

### STATES OF MATTER

1. What is the difference between vapour and gas?

**Ans.** A substance which is in gaseous state at room temperature is called a gas. However, if a substance is not in gaseous state at room temperature but changes into gaseous state on heating, then the gaseous state obtained is called vapour or when a gas is below its critical temperature, it is called vapour.

2. Why mercury is used as a liquid in a barometer? Explain.

**Ans.** Mercury is used as a liquid in a barometer because.

- (i) The height of the column in a barometer is inversely proportional to the density of the liquid, i.e. less dense the liquid, higher will be the column. Because of high density of mercury, it supports column of convenient height in a barometer.
- (ii) Since mercury is not volatile at ordinary temperature, therefore, the pressure exerted by the vapours above the mercury column is very small and can be neglected.

3. The van der Waal's constants for two gases are as follows:

Gas	a(atm L <sup>2</sup> mol <sup>-2</sup> )	b(L mol <sup>-1</sup> )
X	1.39	0.0391
Y	3.59	0.0427

Which of them is more easily liquefiable and which has greater molecular size?

**Ans.** Greater the value of 'a', more easily the gas is liquefiable. Similarly, greater the value of 'b' greater is the molecular size. Hence, gas Y will be more easily liquefiable and will have greater molecular size.

4. Out of N<sub>2</sub> and NH<sub>3</sub>, which one will have greater value of 'a' and which one will have greater value of 'b'?

**Ans.** (I) As NH<sub>3</sub> is more easily liquefiable (due to hydrogen bonding), intermolecular forces of attraction are stronger than in N<sub>2</sub>. Hence, NH<sub>3</sub> will have greater value for 'a'

(II) As NH<sub>3</sub> molecule is larger in size than N<sub>2</sub>, hence NH<sub>3</sub> will have greater value for 'b'

For NH<sub>3</sub>, a= 4.17 L<sup>2</sup> atm mol<sup>-2</sup>, b= 0.0371 L mol<sup>-1</sup>

For N<sub>2</sub>, a= 1.39 L<sup>2</sup> atm mol<sup>-2</sup>, b = 0.0319 L mol<sup>-1</sup>

5. A flask is of capacity of one litre. What volume of air will escape from the flask if it is heated from 27°C to 37°C? Assume pressure constant.

**Ans.**  $V_1=1\text{litre}$                        $V_2=?$   
 $T_1= 27^\circ\text{C}=300\text{k}$ ,                       $T_2=37^\circ\text{C}=310\text{k}$

At Constant pressure,  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$\frac{1}{300} = \frac{V_2}{310}$        $V_2 = 1.0333 \text{ litre}$

Since capacity of flask is one litre

$\therefore$  Volume of air escaped out  
 $= 1.0333-1= 0.0333 \text{ litre} = 33.3\text{ml}$

6. A cylinder containing cooking gas can withstand a pressure of 14.9 atm. The pressure gauge of cylinder indicates 12 atm at 27°C. Due to sudden fire in the building, its temperature starts rising. At what temp. the cylinder will explode?

**Ans.** Suppose the cylinder will burst at  $T_2$  K

Given  $P_1= 12\text{atm}$ ,  $T_1 = (27 + 273) = 300 \text{ k}$

$P_2 = 14.9 \text{ atm}$ ,

Now  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

Here  $V_1 = V_2$  as the volume does not change

$\therefore T_2 = \frac{P_2 T_1}{P_1} = \frac{14.9 \times 300}{12} = 372.5 \text{ k}$

7. 8 g of methane is placed in 5 litre container at 27°C. Find Boyle constant.

**Ans.**  $PV=$  Boyle Constant

But  $PV= nRT = \frac{w}{M} RT$

$= \frac{8}{16} \text{ mol} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ k}$

$= 12.315 \text{ L atm}$

Hence, Boyle constant= 12.315 L atm

8. A mixture of CO and CO<sub>2</sub> is found to have density of 1.50 g L<sup>-1</sup> at 20°C & 740 mm pressure. Calculate the composition of the mixture.

