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CLASS : XI (PHYSICAL CHEMISTRY)

DPP

DAILY PRACTICE PROBLEM

Solutions (PART-II)

DPP-32 to 59

DPP No. # 32

6. $N_2 + 3H_2 \longrightarrow 2NH_3$

Initially a atm b atm

Finally $a - x$ $b - 3x$ $2x$

$\therefore$ $a + b = 1$ and $a + b - 2x = 0.75$

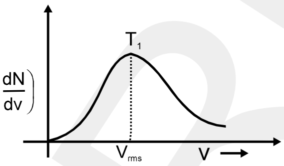
$\therefore$ $P_{NH_3} = 2x = 0.25$ atm

7. $v_{RMS} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1.2 \times 10^5}{4}} = 300$ m/s

8. $[(v_{rms})_X]_{546°C} = [(v_{mp})_Y]_{273°C}$

$\sqrt{\frac{3RT_X}{M_X}} = \sqrt{\frac{2RT_Y}{M_Y}}$ $\frac{3 \times 819}{9} = \frac{2 \times 546}{M_Y}$

$\therefore$ $M_Y = 4$ amu.

9. **(C)** Area under the curve $\left(\frac{1}{N}\frac{dN}{dv}\right)$  $= \int_0^x ydx = \int_0^N \left(\frac{1}{N}\frac{dN}{dV}\right)dV = \frac{1}{N}\int_0^N dN = 1.$

11. **(C,D)**

If two gases haves identical Max wellian plot then their all the speeds will also be identical.

Hence $\frac{T_A}{M_A} = \frac{T_B}{M_B}$. Since all the speeds are proportional to $\sqrt{\frac{T}{M}}$

for SO_2 – $M_1 = 64$, $T_1 = 600$ K ; O_2 – $M_2 = 32$, $T_2 = 300$ K $\Rightarrow \frac{T_1}{M_1} = \frac{T_2}{M_2}$.

DPP No. # 33

1. (a) V.P. depends on temperature.

3. Pressure of air = 750 – 100 = 650 mm of Hg

on compressing P_f = Hg 650 × 3 mm of Hg

= 1950 mm of Hg

so P_T = (1950 + 100) = 2050 mm of Hg

4. $P_{N_2} + P_{H_2O(v)} = 1$ atm, $\because P_{H_2O} = 0.3$ atm

$\therefore P_{N_2} = 0.7$ atm

Now new pressure of N_2 in another vessel of volume V/3 at same T is given by :

$P_{N_2} \times \frac{V_1}{3} = 0.7\,0 \times V_1$

$\therefore P_{N_2} = 2.1$ atm

Since aqueous tension remains constant, and thus total pressure in new vessel.

$= P_{N_2} + P_{H_2O} = 2.1 + 0.3 = 2.4$ atm.

5. $3O_2 \rightleftharpoons 2O_3$

t = 0 60

$t = t_1$ 48 8

so $V_1 = 48 + 8 = 56$ and $V_2 = 48$ (on passing through turpentine oil, O_3 will be absorbed.)

7. $CO_2 + C \longrightarrow 2CO$

At t = 0 x L (1 – x) L

At = t 0 2x L

1 – x + 2x = 1.6

1 + x = 1.6

x = 0.6 L

1 – x = 0.4 L

8. 896 mL.

DPP No. # 34

1. $T_4 < T_3 < T_2 < T_1$

2. A real gas behaves idealy under conditions of low pressure and high temperature .

3. Order of Vander waals constant $CO_2 > CH_4 > N_2 > H_2$

$\therefore$ ease of liqufication $CO_2 > CH_4 > N_2 > H_2$

5.* Z for an ideal gas is equal one.

6. Clearly, from the graph at 80 K = $\frac{PV}{RT}$ = 1 and at 60K, Z < 1

7. $Z = \frac{PV}{nRT} \Rightarrow n = \frac{PV}{ZRT}$

8. Translational energy = (3/2) kT

= (3/2) kT = hcR_H ((1/1) – (1/4))

$= (3/2)\ T = 6.626 \times 10^{-34} \times 2.996 \times 10^{10} \times 109679 \times (3/4)\ \frac{6.02 \times 10^{23}}{8.315}$

= 118331.1 K

T = 118331.1 × 2/3 = 80000 K.

DPP No. # 35

4. For very large value of molar volume (V_m)

$\frac{a}{V_m}$ and b can be neglected, so gas behaves as Ideal

$\therefore PV_m = RT$

5. At low pressure vander waal's equivalent for a real gas is given as

$Z = 1 - \frac{a}{RTV}$

intercept = 1

slop = –ve

7. (i) $Z = \frac{PM}{dRT} = \frac{2 \times 16}{0.8 \times \frac{1}{12} \times 400} = 1.2$

(ii) As Z > 1, so repulsive forces are dominating among gas molecules.

8. At Boyle's temperature, for low pressure regions, Z = 1. However, for high pressure regions, Z > 1.

DPP No. # 36

4. Under low pressure region and below the boyle temperature, Z < 1.

5. Refer class notes.

7.* at very high Pressure $Z = 1 + \frac{Pb}{RT}$

$Z > 1$

for particular realgas above boyle temp Z > 1.

8. [A – r] ; [B – r,s] ; [C – q] ; [D – r].

DPP No. # 37

5. $H_2 + I_2 \rightleftharpoons 2HI$

0.4   0.4   2.4

$K = \frac{2.4 \times 2.4}{0.4 \times 0.4} = 36$ (Since volume term is cancelled)

7. Mol. mass of HI = 1 + 127 = 128

64 g HI = 64 / 128 = 0.5 mole

$[HI] = \frac{0.5}{2}$ M = 0.25 M

DPP No. # 38

1. $K_p = K_c (RT)^{\Delta n}$

$2K_c = K_c (RT)^{\Delta n}$

$2 = (RT)^1$

$T = \frac{2}{0.0821} = 24.36$ K

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

1   3   0

0.5   1.5   1

$P_{H_2} = \frac{1.5}{3} P = P/2$

6. $2NO_2 \rightleftharpoons N_2O_4$

$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \left(= \frac{mol\ L^{-1}}{(mol\ L^{-1})^2}, K_c \text{ has unit of } L\ mol^{-1} \right)$

$K_p = \frac{p_{N_2O_4}}{p^2_{NO_2}} \left(= \frac{atm}{atm^2}, K_p \text{ has unit of } atm^{-1} \right)$

(Since mole fraction is itself unitless hence, K_x is also unitless)

7. (i) Molar concentrations :

$[PCl_5] = \frac{mol}{L} = \frac{1}{2} = 0.5$ mol L^{-1}

$[PCl_3] = \frac{2}{2} = 1.0$ mol L^{-1}

$[Cl_2] = \frac{2}{2} = 1.0$ mol L^{-1}

(ii) Mole fractions :

Total moles at equilibrium = 1 + 2 + 2 = 5

$\therefore \quad X_{PCl_5} = \frac{n_{PCl_5}}{n_{total}} = \frac{1}{5} = 0.2$

$X_{PCl_3} = \frac{n_{PCl_3}}{n_{total}} = \frac{2}{5} = 0.4$

$$X_{Cl_2} = \frac{n_{Cl_2}}{n_{total}} = \frac{2}{5} = 0.4$$

(iii) Equilibrium constants :

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{1\times1}{0.5} = 2\ (mol\ L^{-1})^{-1} \quad = 2\ L\ mol^{-1}$$

8. $K_C = 4.0$.

