 - 2\epsilon$ .

mole fraction of  $N_2$ ,  $H_2$ ,  $NH_3$  are,

$$\frac{1-\epsilon}{4-2\epsilon}, \quad \frac{3(1-\epsilon)}{4-2\epsilon}, \quad \frac{2\epsilon}{4-2\epsilon}$$

The sum of stoichiometric number  $\nu = 2 - 1 - 3 = -2$ .

$$K_p = (k/k_p) P^{-v} = k P^2$$

for ideal behaviour, so that  $K_p = k$ ,  
eq. comp.

$$\therefore \frac{[2\epsilon / (4-2\epsilon)]^2}{(1-\epsilon)/(4-2\epsilon)} [3(1-\epsilon)/(4-2\epsilon)]^3 = 2 \times 10^{-4} P^2$$

$$\text{That is } \frac{4\epsilon^2 (4-2\epsilon)^2}{27(1-\epsilon)^4} = 2 \times 10^{-4} P^2$$

$$\frac{\epsilon (4-2\epsilon)}{(1-\epsilon)^2} = 3.6742 \times 10^{-2} P$$

(a) when  $P = 20$  bar

$$\frac{\epsilon (4-2\epsilon)}{(1-\epsilon)^2} = 0.73485$$

$$2.73785\epsilon^2 - 5.4697\epsilon + 0.73485 = 0$$

$$\text{Solving } \epsilon = 0.1448$$

$$\therefore z = \frac{V_1/\epsilon}{n_{10}} = \epsilon = 0.1448$$

That is conversion of nitrogen = 14.48%

(b) when  $P = 200$  bar

$$\frac{\epsilon (4-2\epsilon)}{(1-\epsilon)^2} = 7.3485$$

$$9.3785\epsilon^2 - 18.697\epsilon + 7.3485 = 0$$

$$\therefore \epsilon = 0.5375$$

So conversion of  $N_2 = 53.75\%$ .  
We see that the increase in pressure favours the formation of ammonia as this reaction is accompanied by a decrease in the number of moles.

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Answer II

## THEORY OF GASES

### Introduction

Molecules have a diameter of the order of  $2 \text{ \AA}$  and the distance between them in a gas is  $20 \text{ \AA}$  while the interaction distance in solids is very small. R. Clausius and J. C. Maxwell developed the mathematical concept of the random motion of the gas molecules in a gas which helped to explain not only the properties of gases but also that of free electrons in metals.

### Postulates of Kinetic Theory of Gases

1. A gas consists of a large number of minute particles known as molecules of the same size and mass.
2. The interaction between molecules is negligible unlike solids.
3. The molecules in a gas are in a state of random motion in all directions with different velocities ranging from zero to infinity.
4. The size of the molecules is negligible in comparison with the volume of a gas.
5. During the motion, molecules collide with each other which is perfectly elastic.
6. The impact of molecules on the walls of the container exerts a pressure. Pressure of a gas is the average force per unit area of the molecules on the walls of the container during impact. Larger the number of impacts, greater will be the pressure.
7. Due to random motion of molecules in gas, the molecules have kinetic energy. The average kinetic energy of a gas molecule varies as absolute temperature.

According to kinetic theory of gases, the molecules of a gas are in random motion. So, the average velocity of the molecules is zero. Hence we find the rms velocity of a molecule.

If  $c_1, c_2, c_3, \dots, c_n$  are the velocities of the molecules of a gas at any instant, the mean square velocity of the molecules of the gas is,  $\bar{c}^2 = \frac{c_1^2 + c_2^2 + c_3^2 + \dots}{n}$ . Hence root mean square velocity of a molecule is

$$c_{rms} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}}$$

### 1.1.3 Pressure Exerted by a Gas

Let us enclose a gas in a cubical box of dimension 1 metre. Let  $m$  be the mass of the molecule and  $n$  be the total number of molecules in this cubical vessel of volume  $1 \text{ m}^3$ .

Consider a molecule D moving in the  $x$ -direction with a velocity  $v$  towards the wall B. It hits the wall B with a velocity  $v$  and rebounds with the same velocity  $v$  as the collision is perfectly elastic. Momentum of the molecule D before collision is  $mv$  and the momentum of the molecule after collision is equal to  $-mv$ . Thus change in momentum of the molecule on the wall B due to a single collision of the molecule D is  $mv - (-mv) = 2mv$ .