**Ans.** Calculation of average molecular mass of the mixture.

$M = \frac{dRT}{P} = \frac{1.50 \text{ g l}^{-1} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{\left(\frac{740}{760}\right) \text{ atm}} = 37.06 \text{ g mol}^{-1}$

Calculation of percentage composition:

Suppose mol% of CO in the mixture= $x$

Then mol% of CO<sub>2</sub> in the mixture=(100-  $x$ )

Average Molecular mass=  $\frac{x \times 28 + (100-x) \times 44}{100}$

$$\frac{28x+4400-44x}{100} = 37.06$$

$$\text{Or } 16x = 4400 - 3706 = 694$$

$$\text{Or } = 694/16 = 43.38$$

$$\text{Mol\% of CO} = 43.38$$

$$\text{and Mol\% of CO}_2 = 100 - 43.38 = 56.62$$

9. Using van der Waals' equations calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atmosphere at a temperature of 300 K. The value of 'b' is 0.05 lit mol<sup>-1</sup>

**Ans.** According to van der Waals' equation

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

$$\left(11 + \frac{a \times 4}{16}\right)(4 - 2 \times 0.05) = 2 \times 0.082 \times 300$$

$$\left(\frac{176 + 4a}{16}\right) \times 3.9 = 49.2$$

$$(176 + 4a) \times 3.9 = 49.2 \times 16$$

$$15.6a = 787.2 - 686.4 \text{ or}$$

$$a = 6.4615 \text{ atm L}^2 \text{ mol}^{-2}$$

10. The compression factor (compressibility factor) for one mole of a van der Waals' gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant 'a'.

$$\text{Ans } Z = \frac{PV}{nRT} \quad \text{i.e., } 0.5 = \frac{100 \times V}{1 \times 0.082 \times 273}$$

$$V = \frac{0.5 \times 0.082 \times 273}{100} \text{ or } V = 0.119 \text{ L}$$

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

If volume of molecules is negligible i.e. b is negligible van der Waals' equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - 0) = RT \text{ or } \left(P + \frac{a}{V^2}\right)V = RT$$

$$\text{Or } PV + \frac{a}{V} = RT \text{ or } \frac{PV}{RT} + \frac{a}{VRT} = 1$$

$$\text{Or } a = \left(1 - \frac{PV}{RT}\right)VRT$$

$$a = (1 - 0.5)0.119 \times 0.082 \times 273$$

$$a = 1.252 \text{ atm L}^2 \text{ mol}^{-2}$$

11. The critical temp. and pressure for NO gas at 177 k and 64.5 atm respectively. Calculate van der Waals constant 'a' & 'b' for the gas.

Ans. Given  $T_c = 177$  k,  $P_c = 64.5$  atm

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

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

$$\text{Or } T_c^2 = \frac{64a^2}{(27)^2 R^2 b^2} = \frac{64a^2 \times 27 P_c}{(27)^2 \times R^2 \times a} = \frac{64 \times a \times P_c}{27 \times R^2}$$

$$\text{Or } a = \frac{27(RT_c)^2}{64P_c} = \frac{27 \times (0.082 \times 177)^2}{64 \times 64.5}$$

$$a = 1.37 \text{ litre}^2 \text{ atm mol}^{-2}$$

$$b = \frac{RT_c}{8P_c} = \frac{0.082 \times 177}{8 \times 64.5} = 0.02717 \text{ litre mol}^{-1}$$

12. One mole of  $\text{CCl}_4$  vapours at  $77^\circ\text{C}$  occupies a volume of 35.0 L. If van der Waal's constants are  $a = 20.39 \text{ L}^2 \text{ atm mol}^{-2}$  and  $b = 0.1383 \text{ L mol}^{-1}$ , calculate compressibility factor Z under,

Ans. (a) Low pressure region (b) High pressure region.

(a) Under low pressure region,  $V_m$  is high  $(V_m - b) = V_m$

$$\rightarrow \left[ P + \frac{a}{V_m^2} \right] V_m = RT$$

$$\rightarrow PV_m + \frac{a}{V_m} = RT$$

$$Z = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

$$[\because Z = 1 - \frac{a}{RTV_m}]$$

(b) Under high pressure region P is high,

$$\left[ P + \frac{a}{V_m^2} \right] = P$$

$$P(V_m - b) = RT \quad \text{or} \quad PV_m - Pb = RT$$

$$P = \frac{RT}{V_m - b}$$

$$Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} = \frac{1}{1 - \frac{b}{V_m}}$$

$$Z = \frac{1}{1 - \frac{0.1383}{35}} = 1.004$$

## THERMODYNAMICS

1. In a thermally insulated flask 50 g H<sub>2</sub>O is taken at temperature 22<sup>o</sup>C. In it 150 g of heated piece of Pb having temp. 100<sup>o</sup>c is poured in it, where final temperature observed is 28.8<sup>o</sup>c. if specific heat of water is 1 cal g<sup>-1</sup>, then calculate the specific heat of Pb.