9. $PCl_3 + Cl_2 \rightleftharpoons PCl_5$

t = 0 n n 0

t = teq. n-y n-y y

$$K_p = \frac{y}{(n-y)\,(n-y)}\left[\frac{P}{2n-y}\right]^{-1}$$

$$K_p = \frac{(2n-y)y}{(n-y)^2 P}$$

DPP No. # 39

8. The equilibrium reaction is

$$2XO\,(g) + O_2(g) \rightleftharpoons 2XO_2\,(g)$$

since the unit of K_c given is lit/mole.

$$2XO(g) \quad + \quad O_2(g) \quad \rightleftharpoons \quad 2XO_2(g)$$

	$2XO(g)$	$O_2(g)$	$2XO_2(g)$
Initial conc.	1	2	0
Conc. at equilib.	$1-2x$	$2-x$	$2x$

$$\therefore \quad K_c = \frac{[XO_2]^2}{[XO]^2[O_2]} = \frac{(2x)^2}{(1-2x)^2(2-x)} = \frac{4x^2}{(1-2x)^2(2-x)} = \frac{4x^2}{2}$$

Since, the value of equilibrium constant is very small (1×10^{-4}), so 2x can be ignored with respect to 1 and x can be ignored with respect to 2.

$$\therefore \quad 1 \times 10^{-4} = \frac{4x^2}{2}$$

$$x = 7.07 \times 10^{-3}$$

we can see that the value of x is very small, so the assumtion made was correct as it is within 1.4% of the actual value. Thus, the assumption made is correct and acceptable.

$\therefore$ $[XO] = 1 - 0.01414 = 0.985$ M

$[O_2] = 2 - 0.00707 = 1.992$ M

$[XO_2] = 0.0141$ M

9.

1	0	0	Initial moles (say)
$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2	
$(1-0.5)$	0.5	0.5	Moles at equilibrium

Total moles at equilibrium = 0.5 + 0.5 + 0.5 = 1.5

$$K_p = \frac{p_{PCl_3}\cdot p_{Cl_2}}{p_{PCl_2}} = \frac{\left(\frac{0.5}{1.5}p\right)\left(\frac{0.5}{1.5}p\right)}{\left(\frac{0.5}{1.5}p\right)} \qquad \text{(p = total pressure)}$$

or $K_p = \frac{1}{3}.p$ or $p = 3K_p$.

DPP No. # 40

3. $2HI \rightleftharpoons H_2 + I_2$

	$2HI$	H_2	I_2
Initial	2moles		
At eqm.	$2-\frac{20}{100}\times 2$	0.2	0.2

$= 2 - 0.4 = 1.6$

$$K = \frac{[H_2][I_2]}{[HI]} = \frac{0.2 \times 0.2}{(1.6)^2} = \frac{1}{64}.$$

7. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

	$H_2(g)$	$Br_2(g)$	$2HBr(g)$
Intial pressures	0	0	10.0 bar
At equilibrium	p/2	p/2	(10.0-p)

$$K_p = \frac{p^2_{HBr}}{p_{H_2} \times p_{Br_2}}$$

$$1.6 \times 10^5 = \frac{(10-p)^2}{(p/2)(p/2)}$$

Taking square root of both sides

$$4 \times 10^2 = \frac{10-p}{p/2}$$

$$200\,p = 10 - p\ ; \quad p = \frac{10}{201}\text{ bar}$$

$$p_{H_2} = p/2 = \frac{1}{2}\left(\frac{10}{201}\right)\text{bar} = 2.5 \times 10^{-2}\text{bar}\ ;\ p_{Br_2} = p/2 = 2.5 \times 10^{-2}\text{ bar}\ ; \qquad p_{HBr} = 10 - p \approx 10\ \text{bar}.$$

8. We have,

10 mole	10 mole		10 mole	10 mole	Initial moles
$CO(g)$	$+\ H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	$+\ H_2(g)$	
$10 - x$	$10 - x$		$10 + x$	$10 + x$	Moles at eqb. or concentration at eqb.

where x is the number of moles of each reactant changed to the products at equilibrium.

$$K = \frac{(10+x)^2}{(10-x)^2} = 9/4 \text{ (given)} \qquad \text{or} \qquad \frac{10+x}{10-x} = 3/2\ ;\ x = 2$$

Mole percent of H_2 (g) at equilibrium = $\frac{10+x}{40} \times 100 = 30$

DPP No. # 41

3. 0.2.

4. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

0.02   0.01

0.02-x   x   0.01+x

$$D = \frac{PM}{RT}$$

Calculate M_{avg}.

$$\frac{(0.02 - x)208.5 + 137.5x + (0.01 + x)71}{0.03 + x} = M_{avg}.$$

5. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

P   P

2P = 1.12

P = 0.56

$K_P = P^2 = (0.56)^2 = 0.3136\ atm^2$

6. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

0.2-x   x   x

$$K_P = P_{CO_2} = 1$$

$$x = \text{mole of } CO_2 = \frac{PV}{RT}$$

Remaining mass of $CaCO_3$ = (0.2 – x) 100 g.

7. $[CaO] = \dfrac{\rho_{CaO(s)}}{M_{CaO(s)}} = \dfrac{1.12}{56} \times 1000$

9.* Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as Δn_g is +ve.

DPP No. # 42

2. $K_p = (p_{H_2O})^4 = 2.56 \times 10^{-10}\ atm^4$

$\therefore$ $p_{H_2O} = 4 \times 10^{-3}$ atm $= 4 \times 10^{-3} \times 760 = 3.04$ torr.

Partial pressure of water vapour in air $= \dfrac{40}{100} \times 12.5 = 5$

So, the amount of water vapour in air should decrease to decrease value of partial pressure of water vapour from 5 torr to the equilibrium value (3.04 torr).

so, mass of $CuSO_4.5H_2O$ will increase and mass of $CuSO_4.H_2O$ will decrease.

3. (A) As reaction is endothermic therefore it will go in the forward direction hence moles of PbO will increase.

(B) With the increase or decrease of volume partial pressure of the gases will remain same.

(C) Due to the addition of inert gas at constant pressure reaction will proceed in the direction in which more number of gaseous moles are formed.

4.* $N_2(g) + O_2(g) \rightleftharpoons 2NO\,(g)$

(A) For changing pressure volume has to be changed, though number of moles of NO(g) do not get changed but its concentration will get changed.

(B) Temperature change will change K_P and hence concentration.

(C) Volume change will change concentration, not the number of moles.

(D) Catalyst does not change equilibrium concentrations.

5.* Number of moles will remain unchanged but due to decreased volume pressure will get increased and also the concentrations.

6. Slope $= -\tan 30° = \dfrac{-1}{\sqrt{3}} = \dfrac{-\Delta H°}{R}$

$\therefore$ $\Delta H° = \dfrac{R}{\sqrt{3}}$

7. As $T \rightarrow \infty$, K = A

$\therefore$ $\ell nA = \ell nK = 46.06$

$\therefore$ $2.303 \log_{10} A = 46.06$

$\therefore$ $A = 10^{20}$

8. $\Delta H° > O$ $\therefore$ Endothermic reaction

Y – intercept = +ve $\therefore$ $\Delta S° > 0$

for endothermic reaction, as $T\uparrow$, $K\uparrow$.

The value of equilibrium constant K is unaffected by pressure changes.

DPP No. # 43

1. $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ $K_C = 50$

$A_2(g)$	$B_2(g)$	$2AB(g)$
1	2	0
$\dfrac{1-x}{3}$	$\dfrac{2-x}{3}$	$\dfrac{2x}{3}$

$50 = \dfrac{\frac{2x}{3}\cdot\frac{2x}{3}}{\frac{1-x}{3}\cdot\frac{2-x}{3}} = \dfrac{4x^2}{(1-x)(2-x)} = \dfrac{4x^2}{2-3x+x^2}$ $\Rightarrow$ $100 - 150x + 50x^2 = 4x^2$

$\therefore$ no. of mol of AB $= \dfrac{2x}{3} = 1.868$.

∴ AB dh eksy la[;k $= \frac{2x}{3} = 1.868$

2. (i) From the graph $0.3 \times n = 0.6$

$n = 2$

(ii) $K = (0.6)^2 / 0.3 = 1.2$ mol / L

3.

	PCl_5 (g) $\rightleftharpoons$	PCl_3 (g) +	Cl_2 (g).
Initial	3	0	1
	(3–x)	x	1+x
	2	1	2

Initial total moles = (3+1) = 4.

Now from Ideal gas equation

$PV = nRT = P \times 100 = 4 \times 0.082 \times 500$

$P = 0.082 \times 20 = 1.64$ atm.

