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CHEMISTRY

CAPS – 5
Chemical Equilibrium
& Surface Chemistry

TARGET : JEE Advanced – 2021

Answer Key

1.	(A)	**2.**	(C)	**3.**	(C)	**4.**	(A)	**5.**	(B)
6.	(D)	**7.**	(A)	**8.**	(D)	**9.**	(D)	**10.**	(C)
11.	(BC)	**12.**	(ABC)	**13.**	(ABD)	**14.**	(CD)	**15.**	(CD)
16.	(AC)	**17.**	(AB)	**18.**	(ACD)	**19.**	(C)	**20.**	(D)
21.	(A)	**22.**	(B)	**23.**	(A)	**24.**	(A → Q; B → P; C → R; D → S)		

25. $\left(K_{p_1} = \frac{1}{20P_0^2}, K_{P_2} = \frac{3}{20P_0^2}\right)$

26. ((i) $k_C = 189.574\ mol^{-2}\ lit^2$, $k_P = 0.05\ atm^{-2}$ (ii) P = 12.4408 atm)

27. (708.3 M^{-1}) **28.** (Ne)

Solution

1. Formation of NH_3 through Haber's Process is an exothermic change so on increasing the temperature concentration of NH_3 obtained at equilibrium will decrease.

2. Given that $Br_{2(l)} + Cl_{2(g)} \rightleftharpoons 2BrCl_{(g)}$; $K_P = 1$ atm

$\therefore$ Initially 0 1 0

at equilibrium (1 – x) 2x

$\because K_P = \frac{[P_{BrCl}]^2}{[P_{Cl_2}]} = 1$ & $P_{BrCl} = 0.1$ atm

$\therefore P_{Cl_2} = 0.01$ atm

Now in a closed container V = constant & at constant T; $P \propto n$

$$\therefore \frac{P_{BrCl}}{P_{Cl_2}} = \frac{n_{BrCl}}{n_{Cl_2}} \text{ or } \left.\frac{0.1}{0.01} = \frac{2x}{1-x}\right\} x = \frac{5}{6}$$

So, moles of BrCl = $2x = \frac{10}{6}$

Since the vapour pressure of Br_2 is same as the partial pressure of BrCl, the moles of bromine in vapour phase will be equal to the moles of BrCl.

Moles of Cl_2 used up = $\frac{5}{6}$

$\therefore$ Moles of Br_2 required = moles of BrCl formed + moles of Cl_2 used = $\frac{15}{6}$

3. Where the stopcock is opened then the total volume of the vessel becomes = 4 lt

Now,	A_2	+	B_2	$\rightleftharpoons$	2AB
at t = 0	$\frac{2}{4}$		$\frac{4}{4}$		0
at t = t_{eq}	$\frac{2-x}{4}$		$\frac{4-x}{4}$		$\frac{2x}{4}$

$$K_C = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left[\frac{2x}{4}\right]^2}{\left[\frac{2-x}{4}\right]\left[\frac{4-x}{4}\right]} = 4$$

or $\quad \frac{4x^2}{(2-x)(4-x)} = 4$

or $\quad x = \frac{4}{3}$

$\therefore \quad [AB]_{\text{at equilibrium}} = \frac{2x}{4} = \frac{2\left(\frac{4}{3}\right)}{4} = 0.66.$

4.

	2A(g)	+	B(g)	$\rightleftharpoons$	C(g)	+	D(g)
at t = 0	2		1		7		3
at t = equilibrium	2- 2x		1 –x		7 + x		3 + x

Given that $K_C = 10^{12} = \frac{[C][D]}{[A]^2[B]} = \frac{(7+x)(3+x)}{(2-2x)^2(1-x)}$

x = 0.9998

$\therefore \quad [A]_{\text{equilibrium}} = 2 - 2x = 2 - 2\,(0.9998) \approx 4 \times 10^{-4}$

5.