**Ans.** In Pb-water System

Heat Given by Pb = Heat absorbed by water

$$\text{and } m_{\text{pb}} \cdot C_{\text{pb}} (\Delta T)_{\text{Pb}} = m_{\text{water}} \cdot C_{\text{water}} (\Delta T)_{\text{water}} \quad (\because Q = mC\Delta T)$$

Given that

$$m_{\text{pb}} = 150 \text{ g} \quad m_{\text{water}} = 50 \text{ g}$$

$$C_{\text{pb}} = ? \quad C_{\text{water}} = 1 \text{ cal g}^{-1}$$

$$(\Delta T)_{\text{Pb}} = (100.0 - 28.8)^{\circ}\text{C}; \quad (\Delta T)_{\text{water}} = (28.8 - 22.0)$$

$$\therefore 150 \times C_{\text{pb}} \times (100.0 - 28.8) = 50 \times 1 \times (28.8 - 22.0)$$

$$\text{i.e. } C_{\text{pb}} = 0.032 \text{ cal g}^{-1}$$

2. A swimming pool contains 1 x 10<sup>5</sup> L of water. How much energy in Joule is required to raise the temperature of water from 20<sup>o</sup>c to 25<sup>o</sup>c ? The specific heat capacity of water is 4.184 J/<sup>o</sup>C g

**Ans.** Volume of water = 10<sup>5</sup> L = 10<sup>8</sup> mL

Mass of water = V x d  $\because$  d = 1g/mL

$$= 10^8 \times 1 = 10^8 \text{ g}$$

Specific heat of water, C<sub>s</sub> = 4.184 J/<sup>o</sup>C

Heat absorbed by the water to raise the temperature may be calculated as,

$$q = mC_s \Delta T$$

$$q = 10^8 \times 4.184 \times 5 = 2.092 \times 10^9 \text{ J}$$

3. A certain gas expands its volume from 3.0 L to 7.0 L at constant temperature. Calculate the work done by the gas if it expands,

(a) Against a vacuum.

(b) Against a constant pressure of 1.2 atm.

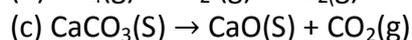
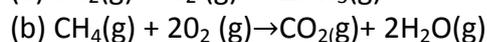
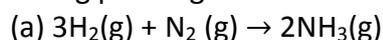
**Ans.** (a) when gas expands into vacuum, P = 0 Therefore, w = -PΔV i.e w = 0

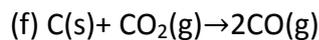
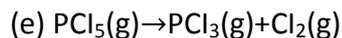
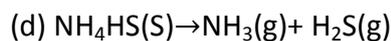
(b) If the external opposing pressure is 1.2 atm, then w = - PΔV

$$W = -1.2(7.0 - 3.0) = -4.8 \text{ L atm}$$

$$W = -4.8 \times 101.3 = -486.24 \text{ J}$$

4. Assign the sign of work done (based on SI Convention) in the following chemical changes taking place against external atmospheric pressure:





**Ans.** We shall consider actually Sign of

$$\Delta n_g = (\text{moles of gaseous products} - \text{moles of gaseous reactants})$$

$\Delta n_g = +ve$  means expansion

= -ve means contraction

= 0 means no change

Chemical Change	$\Delta n_g$	$\Delta W = -P \Delta V$	Nature of work
(a)	-2	+ve	Work is done on the system.
(b)	0	0	-
(c)	+1	-ve	Work is done by the system.
(d)	+2	-ve	-do-
(e)	+1	-ve	-do-
(f)	+1	-ve	-do-

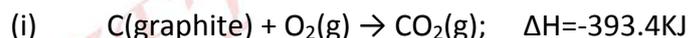
**5.** The enthalpy of combustion of graphite is 393.4 kJ. Calculate

(a) The amount of graphite needed to produce 196.7 KJ of heat.