At equilibrium Total mole = 3 – x + x + 1 + x = (4 + x)

$PV = nRT.$

$2.05 \times 100 = (4+x) \times 0.082 \times 500.$

$2.05 = (4+x) \times 0.41.$

$5 = 4 + x.$

$x = 1.$

$$\alpha = \frac{\text{No. of mole dissociated}}{\text{Initially total mole taken}} = \frac{1}{3} = 0.33.$$

$$P_{PCl_5} = \frac{2}{5} \times 2.05 \quad ; \quad P_{PCl_3} = \frac{1}{5} \times 2.05 \quad P_{Cl_2} = \frac{2}{5} \times 2.05$$

$$K_P = \frac{\left(\frac{1}{5}\times 2.05\right)\left(\frac{2}{5}\times 2.05\right)}{\left(\frac{2}{5}\times 2.05\right)} = \mathbf{[0.41]}$$

4.

	Ag^+ +	$2CN^-$ $\rightleftharpoons$	$[Ag(CN)_2]^-$
t = 0	0.1	0.5	0
t_{eq}	10^{-6}	0.3	0.1

$K_1 = \frac{10}{9} \times 10^6$

	Zn^{2+} +	$4CN^-$ $\rightleftharpoons$	$[Zn(CN)_4]^{2-}$
t = 0	0.1	0.5	0
eq.	10^{-12}	0.1	0.1

$$K_2 = \frac{0.1}{(0.1)^4 \times 10^{-12}} = 10^{15}$$

Substracting two times I^{st} reaction from II^{nd} reaction, we will get the required reaction, so

$$K_{eq} = \frac{10^{15}}{\left(\frac{10}{9}\right)^2 \times 10^{12}} = \frac{10^3 \times 81}{100} = 810$$ **Ans. 810**

5.* When some amount of HCl is added to equilibrium, the first eq will shift in backward direction leading to decrease in amount of O_2. Then, the second eq. will shift in backward direction to increase the amount of O_2. Thus, amount of N_2 gas will increase.

DPP No. # 44

4. (i) Molecules move faster for which $\frac{T}{M}$ greater obviously H_2 molecule move faster.

5. State function : a, b, c, d, g, h, j ; Path function : e, f, i, k

6. Intensive : a, c, d, f, g, h, i, k ; Extensive : b, e, j, l

7. Open system : b, f, g, i, j ; Closed system : a, c, h ; Isolated system : d, e

8. Q = 7.5 KJ

$\Delta U = -12$ KJ

$\Delta U = Q + W$

W = –12 – 7.5 = **–19.5 KJ. Ans.**

Now W = 0,

∴ $\Delta U = Q$ ∴ $Q = \Delta U =$ **– 12 KJ Ans.**

DPP No. # 45

5. $\Delta U_{ab} = Q_{abc} + W_{abc}$

or $\Delta U_{ab} = 100 - 40 = 60$ J

$\Delta U_{ab} = Q_{aeb} + W_{aeb}$

or $60 = Q_{aeb} - 20$

or Q_{aeb} = **80 J** **Ans.**

$\Delta U_{ba} = -60$ J

$W_{bda} = 30$ J

$\Delta U_{ba} = Q_{bda} + W_{bda}$

or $Q_{bda} = \Delta U_{ba} - W_{bda}$

or $Q_{bda} = -60 - 30 =$ **– 90 J** **Ans.**

Since Q_{bda} is (–)ve ∴ Heat is liberated from the system.

6. 4275 J.

7. 6.66 min. (400 sec)

8. Since $\Delta E = q + w$

$= 80 - 30 = 50$

So for ADB

$\Delta E = q + w$

$50 = q - 10$

$q = 60$ J

9. For B to A,

$\Delta E = -50$ J

$w = +20$ J

$q = -50 - 20 = -70$

heat is liberate.

10. In ADB process, DB process is isochoric so $w_{DB} = 0$

So , $\Delta E_{AD} = q_{AD} + w_{AD}$

$-40 = q_{AD} + (-10)$

$q_{AD} = -30$ J

Now , $q_{AB} = q_{AD} + q_{DB}$

$60 = -30 + q_{DB}$

$q_{DB} = 90$ J

DPP No. # 46

1. $w = P_{ext}\,\Delta V$

$w = -1.2 \times 32 = -38.4$ lt atm.

$= -38.4 \times 100$ J $= -3840$ J $= -3.84$ kJ

$\Delta E = q + w$

so, $q = \Delta E - w = -51 + 3.84 = -47.16$.

6. W = 240 L atm.

7. $\Delta U = \Delta H = 0$ Q= -W

$$W = -2.303\, nRT \log \frac{V_2}{V_1} \Rightarrow W = -2.3 \times \frac{20}{40} \times 8.3 \times 300 \log \frac{10}{5} = -859.05 \text{ J.}$$

8. (a) $W = -nRT \ln \frac{V_2}{V_1}$

$$W = -P_1V_1 \ln \frac{V_2}{V_1} = -14 \times 0.03 \ln \frac{0.06}{0.03} \text{ bar m}^3 = -14 \times 0.7 \times 0.03 = \mathbf{-0.294 \text{ bar m}^3}$$ **Ans.**

(b) $P_1V_1 = P_2V_2$

$\therefore \quad P_2 = \frac{P_1V_1}{V_2} = \frac{14 \times 0.03}{0.06} = 7$ bar

$\therefore \quad W = -P_{ext}(V_2 - V_1) = -7(0.06 - 0.03) = -7 \times 0.03 = -0.21$ bar m³.

Efficiency = $\frac{0.21}{0.294}$ = 71.43% **Ans.**

9. (a) F (b) T (c) F (d) T (e) T

DPP No. # 47

1. The product PV is increasing so temperature will keep or increasing in the process, hence
$\Delta H = \Delta E + \Delta(PV)$ will increase constantly.

2. From graph we know that $V_B > V_A$, so expansion has taken place so w will be with –ve sign and ΔH will be +ve as both ΔE and $\Delta(PV)$ have increased.

3. At A and D the temperatures of the gas will be equal, so
$\Delta E = 0, \quad \Delta H = 0$
Now $w = W_{AB} + W_{BC} + W_{CD} = -P_0V_0 - 2P_0V_0 \ln 2 + P_0V_0 = -2P_0V_0 \ln 2$
and $q = -W = 2P_0V_0 \ln 2$

5. Since liquid is expanding against external pressure P_0 hence work done
$w = -P_0(4V_0 - V_0) = -3P_0V_0$
$\Delta U = w = -3P_0V_0$
$\Rightarrow \quad \Delta H = \Delta U + P_2V_2 - P_1V_1 = -3P_0V_0 + 4P_0V_0 - 2P_0V_0$.

7. γ for $O_2 = 1.44$ γ for He = 1.66.

8. Since, ΔH is a state function, and the final state attained by the gas is same as its initial state, so value of $\Delta H = 0$.

9. $q = q_{AB} + q_{BC} + q_{CD} + q_{DA}$

$= -1R \times 300\ell n2 + 1 \times \frac{5R}{2} \times (400 - 300) + 1R \times 400\ell n2 + 1 \times \frac{5R}{2} \times (300 - 400)$

($\because q_{AB} = -W_{AB} = -1R \times 300\ell n2$ since process is reversible isothermal for which $\Delta U = 0$).

($\because q_{BC} = \Delta H_{BC} = 1 \times \frac{5R}{2} \times (400 - 300)$ since process is reversible isobaric).

($\because q_{CD} = -W_{CD} = 1R \times 300\ell n2$ since process is reversible isothermal for which $\Delta U = 0$).

($\because q_{DA} = \Delta H_{AB} = 1 \times \frac{5R}{2} \times (300 - 400)$ since process is reversible isobaric).

So, $q = 100 R\ell n2$.