In 2 metres the molecule undergo 1 collision. For  $v$  metre it will undergo  $\frac{2}{v}$  collisions (in a sec). Thus force exerted by the single molecule on the wall B = change in momentum

$$\times \text{time} = 2mv \times \frac{v}{2} = mv^2.$$

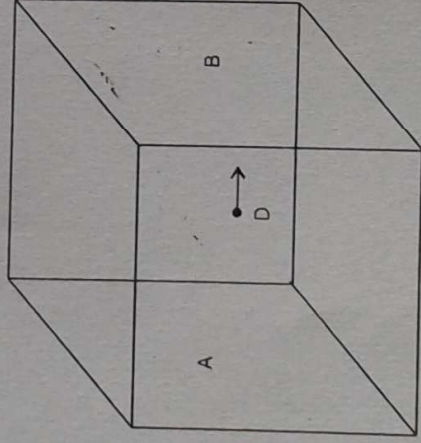


Fig. 1.1

We shall now consider the combined effect of collisions of all molecules on the wall B. All the  $n$  molecules in the cubical vessel are not moving along the  $x$ -axis between the walls B and A. Since there are only three independent directions  $x, y$  and  $z$ , it is reasonable

to assume that, at any instant, there may be  $\frac{n}{3}$  molecules moving along the x-axis between walls B and A.

Therefore, force exerted by the molecules on the walls  $B = \frac{1}{3} m n v^2$ . Being the area of the surface B is 1 sq. m., the pressure exerted on the wall B is

$$P = \frac{1}{3} m n v^2$$

But all molecules are not moving with the same velocity. Hence it is reasonable to substitute  $\bar{c}^2$ , the mean square velocity of the molecule, for  $v^2$ . If  $c_1, c_2, c_3, \dots, c_n$  are the velocities of the molecules at any instant, then

$$\bar{c}^2 = c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2$$

$$P = \left( \frac{1}{3} \right) m n \bar{c}^2$$

Therefore,

Since  $m$  is the mass of the molecule and  $n$  is the number of molecules per unit volume of the gas, then

$$\rho = \frac{m n}{1}$$

$$P = \frac{1}{3} \rho \bar{c}^2$$

i.e.,

Further discussion is possible by choosing unit volume or molar volume ( $V_m$ ). Let us consider one mole of a gas which occupies a volume  $V_m$ . The pressure exerted by the gas is

$$P = \frac{1}{3} m N_A \bar{c}^2$$

$P V_m = \frac{1}{3} m N_A \bar{c}^2 = R T$ , where  $R$  is universal gas constant. Thus

$$m \bar{c}^2 = \frac{3 R T}{N_A} = 3 k_B T$$

as Boltzmann constant  $k_B = \frac{R}{N_A}$ .

or 
$$\frac{1}{2} m \bar{c}^2 = \frac{3}{2} k_B T \quad \dots(1)$$

This is kinetic energy of a molecule.

Hence, average kinetic energy of one mole of the gas is 
$$\frac{1}{2} m \bar{c}^2 N_A = \frac{3}{2} N_A k_B T = \frac{3}{2} RT \quad \dots(2)$$

It is now evident that K.E. of a molecule of the gas is  $\frac{3}{2} k_B T$  or K.E.  $\mu T$ .

*Conclusion:* Let us consider any amount of a gas. Let  $P$ ,  $V$ ,  $T$  and  $n$  be the pressure, volume, temperature and number of the molecules of the gas.

K.E. of a molecule of a gas  $= \frac{3}{2} k_B T$

Hence, K.E. of the gas  $= \frac{3}{2} n k_B T$ . If  $M$  is the mass of a given gas with  $V$  as the volume,

then

$$PV = \frac{1}{3} M \bar{c}^2 = \frac{2}{3} \times \frac{1}{2} M \bar{c}^2 = \frac{2}{3} \times \text{K.E. of the gas} \quad \dots(3)$$

$$= \frac{2}{3} \times \frac{3}{2} n k_B T$$

or  $PV = nk_B T \quad \dots(4)$

#### 1.1.4 Boyle's Law and Charles Law

(i) Kinetic energy of a gas is directly proportional to the absolute temperature. Hence from equations (1) and (2), it is obvious that at constant temperature  $PV = \text{constant}$

or  $V \propto \frac{1}{P}$ . This is Boyle's law.

(ii) Since K.E. of the gas is proportional to the absolute temperature, from equations (3) and (4),  $PV \propto T$ .