(b) The number of moles of  $\text{CO}_2$  formed when 196.7 KJ of heat is produced.

(c) The volume of oxygen required at S.T.P. to from 24.0 g of graphite in this process.

**Ans.** We are given



(a) From the above equation, we know that 393.4 KJ of heat is produced by 12 g of graphite.

$\therefore$  196.7 kJ of heat is produced by

$$\frac{12}{393.4} \times 196.7 = 6 \text{ g of graphite}$$

(b) From equation (i) we can say that

Production of 393.4 KJ of heat is accompanied by the formation of 1 mole of  $\text{CO}_2$ .

$\therefore$  Production of 196.7 KJ of heat is accompanied by the formation of 0.5 mole of  $\text{CO}_2$ .

(c) Volume of oxygen required at S.T.P to burn 12 g of graphite = 22.4 litres.

Volume of oxygen required at S.T.P to burn 24 of graphite =  $22.4 \times 2 = 44.8$  litres.

**6.** 150 mL of 0.5 N nitric acid solutions at  $25.35^\circ\text{C}$  was mixed with 150 mL of 0.5 N sodium hydroxide solutions at the same temp. The final temperature was recorded to be  $28.77^\circ\text{C}$ . Calculate the heat of neutralization of nitric acid with sodium hydroxide.

**Ans.** Total mass of solution = 150 + 150 = 300 g

Q = Total heat produced

$$= 300 \times (28.77 - 25.35) \text{ cal}$$

$$= 300 \times 3.42 = 1026 \text{ cal}$$

$$\text{Heat of neutralization} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ Kcal}$$

Since heat is liberated, heat of neutralization should be negative. So heat of neutralization = -13.68 Kcal

**7.** Predict the sign of entropy change in each of the following :

(I)  $\text{H}_2$  (at 298 K, 1 atm)  $\rightarrow$   $\text{H}_2$  (at 298K, 10 atm)

(II)  $\text{H}_2\text{O}$  (at 298 K, 1 atm)  $\rightarrow$   $\text{H}_2\text{O}$  (at 330 K, 1 atm)

(III)  $2\text{NH}_4 \text{NO}_3(\text{s}) \rightarrow \text{N}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$

(IV) Crystallization of copper sulphate from its saturated solution.

(V)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2\text{SO}_3(\text{g})$

**Ans.** Entropy is a measure of randomness or disorder of a system. If randomness increases entropy increases.

(I) Gas at lower pressure has greater randomness than  $\Delta$  at high pressure (compressed gas) at the same temperature. Hence, entropy decreases, i.e.  $\Delta S$  is -ve.

(II) Molecules at higher temperature have greater randomness at the same pressure. Hence,  $\Delta S$  is +ve.

(III) Gaseous molecules have greater randomness than the solid. Hence,  $\Delta S$  is positive.

(IV)  $\text{CuSO}_4$  crystals have ordered arrangement whereas ions in sol. Have greater randomness. Hence  $\Delta S$  is -ve.

(V) There are 3 moles of two different gaseous reactants which have greater randomness than 2 moles of the only gaseous product,  $\text{SO}_3$ . Hence, randomness decreases i.e.  $\Delta S$  is -ve.

**8.** Under what conditions will the reaction occur, if

(I) Both  $\Delta H$  and  $\Delta S$  are positive

(II) Both  $\Delta H$  and  $\Delta S$  are negative ?

**Ans.**  $\Delta G = \Delta H - T\Delta S$ . For a reaction to occur,  $\Delta G$  should be -ve.

(i) If both  $\Delta H$  and  $\Delta S$  are positive,  $\Delta G$  can be -ve only if  $T\Delta S > \Delta H$  in magnitude. Thus, either  $\Delta S$  has large +ve value so that even if T is low,  $T\Delta S$  is greater than  $\Delta H$  or if  $\Delta S$  is small, T should be high so that  $T\Delta S > \Delta H$ .

(ii) If both  $\Delta H$  and  $\Delta S$  are negative,  $\Delta G$  can be -ve only if  $T\Delta S < \Delta H$  in magnitude or  $\Delta H > T\Delta S$  in magnitude. This is possible only if either  $\Delta H$  has large negative value or T is so low that  $T\Delta S < \Delta H$ .

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