10. Since, for a cyclic process, $\Delta U = 0$.
So, $W = -q = -100 R\ell n2$.

DPP No. # 48

1. $TV^{\gamma-1}$ = constant

$\gamma = \frac{5}{3} \quad \therefore \quad \gamma - 1 = \frac{2}{3}$

$\therefore \quad 300 \times (8)^{2/3} = 250 \times (V_2)^{2/3} \quad \Rightarrow \quad (V_2)^{2/3} = 4.8$

$\Rightarrow \quad V_2 = (4.8)^{3/2} \cong 4.8 \times 2.2 = 10.5$ L

8. $\gamma_{mix} = \frac{n_AC_{P_A} + n_BC_{P_B}}{n_AC_{V_A} + n_BC_{V_B}} = \frac{2(4R) + 4(5R/2)}{2(3R) + 4(3R/2)} = \frac{18R}{12R} = \frac{3}{2}$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad (\gamma = \gamma_{mix} = 1.5)$

$\therefore \quad T_2 = 320\left(\frac{2}{8}\right)^{1.5-1} = 320 \times \frac{1}{2} = 160$ K

$\therefore \quad W = \frac{nR}{\gamma - 1}(T_2 - T_1) = \frac{6R}{1.5 - 1}(160 - 320) = -1920 R = 1920 \times 2 = -3840$ calories.

9. The process can be described on a p-V diagram as

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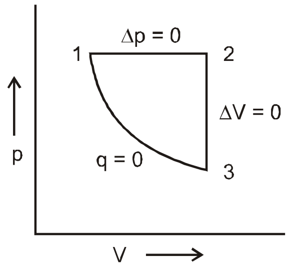


At 1 : p = 10 atm T = 400 K $V = V_1$
At 2 : p = 10 atm T = 800 K $V = V_2 = 2V_1$
At 3 : p = ? $T = T_3$ $V = V_3 = V_2 = 2V_1$
Therefore,

$W_{12} = -p\Delta V = -nRT = -400\ R$

$W_{23} = 0$ $[\because \Delta V = 0]$

Between 3 and 1 ; $TV^{\gamma-1}$ = constant

$T_3\,(2V_1)^{\gamma-1} = 400(V_1)^{\gamma-1}$

$\Rightarrow \quad T_3 = 400\left(\frac{1}{2}\right)^{2/3} = 252\ K$

$\Rightarrow \quad W_{31} = \Delta E_{31} = nC_V(T_1 - T_3) = \frac{3}{2}R(400 - 252) = 222\ R$

$\Rightarrow \quad W_{12-31} = W_{12} + W_{23} + W_{31} = -178\ R$

10. $W = -\int PdV$

$= -\int \frac{K}{V^n}dV = -\frac{K}{1-n}\left[V^{-n+1}\right]_{V_1}^{V_2} = \frac{K}{n-1}[V_2^{1-n} - V_1^{1-n}]$

$= \frac{P_1V_1^n}{n-1}\left[V_2^{1-n} - V_1^{1-n}\right] = \frac{P_1V_1^{n+1-n}}{n-1}\left[\left(\frac{V_2}{V_1}\right)^{1-n} - 1\right]$

DPP No. # 49

1. Standard molar enthalpy of formation (ΔH^o_f) of element in their stable state of agregation is zero.
$\therefore \quad \Delta H^o_f\,(O_2, g) = 0$

4. Some of the heat is used to vaporise the $H_2O\,(\ell)$
$\therefore \quad x_1 > x_2$

5. $CS_2(\ell) + 3O_2(g) \longrightarrow CO_2\,(g) + 2SO_2(g)$; $\Delta H^o_{rxn.} = 5 \times -215 = -1075$ kJ
$\Delta H^o_{rxn.} = \Delta H^o_f\,(CO_2) + 2 \times \Delta H^o_f\,(SO_2) - \Delta H^o_f\,(CS_2)$
$\Delta H^o_{rxn.} = (-393.5 - 2 \times 296.8) - (-1075)$
$\Delta H^o_{rxn.} = 87.9$

6. Refer Class notes.

8. Eq (i) + Eq (ii)
$C_{diamond} + O_2\,(s) \longrightarrow CO_2(g)$
$\Delta H = \Delta H_1 + \Delta H_2$

DPP No. # 50

2. Since it is neutralisation of a weak acid with strong base.

3. enthalpy of dissociation = (13.7 – 3) KCal = 10.7 KCal

6. $n_{CH_4} = \frac{280}{22.4}$

$\therefore \quad \Delta H_{obntained} = \frac{240 \times 280}{22.4}$ KCal

$\therefore \quad m = \frac{240 \times 280}{22.4 \times 2 \times 1 \times 180}$ kg = 8.33 kg.

7. Heat generated = $C_T \Delta T$ = 1260 × 0.667 cal.

$\therefore \quad n_{CH_4} = \frac{1260 \times 0.667}{210 \times 10^3}$

$n_{total} = \frac{PV}{RT} = 4 \times 10^{-2}$ $\therefore$ mol% = $\frac{4 \times 10^{-3}}{4 \times 10^{-2}} \times 100\% = 10\%$ Ans.

8. $\Delta H_2 - 24 = -0.024 \times (523 - 473)$ Cal/g.
$\therefore \quad \Delta H_2 = 22.8$ Cal/g.

9. **Target eq** $1/2\ H_2\ (g) + 1/2\ Cl_2\ (g) \longrightarrow HCl\ (g)$
$NH_3\ (aq) + HCl\ (aq) \longrightarrow NH_4Cl\ (aq)$ $\Delta H = -12.1$ ....(1)
$1/2N_2(g) + 3/2H_2(g) \longrightarrow NH_3(g)$; $\Delta H = -11$ ....(2)
$1/2N_2 + 2H_2 + 1/2Cl_2\ (g) \longrightarrow NH_4Cl(s)$; $\Delta H = -75.3$ ....(3)
$NH_3(g) + aq \longrightarrow NH_3\ (aq)$ $\Delta H = -8.8$ ....(4)
$NCl(g) + aq \longrightarrow HCl\ (aq)$ $\Delta H = 17.5$ ....(5)
$NH_4Cl(s) + aq \longrightarrow NH_4Cl\ (aq)$ $\Delta H = 3.8$ ....(6)
ΔH = eq (6) – eq (3) + eq (2) + eq (4) + eq (5)
= – 12.1 – 3.8 – (–75.3) – 11 – 8.8 – 17.5
= + 22.1
from this we get equation
$HCl\ (g) \longrightarrow 1/2\ H_2(g) + 1/2\ Cl_2\ (g)$
$\therefore$ ΔH of target eq = – ΔH = – 22.1 Kcal Ans.

DPP No. # 51

1. - 372.0 kCal.
2. - 136.8 kJ.
3. - 121 kJ/mole.
4. $\Delta H = -67710$ Cal
5. - 22 kCal/mol.
6. $C_2H_4(g) + H_2 \longrightarrow C_2H_6$
$\Delta H = (\Delta H)_{sup} - (\Delta H)_{req}$
$\Delta H = [145 + 104] - [80 + 2 \times 99]$
$\Delta H = -29$ kCal/mol
7. $C_2H_4\ (s) \longrightarrow 2C(o) + 4H\ (g)$
$\Delta H_{reaction} = 4 \times 52.1 + 2 \times 170.9 - 12.5 = 53.7 = \Delta H_{C=C} + 4 \times 99$
$\Delta H_{C=C} = 141.7$
8. $= \frac{3y - 4x}{3}$ kCal mol^{-1}.
9. 49 kCal/mol.
11. $-49.86 = \Delta H_{ioni} - 55.84$
$\Delta H_{ion} = 55.84 - 49.86 = 5.98$ KJ/mol.

DPP No. # 52

1. - 41.104 kCal.
2. $C_6H_6\ (g) + \frac{15}{2} O_2\ (g) \longrightarrow 6CO_2\ (g) + 3H_2O(\ell)$ $\Delta_r u_1 = -800$ kcal/mole

$C_2H_2\ (g) + \frac{5}{2} O_2\ (g) \longrightarrow 2CO_2\ (g) + H_2O(\ell)$ $\Delta_r u_2 = -300$ kcal/mole

$\therefore \quad 3C_2H_2(g) \longrightarrow C_6H_6(g) \qquad \Delta_r u = -100$ kcal/mole

$\Delta_r H = \Delta_r u + (-2) \times 2 \times 300 \times 10^{-3}$

$\Delta_r H = -100 - 1.2 = -101.2$ kcal/mol.