	$2SO_3(g)$	$\rightleftharpoons$	$2SO_2(g)$	+	$O_2(g)$
Mole at t = 0	1 mole		0		0
Mole at t = eq	1 – 2x		2x		x

$KMnO_4/H^+$ used reacts with SO_2 only.

No. of equivalents of $KMnO_4$ used = 0.2 × 5 = 1

So, no. of equivalents of SO_2 = 1 = n × n_f

$n = \frac{1}{2} = 0.5$

Hence no. of moles of SO_2 at equilibrium = 0.5

$2x = 0.5 \Rightarrow x = \frac{1}{4}$

At equilibrium

$[SO_3] = 1 - \frac{1}{2} = \frac{1}{2} \quad [SO_2] = \frac{1}{2} \quad [O_2] = \frac{1}{4}$

$$K_C = \frac{\left(\frac{1}{4}\right)\left(\frac{1}{2}\right)^2}{\left(\frac{1}{2}\right)^2} = 0.25$$

6. Pure T_2O at 298 K

$T_2O \rightleftharpoons T^+ + OT^-$

$10^{-7.62}$ $10^{-7.62}$

	TCl	+	NaOT	→	T_2O	+	NaCl
t = 0	2 mmoles		3.75 mmoles		0		0
t = eq	0		1.75		2		2

Total volume = 25 ml

$$\left[OT^-\right] = \frac{1.75}{25} = 0.07$$

$P^{OT} = 2 - \log 7$

$P^{T} = 15.24 - (2 - \log 7)$

$= 13.24 + \log 7$

7. Physical adsorption is an exothermic process, i.e., change in enthalpy is -ve. Thus, H decreases as reaction progresses.

8. Lyophilic sols are reversible sols. Few examples include organic substances like starch in suitable solvents. They are neutral and thus cannot be readily coagulated and thus they are self-stabilized.

9. Below CMC, salt behave as normal electrolyte.

10. Number of sodium lauryl sulphate molecules ($CH_3(CH_2)11SO_4^-Na^+$) in 1 litre solution

$= 10^{-3} \times 6 \times 10^{23}$

$= 6 \times 10^{20}$

No. of sodium lauryl sulphate molecules per mm^3 = 6 × 1014

Number of colloidal particles per $mm^3 = 10^{13}$

Number of molecules per colloidal particle

$$= \frac{6 \times 10^{14}}{10^{13}} = 60$$

11. A catalyst provides a different pathway, i.e., mechanism to the reaction, with less activation energy.

12. Fact based.

13. For this reaction

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -22.4$ Kcal

$\Delta n = -ve$

When an inert gas like He is added to the above equilibrium at constant temperature and pressure then to maintain a constant temperature and pressure then to maintain a constant pressure condition the volume of the system must increase. Because of this, the concentration of all species involved in the reaction immediately decreases. The reaction then tries to re achieve equilibrium by shifting in the backward direction which would increase the amount of N_2 & H_2 and decrease the amount of NH_3.

14.

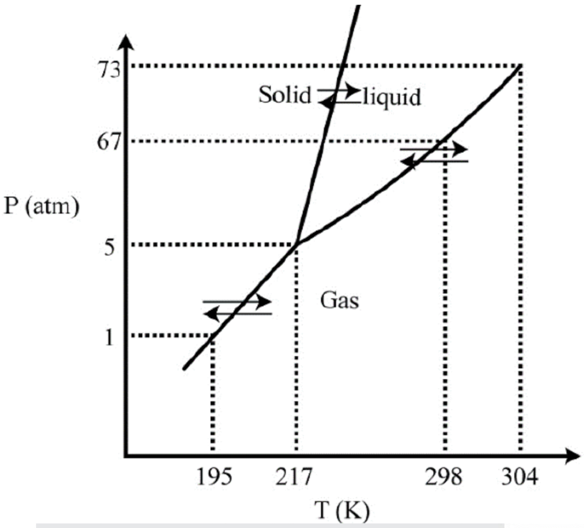
$$\begin{array}{ccccccc} AB_2 & + & B_2C & \rightleftharpoons & AB_3 & + & BC \\ 1-x & & 1-x-y & & x & & x-y \\ BC & + & B_2C & \rightleftharpoons & B_3C_2 & & \\ x-y & & 1-x-y & & y & & \end{array}$$

Since $x > y$

$\therefore \quad [AB_3]_{equm} > [BC]_{equm}$

$[AB_3]_{equm} > [B_3C_2]_{equm}$

15.