#### Conclusions

(a) At constant pressure [from Eqns. 3 and 4]

$V \propto T$ . This is Charles first law

(b) At constant volume

$P \propto T$ . This is Charles second law.

solution 7

**Maximum Work Obtainable from Two Finite Bodies at Temperatures  $T_1$  and  $T_2$**

Let us consider two identical finite bodies of constant heat capacity at temperatures  $T_1$  and  $T_2$  respectively,  $T_1$  being higher than  $T_2$ . If the two bodies are merely brought together into thermal contact, delivering no work, the final temperature  $T_f$  reached would be the maximum.

$$T_f = \frac{T_1 + T_2}{2}$$

If a heat engine is operated between the two bodies acting as thermal energy reservoirs (Fig. 7.17), part of the heat withdrawn from body 1 is converted to work  $W$  by the heat engine, and the remainder is rejected to

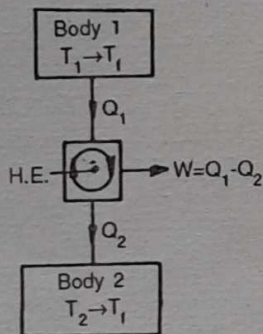


FIG. 7.17 Maximum work obtainable from two finite bodies

body 2. The lowest attainable final temperature  $T_f$  corresponds to the delivery of the largest possible amount of work, and is associated with a reversible process.

As work is delivered by the heat engine, the temperature of body 1 will be decreasing and that of body 2 will be increasing. When both the bodies attain the final temperature  $T_f$ , the heat engine will stop operating. Let the bodies remain at constant pressure and undergo no change of phase.

Total heat withdrawn from body 1

$$Q_1 = C_p (T_1 - T_f)$$

where  $C_p$  is the heat capacity of the two bodies at constant pressure.

Total heat rejected to body 2

$$Q_2 = C_p (T_f - T_2)$$

$\therefore$  Amount of total work delivered by the heat engine

$$\begin{aligned} W &= Q_1 - Q_2 \\ &= C_p (T_1 + T_2 - 2T_f) \end{aligned}$$

For given values of  $C_p$ ,  $T_1$  and  $T_2$ , the magnitude of work  $W$  depends on  $T_f$ . Work obtainable will be maximum when  $T_f$  is minimum. Now, for body 1, entropy change  $\Delta S_1$  is given by

$$\Delta S_1 = \int_{T_1}^{T_f} C_p \frac{dT}{T} = C_p \ln \frac{T_f}{T_1}$$

For body 2, entropy change  $\Delta S_2$  would be

$$\Delta S_2 = \int_{T_2}^{T_f} C_p \frac{dT}{T} = C_p \ln \frac{T_f}{T_2}$$

Since the working fluid operating in the heat engine cycle does not undergo any entropy change,  $\Delta S$  of the working fluid in heat engine =  $\oint dS = 0$ .

Applying the entropy principle

$$\Delta S_{\text{univ}} \geq 0$$

$$\therefore C_p \ln \frac{T_f}{T_1} + C_p \ln \frac{T_f}{T_2} \geq 0$$

$$C_p \ln \frac{T_f^2}{T_1 T_2} \geq 0$$

From equation (7.20), for  $T_f$  to be a minimum

$$C_p \ln \frac{T_f^2}{T_1 T_2} = 0$$

$$\ln \frac{T_f^2}{T_1 T_2} = 0 = \ln 1$$

or

$$T_f = \sqrt{T_1 T_2}$$

For  $W$  to be a maximum,  $T_f$  will be  $\sqrt{T_1 T_2}$ . From equation

$$W_{\text{max}} = C_p (T_1 - T_2 - 2\sqrt{T_1 T_2}) = C_p (\sqrt{T_1} - \sqrt{T_2})^2$$

The final temperatures of the two bodies, initially at  $T_1$  and  $T_2$ , can range from  $(T_1 + T_2)/2$  with no delivery of work to  $\sqrt{T_1 T_2}$  with maximum delivery of work.

**Maximum Work Obtainable from a Finite Body and a Thermal Energy Reservoir (TER)**

Let one of the bodies considered in the previous section be a thermal energy reservoir. The finite body has a thermal capacity  $C_p$  and is at temperature  $T$  and the TER is at temperature  $T_0$  such that  $T > T_0$ . Let a heat engine operate between the two (Fig. 7.18). As heat is withdrawn from the body, its temperature decreases. The temperature of the TER would, however, remain