3. 80 kCal/mol.

4. 100 kJ/mol.

5. $P_4(s) \rightarrow 4P(g) \quad \Delta H = 53.2 \times 6$

$H_2(g) \rightarrow 2H(g) \quad \Delta H = 104.2$

$$\frac{1}{4}P_4(s) + \frac{3}{2}H_2(g) \rightarrow PH_3(g) \; \Delta H = 5.5$$

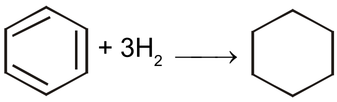
$$\frac{1}{4} \times 6 \times 53.2 + \frac{3}{2} \times 104.2 - 3\epsilon_{P-H} = 5.5$$

$\Rightarrow \quad \epsilon_{P-H} = 76.866$ i.e. 76.9 kcal mol^{-1}

6. C - H = 99 kCal ; C - C = 82 kCal

7. - 56.5 kJ.

8. -152 KJ mol^{-1}



$\Delta H_{calculated} = 3 \times (-119) = -357$ KJ mol^{-1}

$$\Delta H_{experimental} = \sum(\Delta H^\circ_f)_{product} - \sum(\Delta H^\circ_f)_{reactant}$$

or $\Delta H_{expt} = -156 - (49 + 0) = -205$ KJ mol^{-1}

Resonance energy $= -357 - (-205) = -152$ KJ mol^{-1}

9. $-$ 18.7 kCal

10. -167.2 kJ/mol.

DPP No. # 53

2. Latent heat of fusion of ice per mole = 80 × 18 = 1440 cal.

Latent heat of vpourisation of liquid water per mole = 596 × 18 = 10728 cal.

$\therefore$ Total q = (1440 + 10728) cal = 12168 cal.

$\therefore$ $q_p = \Delta H = 12168$ cal Ans.

$\Delta E = \Delta H - P\Delta V = q_p - P\Delta V$

V_2 = volume of 1 mole of H_2O (g) and $V_t \approx 0$.

$\therefore$ $P\Delta V = 546$ Cal

$\therefore$ $\Delta E = (12168 - 546)$ cal = 11622 Cal.

3. W = 0.1 KJ, q = 2KJ, DE = 2.1 KJ.

4. n_{O_2} (inhaled) $= \frac{640}{32} = 20$

12 mole O_2 consumes 1 mole = 342 g sucrose.

$\therefore$ Mass of sucrose consumed $= \frac{342}{12} \times 20$ g = 570 g.

and heat liberated $= \frac{5472}{342} \times 570$ kJ. = 9120 kJ.

5. $$\Delta H_{vap}(0^\circ C) = \int_{273}^{373} C_p\,(\text{liquid})\,dT + \Delta H_{vap}(100^\circ C) + \int_{373}^{273} C_p\,(\text{gas})\,dT$$

$= 75 \times 100 + 40{,}000 - 30 \times 100$

$= 44{,}500$ J $mole^{-1}$ = 44.5 kJ $mole^{-1}$

6. $\Delta H_{sub}(223K) = \int_{223}^{273} C_p\ (solid)\ dT + \Delta H_{fus}\ (0^oC) + \int_{273}^{373} C_p\ (liquid)\ dT + \Delta H_{vap}\ (100^oC) + \int_{373}^{223} C_p\ (gas)\ dT$

$= 50 \times 40 + 6000 + 100 \times 75 + 40000 - 150 \times 30$

$= 51$ kJ/mole.

7. $\Delta H_2^o = \Delta H_1^o + \Delta C_p (T_2 - T_1) = 43.285 + (-45 \times 100)$

$= 38785$ J mole^{-1}.

8. $\Delta C_p = -ve$

$C_{p\ (products)} < C_{p\ (Reactants)}$ so $q_2 < q_1$

9. $\Delta H_0^2 = [-30 \text{ kJ/mole}] + [\{2 \times 2 \times 17 - 28 - 3 \times 2 \times 10\}\ (100) \text{ J/mole}]$

$= (-30 \text{ kJ/mole}) + (-2000 \text{ J/mole}) = -32$ kJ/mole.

DPP No. # 54

1. Polymerisation leads to more ordered structure.

2. Δn_g is + ve

3. Δn_g is most – ve

4. For same amount of gas at constant temperature, lesser is the volume, lower will be the entropy.

6. For a reversible adiabatic process,

$\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$

7. For initinal state $P_i \times 22.4 = 2 \times R \times 546$ $\quad \therefore P_i = 4$ atm

Now, $P_i V_i = P_f V_f$ ($\because$ process is Isothermal)

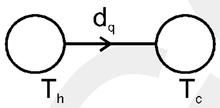
$4 \times 22.4 = 2 \times V_f$ $\quad \therefore V_f = 44.8$ L

$\therefore \Delta S_{sys} = nR \ln \left(\frac{V_f}{V_i}\right) = 2 R \ln \left(\frac{44.8}{22.4}\right) = 2 R \ln 2 = R \ln 4$

8. **(a)** $\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T} = \frac{26 \times 10^3}{325} = 80$ JK^{-1} mol^{-1}.

(b) $\Delta S_{cond.} = \frac{\Delta H_{cond}}{T} = -80$ JK^{-1} mol^{-1}.

9.



For a small exchange in heat at time 't'

change entropy for hot piece $= \frac{dq}{T_h^1}$

where T_h^1 is temp of hot piece at time 't'

change of entropy by cold piece $= \frac{dq}{T_c^1}$.

As heat capacities of the pieces is same.

$T_c + T_h = T_c^1 + T_h^1 = 2T_f$

where T_f is final temperature of each piece.

ΔS for hot piece $= \int \frac{dq}{T_h^1} = mS \int_{T_h}^{T_f} \frac{dT}{T_h^1} \quad = mS \ln \frac{T_f}{T_h}$

ΔS for cold piece $= mS \ln \frac{T_f}{T_c}$.

$\therefore$ Total $\Delta S = mS \ln \frac{T_f^2}{T_h T_c} = ms \ln \frac{(T_C + T_h)^2}{4T_h T_C}$

10. For isoentropic process $\Delta S_{system} = 0$

$$\therefore nC_{p,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0$$

$$\Rightarrow \ln (P_2) = \frac{5}{2} \times \ln \left(\frac{600}{300}\right) \qquad = 1.75 \text{ atm}$$

DPP No. # 55

1. $W = -P_{ext}(V_f - V_i) = -(1 \text{ atm})(8-2) L = -6 \text{ L atm}$
as q = 0 so

$$\Delta E = W = n\left(\frac{6}{2}R\right)\left(\frac{P_f V_f}{nR} - \frac{P_i V_i}{nR}\right) \qquad \text{Here } \Delta E = nC_V \Delta T$$

$3(8P_f - 12) = -6$

therefore, $8P_f = 12 - \frac{6}{3} = 10 \quad \Rightarrow \quad P_f = \frac{5}{4}$ atm

so, $\frac{T_f}{T_i} = \frac{\frac{5}{4}\times 8}{6\times 2} = \frac{10}{12}$

so $\Delta S = 3\frac{12}{300}\ln\left(\frac{10}{12}\right) + \frac{12}{300}\ln 4 = 3.312$ J/K

2. P^2V = constant $\therefore \left(\frac{nRT}{V}\right)^2 V$ = constant $\therefore \frac{T^2}{V}$ = constant

$$\therefore \frac{T_1^2}{V_1} = \frac{T_2^2}{V_2} \therefore \frac{(300)^2}{1} = \frac{T_2^2}{4} \therefore T_2 = 600K$$

$$\Delta S_{sys} = nC_V \ell n \frac{T_2}{T_1} + nR\ell n \frac{V_2}{V_1} = 2 \times \frac{3R}{2}\ell n\left(\frac{600}{300}\right) + 2 \times R\ell n\left(\frac{4}{1}\right) = 7R\ell n\, 2$$

$\therefore$ X = 7

4.* For isothermal free expansion of an ideal gas,
$\Delta T = 0$ Therefore, $\Delta H = \Delta E = 0$
Also, W = 0 (since $P_{ext.} = 0$)
Therefore, from first law, q = 0. Therefore, $\Delta S_{surr.} = 0$.
Since gas is expanding, $\Delta S_{sys.} > 0$.