- At temp. above 195 K we final CO_2 to have gaseous phase.
- Both m.pt. and B.pt. of CO_2 increases with pressure.

16.

$$\left.\begin{array}{l} A_{(g)} \rightleftharpoons B_{(g)}; K_1 = ? \\ B_{(g)} \rightleftharpoons C_{(g)}; K_2 = 0.4 \\ C_{(g)} \rightleftharpoons A_{(g)}; K_3 = 0.6 \end{array}\right\} K_1 = \frac{1}{K_1 \times K_2} = \frac{1}{0.24}$$

$$\left.\begin{array}{ll} A & \rightarrow B \\ 1-x & x \end{array}\right\} K_1 = \frac{1}{0.24} \text{and} \quad \begin{array}{ll} A & \rightarrow C \\ 1-x-y & y \end{array}$$

$\therefore \quad [A] = 1 - x - y$

$[B] = x$

$[C] = y$

So, $[A] + [B] + [C] = 1$

or $\dfrac{x}{1-x} = \dfrac{1}{0.24}$

or, $1.24x = 1$

$x = 0.8$

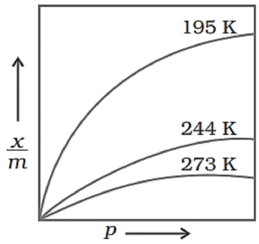
and $\dfrac{y}{1-x-y} = \dfrac{1}{0.6}$

or $1.6y = 1 - x$

or $1.6y = 0.2$

$y = 0.125$

17. When excess of $AgNO_3$ is added, Ag^+ will get adsorbed onto AgI giving it a positive charge. The effect of pressure on physical adsorption is high if temperature is low. It is clear from the graph –



Adsorption isotherm

18. Low temperature is favorable for physical adsorption.

Chemical adsorption requires activation energy.

19. **(Q. 19, 20)**

	$2A_2$	$\rightleftharpoons$	A_4
Initial	3p		–
At eqm.	3p – x– y		$\frac{x}{2}$

	A2	+	2C	$\rightleftharpoons$	A_2C_2
Initial	3p		p		–
At eqm.	3p – x – y		p – 2y		y – a

	A_2C_2	$\rightleftharpoons$	2AC
Initial	–		–
At eqm.	y – a		2a

According to the question,

$$P_{A_4} = \frac{1}{2} \Rightarrow \frac{x}{2} = \frac{1}{2} \Rightarrow x = 1$$

$$P_{Ac} = \frac{1}{2} \Rightarrow 2a = \frac{1}{2} \Rightarrow a = \frac{1}{4}$$

Now, $K_{P_1} = \frac{2}{81} \Rightarrow \frac{P_{A_4}}{\left(P_{A_2}\right)^2} = \frac{2}{81}$

$$\Rightarrow \quad \frac{1}{2\left(P_{A_2}\right)^2} = \frac{2}{81} \Rightarrow P_{A_2} = \frac{9}{2}$$

Thus, $3p - x - y = \frac{9}{2}$

or $3p - 1 - y = \frac{9}{2}$

$\Rightarrow \quad 3p - y = \frac{11}{2}$ .....(1)

Also,

$$P_{A_2} + P_{A_4} + P_C + P_{A_2C_2} + P_{AC} = \frac{27}{4}$$

$\Rightarrow \quad \frac{9}{2}+\frac{1}{2}+p-2y+y-\frac{1}{4}+\frac{1}{2}=\frac{27}{4}$