5. **I.** Molar entropy of gas is much greater than that of solid and liquid.
II. Entropy change is positive if Δn_g is positive.
III. Molar entropy of a crystalline solid will be zero at absolute zero.
IV. In irreversible process both system and surroundings are not restored if path is reversed.
V. Refractive index and molarity are intensive properties.

7. If $\Delta H < 0$ and $\Delta S < 0$, then reaction is non-spontaneous at high temperatures and spontaneous at low temperatures.

8. $H_2O(\ell, 1bar, 373K) \longrightarrow H_2O(g, 1bar, 373\,K)$
$\Delta S > 0$
$\Delta H > 0$
$\Delta G = 0$

9. $(C_p)_m = aT^3 \therefore 0.375 = a(10)^3 \therefore a = \frac{3}{8} \times 10^{-3}$

$$S_m = \int_0^{20} \frac{(C_P)_m dT}{T} = \int_0^{20} aT^2 dT = \left.\frac{aT^3}{3}\right|_0^{20} = \frac{8000a}{3} = \frac{8000}{3} \times \frac{3}{8} \times 10^{-3} = 1 J/K\text{–}mol$$

10. $\Delta G = nRT\ \ell n\left(\frac{P_f}{P_i}\right) = \left(\frac{144}{18}\right) \times \frac{2}{1000} \times 373\ell n\left(\frac{4}{1}\right) \approx 8Kcal.$

DPP No. # 56

1. Gram mol. wt. of $C_6H_{12}O_6$ = 180 g
i.e. wt. of 6.023 × 10^{23} molecules = 180

so wt. of 1 molecules = $\frac{180}{6.023 \times 10^{23}}$ = 2.988 × 10^{-22} g.

2. No. of carbon atom in glucose $= \frac{1.71}{342} \times 12\ N_a$

$= 3.6 \times 10^{22}$

4. $x \times \frac{0.5}{100} = 78.4 \quad \Rightarrow \quad x = \frac{78.4 \times 10^2}{5 \times 10^{-1}} = \frac{78.4}{5} \times 10^3 = 1.568 \times 10^4.$

6. At NTP, weight of 1 litre gas = 0.178 gm
so weight of 22.4 litre gas = weight of 1 mole gas = molar mass of gas = 0.178 × 22.4 gm
vapour denstiy = molar mass of gas / 2

so V.D. = $\frac{0.178 \times 22.4}{2}$ = 2

7. $C_8H_{18} + \frac{25}{2} O_2 \longrightarrow 8CO_2 + 9\,H_2O$

M = 1.425 × 1000 × 0.8 = 1140 g

mol $= \frac{1140}{114}$ = 10 mol

Now from mole–mole analysis

$$\frac{\text{mole of } C_8H_{18}}{1} = \frac{\text{mole of } O_2}{25/2}$$

$$\frac{10}{1} = \frac{\text{mole of } O_2}{25/2} \quad \Rightarrow \text{mole of } O_2 = \frac{25}{2} \times 10 = 125 \text{ mol.}$$

8. $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$\frac{100}{64}$ (excess)

From mole-mole analysis

$\frac{100}{64} = \frac{n_{C_2H_2}}{1}$ (here n = mole)

vol. = $n_{C_2H_2}$ × 22.4 (at N.T.P) (N.T.P ij)

$= \frac{100}{64} \times 22.4 = 35$ lit.

9. $3BaCl_2 + 2Na_3PO_4 \longrightarrow Ba_3(PO_4)_2 + 6\,NaCl$

mole 0.5 0.1

$\frac{0.5}{3}$ $\frac{0.1}{2}$ (L.R is Na_3PO_4)

Now from mole– mole analysis vc eksy&eksy fo'ys"k.k ls

$$\frac{\text{mole of } Na_3PO_4}{2} = \frac{\text{mole of } Ba_3(PO_4)_2}{1}$$

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$= \frac{0.1}{2}$ = mole of $Ba_3(PO_4)_2$ $Ba_3(PO_4)_2$ ds eksy

$\Rightarrow$ mole of $Ba_3(PO_4)_2$ = 0.05 mol. $Ba_3(PO_4)_2$ ds eksy = 0.05 mol.

10. $Ag + HMO_3 \xrightarrow{NaCl} AgCl$

21.6 14.35

mole $\frac{21.6}{108} = 0.2$

Ag Atom remain conseved

So No. of mole of Ag = No. of mole of Ag Cl

So. No. of mole of AgCl = 0.2

Weight of AgCl = 28.7

% Yield = $\frac{14.35}{28.7} \times 100 = 50$ %.

11. $[NO_3^-] = \frac{0.1V + 0}{2V} = \frac{0.1}{2} = 0.05$ M.

12. $[Cl^-] = \frac{300 \times 3 + 200 \times 4 \times 2}{500}$

$= \frac{2500}{500} = 5$ M

13. $2Al + KClO_3 \longrightarrow Al_2O_3 + KCl$

(excess) 1 mole ($KClO_3$ is L.R.) 1 mole ($KClO_3$ L.R. gS)

From mole-mole analysis

$\frac{n_{KClO_3}}{1} = \frac{n_{Al_2O_3}}{1}$

$\Rightarrow n_{Al_2O_3} = 1$ mole.

15. Mole fraction of A i.e. $X_A = \frac{n_A}{\text{Total moles}}$

So $X_{H_2O} = \frac{n_{H_2O}}{\text{Total moles}}$

Now $\frac{X_A}{X_{H_2O}} = \frac{n_A}{n_{H_2O}}$

and molality $= \frac{n_A \times 1000}{n_{H_2O} \times 18} = \frac{X_A \times 1000}{X_{H_2O} \times 18} = \frac{0.2 \times 1000}{0.8 \times 18}$ = **13.9 Ans.**

16. Let wg water in added to 16 g CH_3OH

molality $= \frac{16 \times 1000}{W \times 32} = \frac{500}{W}$

$\frac{500}{W} = \frac{x_A \times 1000}{(1 - x_A)m_B} = \frac{0.25 \times 1000}{0.75 \times 18}$ W = 27 gm.

17. (A) Molarity of second solution is $= \frac{10 \times d \times x}{M} = 1$ M (B) Volume = 100 + 100 = 200 ml

(D) Mass of $H_2SO_4 = \frac{200 \times 1}{1000} \times 98 = 19.6$ gm.

18. $NaN_3 \Rightarrow 1(+1) + 3(x) = 0 \therefore x = -1/3$

$N_2H_2 \Rightarrow 2(x) + 2(+1) = 0 \therefore x = -1$

NO $\Rightarrow$ 1(x) + 1(–2) = 0 $\therefore$ x = + 2

N_2O_5 $\Rightarrow$ 2(x) + 5(–2) = 0 $\therefore$ x = + 5

19. (D) SO_3 SO_2 H_2S S_8
6 4 –2 0

20. $MnO_4^- + C_2O_4^{2-} + H^+ \longrightarrow Mn^{2+} + CO_2 + H_2O$

V.f. = 5 V.f. = 2

$\therefore$ Balanced equation : $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Topic : Atomic Structure

3. For photoelectric effect to take place, $E_{light} \geq W \therefore \frac{hc}{\lambda} \geq \frac{hc}{\lambda_0}$ or $\lambda \leq \lambda_0$.

4. More energy means less wavelength.

5. Power = $\frac{nhC}{\lambda \times t}$ $\Rightarrow$ $40 \times \frac{80}{100} = \frac{n \times 6.62 \times 10^{-34} \times 3 \times 10^8}{620 \times 10^{-9} \times 20}$ $\Rightarrow$ n = 2 × 10^{21}

9. $r \propto n^2$

11. This is the range of visible region.

12. infrared lines = total lines – visible lines – UV lines $= \frac{6(6-1)}{2} - 4 - 5$ = 15 – 9 = 6.