$\Rightarrow \quad \left(\frac{11}{2}-\frac{1}{4}\right)+p-y=\frac{27}{4}$

$\Rightarrow \quad \frac{21}{4}+p-y=\frac{27}{4}$

$\Rightarrow \quad p-y=\frac{6}{4}=\frac{3}{2} \quad .....(2)$

Substituting value of y in eq. (1),

$3p-\left(p-\frac{3}{2}\right)=\frac{11}{2}$

$\Rightarrow \quad 2p+\frac{3}{2}=\frac{11}{2}$

$\Rightarrow \quad 2p=\frac{11}{2}-\frac{3}{2}$

$\Rightarrow \quad 2p = 4 \Rightarrow p = 2$

and $\quad p=y=\frac{3}{2}$

$2-y=\frac{3}{2}$

$\Rightarrow \quad \boxed{y=\frac{1}{2}}$

Thus, $\quad \boxed{P_{A_2C_2}=y-a=\frac{1}{2}-\frac{1}{4}=\frac{1}{4}}$

And $\quad \boxed{\frac{n_{A_2}}{n_{AC}}=\frac{P_{A_2}}{P_{AC}}=\frac{\frac{9}{2}}{\frac{1}{2}}=9}$

21. $SnCl_2.6H_2O(s) \rightleftharpoons SnCl_2.2H_2O(s) + 4H_2O(g)$

KP = $(P_{H_2O})^4$

$\Rightarrow \quad P_{H_2O}=\sqrt[4]{5\times10^{-12}}\approx1.5\times10^{-3}\text{atm}$

$Na_2HPO_4.12H_2O(s) \rightleftharpoons Na_2HPO_4.7H_2O(s) + 5H_2O(g)$

$K_p=\left(P_{H_2O}\right)^5$

$\Rightarrow \quad P_{H_2O}=\sqrt[5]{243\times10^{-15}}$

$\Rightarrow \quad P_{H_2O}=3\times10^{-3}\text{atm}$

$Na_2SO_4 + 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$

$K_P=\left(P_{H_2O}\right)^{10}$

$\Rightarrow \quad P_{H_2O}=\sqrt[10]{1024\times10^{-30}}$

$\Rightarrow \quad P_{H_2O}=2\times10^{-3}\text{atm}$

Since the vapour pressure of water will decrease to the minimum value in case of $SnCl_2.2H_2O$, it will be the best drying agent at 0°C.

22. At equilibrium, relative humidity in $Na_2SO_4.\ 10H_2O(s)$ is,

$$\text{relative humidity} = \frac{PP_{H_2O}}{VP_{H_2O}} \times 100$$

$$= \frac{2 \times 10^{-3} \times 760}{4.56} \times 100 = 33.33\%$$

Now, if relative humidity is less than 33.33% reaction will occur in forward direction as ($Q_P < K_P$). This will lead to release of moisture.

23. As discussed in Q.23, the R.H at equilibrium in $Na_2SO_4.10H_2O$ is 33.33 %. For the substance to show deliquescent behavior, the reaction should occur in backward direction, i.e., QP > KP. Thus, R.H. should be more than 33.33%.

24. Fact

25. $K_{p_1} = \frac{1}{20P_0^2}, K_{P_2} = \frac{3}{20P_0^2}$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Initial	$9x$	$13x$	–
eqm.	$9x - a - b$	$13x - 3a - 2b$	$2a$

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$$

Initial	$9x$	$13x$	–
eqm.	$9x - a - b$	$13x - 3a - 2b$	$2a$

Now, $P_{NH_2} = 2a = P_O \Rightarrow a = \frac{P_0}{2}$

Ans, $13x - 3a - 2b = 2P_O$

$\Rightarrow$ $13x - 2b = 2P_O + \frac{3P_O}{2}$

$13x - 2b = \frac{1P_O}{2}$ .....(1)

And $P_{N_2} + P_{H_2} + P_{NH_3} + P_{N_2H_4} = 7P_O$

$\Rightarrow$ $9x - a - b - 2P_O + P_O + b = 7P_O$

$\Rightarrow$ $9x - a = 4P_O$

$\Rightarrow$ $9x = 4P_O + a$

$\Rightarrow$ $9x = 4P_O + \frac{P_O}{2}$

$\Rightarrow$ $9x = \frac{9P_O}{2}$

$\Rightarrow$ $x = \frac{P_O}{2}$

Substituting in eq. (1),

$$\frac{13P_O}{2} - 2b = \frac{7P_O}{2}$$

$\Rightarrow \quad 3P_O = 2b$

$\Rightarrow \quad b = \frac{3P_O}{2}$

Thus, $K_{P_1} = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3} = \frac{{P_O}^2}{\left(\frac{5P_O}{2}\right)(2P_O)^3}$

$\Rightarrow \quad K_{P_1} = \frac{1}{20P_O^2}$

$$K_{P_2} = \frac{(P_{N_2H_4})}{(P_{N_2})(P_{H_2})^2} = \frac{\left(\frac{3P_O}{2}\right)}{\left(\frac{5P_O}{2}\right)(2P_O)^2} = \frac{3}{20P_O^2}$$

26. $(P_{CO})_{initial} = \frac{nRT}{V} = \frac{0.15 \times 0.0821 \times 750}{2.5} = 3.6945\,atm$

$(P_{CH_3OH})_{at\ eqm} = \frac{nRT}{V} = \frac{0.08 \times 0.0821 \times 750}{2.5} = 1.9704\,atm$

Thus,

	CO	+	$2H_2$	$\rightleftharpoons$	CH_3OH
Initial	3.6945		x		–
Final	3.6945−y		x−2y		y

Here, y = 1.9704 (as calculated above)

and, $\quad P_T = 3.6945 – y + x – 2y + y$

$\Rightarrow \quad 8.5 = 3.6945 + x − 3.9408$

$\Rightarrow \quad 8.5 = x – 0.2463$

$\Rightarrow \quad x = 8.7463$

Thus, $(P_{CO})_{at\ eqm} = 3.6945−1.9704=1.7241$ atm

$(P_{H_2})_{at\ eqm} = x – 2y = 8.7463 − 2×1.9704 = 4.8055$ atm

Thus, $K_P = \frac{P_{CH_3OH}}{(P_{H_2})^2(P_{CO})} = \frac{1.9704}{(4.8655)^2(1.7241)}$

$\Rightarrow \quad K_P = 0.05\ atm^{-2}$

Now, $\quad K_P = K_C(RT)^{\Delta ng}$

$\Rightarrow \quad 0.05 = KCl(0.0821 \times 750)^{-2}$

$\Rightarrow \quad K_C = 0.05(0.0821 \times 750)^2$

$\Rightarrow \quad K_C = 189.575\ M^{-2}$

(ii) If no reaction takes place, total pressure will be the sum of initial pressure of CO and H_2,

$P_T = 3.6945 + x$

= 3.6945+8.7463

=12.4408 atm

27. At equilibrium, 0.33 gm I^2 will remain in the solution, rest 12.17 gm will react with I^- to give I_3^-.

Thus,

$$[I_2]_{eqm} = \frac{0.33}{254}$$

$$[I^-]_{eqm} = 0.1 - \frac{12.17}{254} = \frac{13.23}{254}$$

$$[I_3^-]_{eqm} = \frac{12.17}{254}$$

Thus, $K_C = \dfrac{[I_3^-]}{[I_2][I^-]}$

$$= \frac{\frac{12.17}{254}}{\frac{0.33}{254} \times \frac{13.23}{254}}$$

$K_C = 708.03\ M^{-1}$

On adding water (volume increases), the equilibrium will shift in backward direction.

28. Ne, because of greater Van der Waal's forces of attraction in Ne than that of He.