(visible lines = 4 $6\to2, 5\to2, 4\to2, 3\to2$) (UV lines = 5 $6\to1, 5\to1, 4\to1, 3\to1, 2\to1$)

13. For third line of Bracket series ($4 \to 7$)

$$\frac{1}{\lambda} = R\left(\frac{1}{16} - \frac{1}{49}\right) \Rightarrow \lambda = \frac{784}{33R}$$

14. $\lambda = \frac{h}{mv} = 0.4 \times 10^{-33}$ cm

15. $\lambda = \frac{h}{\sqrt{2mK}} = 3.328 \times 10^{-10}$ m.

18. Number of radial nodes = n – ℓ – 1 = 1, n = 3. $\therefore$ ℓ = 1.

Orbital angular momentum = $\sqrt{\ell(\ell+1)}\frac{h}{2\pi} = \sqrt{2}\frac{h}{2\pi}$.

19. After np orbital, (n + 1) s orbital is filled.

20. Rb_{37} : [Kr] $5s^2$. $\therefore$ n = 5, ℓ = 0, m = 0, s = $\pm\frac{1}{2}$.

DPP No. # 57

1. $PV = \left(P + \frac{1}{100}P\right)V_2$

$V_2 = \frac{PV}{\frac{101}{100}P}$ $\Rightarrow$ $V_2 = \frac{100}{101}V$

% decrease ¼% deh½ = $\frac{\frac{100}{101}V}{V}$ = $\frac{100}{101}$ %

2. V_1 = 100 ml V_2 = 80 ml

$T_1 = 300$ K $\quad T_2 = ?$
$P_1 = 740$ mm $\quad P_2 = 740$ mm
Applying charles law $V \propto T$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{100}{300} = \frac{80}{T_2}$$

$$T_2 = \frac{300 \times 80}{100} = 240\text{ K} = 24 - 273 = 240 - 273^\circ\text{C} = -33^\circ\text{C}.$$

3. $V \propto T$ (at constant n and P).

4. Apply Dalton's law of partial pressure

Initially $\quad n_1 = \frac{P_1V}{RT} = \frac{100 \times V}{RT} \quad ; \quad n_2 = \frac{P_2V}{RT} = \frac{400 \times V}{RT}$

5. $P.P_{H_2} = \frac{\frac{w}{2}}{\frac{w}{2} + \frac{w}{16}} \times P \quad \Rightarrow \quad P.P_{H_2} = \frac{8}{9}P$

6. $\frac{1}{6} = \sqrt{\frac{2}{x}}$ (Where X is molecular weight of gas)

$$\frac{1}{36} = \frac{2}{x}$$

x = 72

7. $\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{d_{O_2}}{d_{H_2}}}$

$$\frac{1}{r_{O_2}} = \sqrt{\frac{1.44}{0.09}}$$

$$r_{O_2} = \sqrt{\frac{1}{16}}$$

$$r_{O_2} = \frac{1}{4}$$

8. $\frac{\frac{50}{20}}{\frac{40}{t}} = \sqrt{\frac{32}{2}}$

$$\frac{50t}{20 \times 40} = 4$$

t = 64 min.

9. K.E. $\propto$ T
(T will same)

10. $V_{mps} : V_{av} : V_{rms}$

$\Rightarrow \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} \quad \Rightarrow \quad \sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$

11. Average K.E. for one mole = $\frac{3}{2}RT$

Average K.E. for 14 g of N_2 $\left(\frac{1}{2}\text{mole}\right) = \frac{3}{2} \times \frac{8.314}{2} \times 400 = 2494$ J.

12. $\frac{V_{rms,SO_2}}{V_{rms,He}} = \sqrt{\frac{T_{SO_2}}{T_{He}} \times \frac{M_{He}}{M_{SO_2}}}$

$\frac{1}{2} = \sqrt{\frac{T_{SO_2}}{300} \times \frac{4}{64}}$

$4 = \frac{T_{SO_2}}{300}$

$T_{SO_2} = 1200$ K

13._ A real gas approaches the behaviour of ideal gas when the pressure is low and the temperature is high.

15._ For ideal gas, compressibility actor (Z) = 1.

16._ $T_c = \frac{8a}{27Rb}$. Thus $T_c \propto \frac{a}{b}$

17. $PV = nRT = \frac{w}{M}RT$

or $P = \frac{w}{V}\frac{RT}{M} = \frac{dRT}{M}$

Thus $P \propto d$, $P \propto T$. Hence,

$$\frac{P_1}{P_2} = \frac{d_1}{d_2} \times \frac{T_1}{T_2} = \frac{1}{2} \times \frac{2}{1} = 1 : 1.$$

18. $U_{rms} = \sqrt{\frac{3RT}{M}}$ using ideal gas equation,

$PV = nRT = \frac{w}{M}RT$; $\frac{RT}{M} = \frac{RV}{w} = \frac{P}{d}$ where d is the density of the gas

$\therefore$ $U_{rms} = \sqrt{\frac{3P}{d}}$ at constant pressure, $U_{rms} \propto \frac{1}{\sqrt{d}}$

19. Pressure of helium = 8 bar

Pressure of CH_4 = 2 bar

$$\frac{r_{He}}{r_{CH_4}} = \frac{P_1}{P_2}\sqrt{\frac{M_{CH_4}}{M_{He}}} = \frac{8}{2}\sqrt{\frac{16}{4}} = \frac{8}{1} = 8 : 1$$

20. At constant temperature,

$P_1 V_1 + P_2 V_2 = P_3 (V_1 + V_2)$

(4.0 bar) (4.0 dm^3) + (6.0 bar) (6.0 dm^3) = P_3 (4.0 + 6.0 dm^3)

or $P_3 = \frac{16+36}{10} = \frac{52}{10} = 5.2$ bar.

21. $HCOOH \longrightarrow H_2O + CO$

a mole   0   0

a   a

$H_2C_2O_4 \longrightarrow H_2O + CO + CO_2$

b mole   0   0   0

b   b   b

H_2O absorb by H_2SO_4 and CO_2 absorbed by KOH

volume of CO_2 / total volume = b/a + 2b = 1/6

a/b = 4/1

the molar ratio of HCOOH and $H_2C_2O_4$ is 4 : 1.

DPP No. # 58

1. $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ $K_p = 4\times10^{-3}$

$SO_3 \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$ $K^1{}_p = \frac{1}{Kp}$

$K^1{}_p = \left(\frac{1}{4\times10^{-3}}\right)$

$2SO_3 \rightleftharpoons 2SO_2 + O_2(g)$

$K^{II}{}_p = (K^I{}_p)^2 = \left[\frac{1}{4\times10^{-3}}\right]^2 = \left[\frac{1000}{4}\right]^2 = 6250 = 625\times10^2$ **6.25×10^4 atm.**

2. $\log\frac{K_P}{K_C} + \log RT = 0$

$\log\left(\frac{K_P}{K_C}.RT\right) = 0$

$K_P = K_C (RT)^{-1}$

$\because K_P = K_C (RT)^{\Delta n}$; $\Delta n = -1$

This is possible one for option (B).

3. Equilibrium const. is temp. dependent only.

4. $C_2H_5OH(\ell) + CH_3COOH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$.

a a 0 0

a 0.33a a – 0.33a 0.33a 0.33a

$$K_C = \frac{(0.33a)\times(0.33a)}{(0.67a)\times(0.67a)} = K_C = 1/4.$$

5. Since, K_p is temperature dependent only.

8. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$\alpha = .2$, initially, $K_P = \frac{\alpha^2}{1-\alpha^2}P = \frac{(0.2)^2}{1-(.2)^2}\times1 = \frac{.04}{.96} = .042$

If $\alpha = .5$, thus, $\frac{(.5)^2}{1-(.5)^2}\times P = .042$, $P = .126$

9. Since inert gas addition has no effect at const. volume.

12. $P_{NH_3} = P_{H_2S} = \frac{P}{2}$ Hence $K_p = P_{NH_3}\times P_{H_2S} = \frac{P}{2}\times\frac{P}{2} = \frac{P^2}{4}$

13. At room temperature, K = 4.32

and at 425°C, equilibrium constant become 1.24×10^{-4} i.e. it is decreases with increase in temperature. So, it is exothermic reaction.

14. $K = [B(g)]^2 [C(g)]^3 = x^2y^3$. If [C(g)] is doubled

i.e. = 2y. Suppose [B(g)] is z. Then

$K = z^2 (2y)^3 = x^2y^3$ or $z^2 = \frac{1}{8}x^2$ or $z = \frac{1}{\sqrt{8}}x = \frac{1}{2\sqrt{2}}x$.

17. On mixing some quantity of 0.01 MHCl in aqueous solution of CH_3COOH, equilibrium concentration of CH_3COO^- will be increase.

18. $N_2O_4(g) \rightleftharpoons 2NO_2(s)$

t = 0	0.1 mole	0
t = eq	0.05	0.1

$$k = \frac{(0.1)^2}{0.05} = 0.2$$

19. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(s)$

at eq, mole of PCl_3 = mole of Cl_2

$$\text{So } K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left[\frac{0.2}{10}\right]\left[\frac{0.2}{10}\right]}{\frac{0.1}{[10]}} = 0.04$$

DPP No. # 59

2. First law of thermodynamics is the law of conservation of energy.

4. Work done by the gas in the cyclic process = Area bounded (ABCA) = $5P_1V_1$

6. From I law of thermodynamics $\Delta E = Q + W$

where Q = 0 for adiabatic process.

7. $\Delta U = W$

$nCv (T_2 - T) = - P \times (V_2 - V_1)$

$\frac{3}{2} R (T_2 - T) = -1 \Rightarrow \therefore T_2 = T - \frac{2}{3 \times 0.0821}$

8. $q = 0 \quad \therefore \quad \Delta U = w$

$$\Rightarrow nC_{v,m} (T`_2 - T_1) = -P_{ext}\left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right]$$

$$\therefore C_{v,m} [T_2 - T_1] = P_{ext} . R \left[\frac{T_1}{P_1} - \frac{T_2}{P_2}\right] \Rightarrow \frac{3}{2} R [T_2 - 300] = 2 \times R \left[\frac{300}{5} - \frac{T_2}{2}\right] \Rightarrow T_2 = 228 \text{ K}$$

9. When one mole of NH_3 is formed from its constituent elements the enthalpy change = – 46.0 kJ

Therefore when one mole of NH_3 decompose to give its constituent elements enthalpy change = 46.0 kJ

$\Rightarrow$ When 2 mole NH_3 decompose, enthalpy change = 2 × 46 = 92.0 kJ

10. Combustion reaction of solid boron

$$B(s) + \frac{3}{4} O_2(g) \longrightarrow \frac{1}{2} B_2O_3$$

$$\Delta H^\circ_r = \Delta H^\circ_c = \frac{1}{2}\Delta H^\circ_f (B_2O_3, s) - \Delta H^\circ_f (B, s) - \frac{3}{4}\Delta H^\circ_f (O_2, g)$$

ΔH_f° of element in stable state of aggregation is assumed to be zero.

$$\mathbf{\Delta H^\circ_c = \frac{1}{2}\Delta H^\circ_f (B_2O_3)}$$

11. (1) $H_2O(\ell) \longrightarrow H_2O(g)$ $\quad \Delta H = 40.6$ KJ/mole

(2) $2H(g) \longrightarrow H(g)$ $\quad \Delta H = –435.0$ KJ/mole

(3) $O_2(g) \longrightarrow 2\,O_2(g)$ $\quad \Delta H = –49836$ KJ/mole

(4) $2H_2(g) + O_2(g) \longrightarrow H_2O(\ell)$ $\quad \Delta H = –571.6$ KJ/mole

$2H_2(g) \downarrow 4H(g)$; $O_2(g) \downarrow 2O(g)$; $4H(g) + 2O(g) \longrightarrow \uparrow H_2O(\ell)$

(1) **Calculation of $\Delta H^\circ_f (H_2O,\ell)$**

$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$ $\Delta H = -571.6$ KJ/mole

$\Delta H^\circ_r = 2\Delta H^\circ_F(H_2O, \ell) - 2\Delta H^\circ_F\{H_2,(g)\} - \Delta H^\circ_F(O_2, g)$

(where $\Delta H^\circ_F\{H_2,(g)\}$ → Zero and $\Delta H^\circ_F(O_2, g)$ → Zero)

$-571.6 = 2\Delta H^\circ_F(H_2O, \ell)$ so $\quad \Delta H^\circ_F(H_2O, \ell) = -285.5$

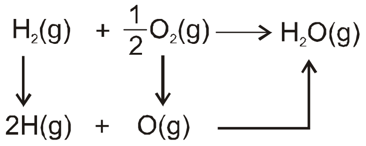
(2) Calculation of $\Delta H^\circ_F(H_2O, g)$

$H_2O(\ell) \longrightarrow H_2O(g) \qquad \Delta H = 40.6$

$\Delta H_r = \Delta H^\circ_F(H_2O, g) - \Delta H^\circ(H_2O, \ell)$

$\Delta H^\circ_F(H_2O, g) = \Delta H^\circ_F(H_2O, \ell) + \Delta H_r$

$= -285.8 + 40 = -245.8$

(3) 

$\Delta H = -245.8$

$\Delta Hr = \epsilon_{H-H} + \frac{1}{2}\epsilon_{O-O} - 2\,\epsilon_{O-H} \quad \Rightarrow \quad -245.8 = +435 + \frac{1}{2}(489.6) - 2 \times \epsilon_{O-H}$

$2\epsilon_{O-H} = 435 + 244.8 + 245.8 \quad \Rightarrow \quad 2\epsilon_{O-H} = 925.6$

ϵ_{O-H} **= 462.5**

13. $nCH_2 = CH_2 \longrightarrow (-CH_2-CH_2-)_n \qquad \Delta H = -100$ KJ/mole

n [C = C] + n[C – H]4 – n [C – H] 4 – n[C – C] × 2 = – 100

n[C = C] – 2n[C – C] = – 100 ⇒ [C = C] – 2[C – C] = – 100

⇒ + 600 – 2[C – C] = – 100 ⇒ – 2 [C – C] = – 700 KJ/mole ⇒ (C – C) = – 350

14. Process is Reversible and adiabatic (Q = 0)

So, $\Delta S = 0$

15.* Process is endothermic i.e., ΔH = + ve and process is also spontaneous i.e., ΔG = – ve

Hence, from Gibbs-Helmholtz equation

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

ΔS must be positive so that ΔG may be negative.

16.* It is because of the fact that for spontaneity, the value of $\Delta G = (\Delta H - T\Delta S)$ should be < 0. If ΔH is – ve, the value of $T\Delta S$ shall have to be less than ΔH or the value of ΔS has to be less than $\frac{\Delta H}{T}$ i.e., $\frac{x}{298}$.

18. The assertion that the increase in internal energy for vaporisation of one mole of water at 1 atm and 373 K is zero is true because for all isothermal process change in internal energy is zero.

19. $H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(g) \quad ; \quad \Delta H_f = -\varepsilon_1, \qquad ....(i)$

$H_2O(g) \longrightarrow H_2O(l) \quad ; \quad \Delta H_f = -\varepsilon_2, \qquad ....(ii)$

and (i) and (ii).

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l).\ ; \qquad \Delta H = -(\varepsilon_1 + \varepsilon_2)$.

20. Heat of neutralisation for strong acid and strong base combination is constant is equal to – 13.7 Kcal or – 57.1 KJ.

22. Enthalpy of formation of 3 carbon-carbon double bonds

= ΔH_F () – ΔH_f ()

= –156 – (+ 49) kJ = –205 kJ.

Given that,  + H_2 ⟶  ΔH = 119 kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

= 3 × (–119) kJ = – 357 kJ.

∴ resonance energy of benzene = – 357 – (–205) kJ = –152 kJ mole^{-1} ®