Q1. Calculate the equilibrium constant for the reaction,

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-,$$

if the equilibrium constant for the reaction,

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+,$$

is 5.55×10^{-10}.

Q2. The ionisation constant of HF, HCOOH and HCN at 298 K are 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9}, respectively. Calculate the ionisation constants of the corresponding conjugate bases.

Q3. Two moles of each reactant A and B are taken in a reaction flask. They react in the following manner:

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

If at equilibrium, the concentraction of C is tripled to that of B, calculate the equilibrium constant for the reaction.

Q4. If 10 mL 0.01 M H_2SO_4 is mixed with 10 mL 0.1 M $Ca(OH)_2$, then calculate the pH of the resultant solution.

Q5. The equilibrium constant K_p for the thermal dissociation of PCl_5 at 200°C is 1.6 atm. What is the pressure (in atm) at which it is 50% dissociated?

Q6. A mixture of 1.57 moles of N_2, 1.92 moles of H_2 and 8.13 moles of NH_3 is introduced into a 20 L reaction vessel at 500 K, At this temperature, the equilibrium constant, K_c for the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2. Predict the direction of the reaction.

Q7. (a) Four moles of PCl_5 are heated in a closed $4\,dm^3$ container to reach equilibrium at 400 K. At equilibrium, 50% of PCl_5 is dissociated. what is the value of K_c for the dissociation of PCl_5 into PCl_3 and Cl_2 at 400 K?

(b) What effect will be observed on the state of equilibrium by the addition of inert gas at constant pressure?

Q8. α-(D)-glucose $\rightleftharpoons \beta$-(D)-glucose. The equilibrium constant for the given reaction is 1.8. What is the percentage of α-(D)-glucose at equilibrium?

Q9. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of strong acid having pH = 6 and pH = 4, respectively.

Q10. A buffer solution contains 0.40 mol of ammonium hydroxide and 0.50 mol of ammonium chloride to make a buffer solution of 1 L. Calculate the pH of the resulting solution. (Dissociation constant of ammonium hydroxide at 25°C is 1.81×10^{-5})

Q11. The degree of ionisation of a 0.1 M bromoacetic acid is 0.1.32. Calculate the pH of the solution and pK_a of bromoacetic acid.

Q12. What is the pH of 0.001 M aniline solution? The ionisation constant of aniline is 4.27×10^{-10}. Calculate the degree of ionisation of aniline in the solution.

Q13. (a) Write a relation between ΔG and Q with usual meaning of each term.

(b) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$?

(c) Explain the effect of increase in pressure in terms of reaction quotient, Q for the reaction,

$$CO\,(g) + 3H_2\,(g) \rightleftharpoons CH_4\,(g) + H_2O\,(g)$$

Q14. Reaction between N_2 and O_2 takes place as follows:

$$2N_2\,(g) + O_2\,(g) \rightleftharpoons 2N_2O\,(g)$$
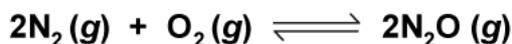
If a mixture of 0.482 mol N_2 and 0.933 mol O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-37}$, determine the composition of equilibrium mixture.

Q15. (a) A sample of HI (g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium?

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

(b) Write the conjugate acids for the following Bronsted bases:

NH_2^-, NH_3 and $HCOO^-$

$$\text{Base} + H^+ \rightleftharpoons \text{Conjugate acid.}$$
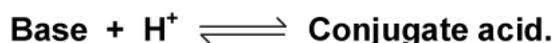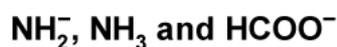
Q16. (a) The equilibrium constants for the reactions

$$SO_2\,g + \frac{1}{2}O_2\,g \rightleftharpoons SO_3\,g \quad \text{and} \quad 2SO_2\,g + O_2\,g \rightleftharpoons 2SO_3\,g$$

are K_1 and K_2, respectively. Derive the relation between K_1 and K_2.

(b) What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH? ($K_a = 1.74 \times 10^{-5}$)

Q17. At 1127 K and 1 atm pressure, a gaseous mixture of CO and CO_2 in equilibrium with solid carbon has 90.55% CO by mass.

$$C\,(s) + CO_2\,(g) \rightleftharpoons 2CO\,(g)$$
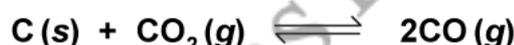
Calculate the value of K_c for this reaction at the above temperature.

Q18. Calculate the pressure of O_2 (in atm) over a sample of NiO at 25°C if $\Delta G° = 212$ kJ for the reaction:

$$NiO\,(s) \rightleftharpoons Ni\,(s) + \frac{1}{2}O_2\,(g)$$

Q19. (a) At 700 K, equilibrium constant for the reaction, $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$ is 54.8. If 0.5 mol L^{-1} of HI (g) is present in equilibrium at 700 K, what are the concentrations of $H_2\,(g)$ and $I_2\,(g)$, assuming that we initially started with HI (g) and allowed it to reach at equilibrium at 700 K?

(b) What will be the K_p for the reaction, $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$ at 1000 K? Given that K_C at 1000 K is 3.75×10^{-6}?

Q20. The concentration o sulphide ion in 0.1 M HCl solution saturated with hydrogen sulphide is 1.0×10^{-19} M. If 10 mL of this added to 5 mL of 0.04 M solution of the $FeSO_4$, $MnCl_2$, $ZnCl_2$ and $CdCl_2$, in which of these solutions, precipitation will take place?

(Given, K_{sp} of FeS $= 6.3 \times 10^{-18}$, $K_{sp} = MnS = 2.5 \times 10^{-13}$

K_{sp} of ZnS $= 1.6 \times 10^{-24}$, $K_{sp} = CdS = 8.0 \times 10^{-27}$).
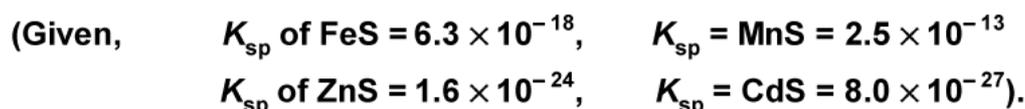
Q21. The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate the ionisation constant and pK_b.

Q22. (a) Equal volumes of 0.002 M solutions of sodium iodate and copper chromate are mixed together. Will it lead to precipitation of copper iodate?

(For copper iodate, $K_{sp} = 7.4 \times 10^{-8}$)

(b) The value of Kw is 9.55×10^{-14} at a a certain temperature. Calculate the pH of water at this temperature.

Q23. Nitric oxide reacts with Br_2 and gives nitrosyl bromide as per reaction given below:

$$2NO\,(g)\ +\ Br_2\,(g) \rightleftharpoons 2NOBr\,(g)$$
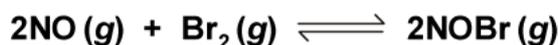
When 0.087 mol of NO and 0.0437 mol of Br_2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate the equilibrium amount of NO and Br_2.

Q24. The solubility product of Al $(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in gL^{-1} and pH of this solution. (Atomic mass of Al = 27u)

S1. NH_4^+ ion is the conjugate acid of NH_3.

$\therefore$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

$$K_b = \frac{[NH_4OH][H^+]}{[NH_4^+]} = 5.55 \times 10^{-10}$$

$\therefore$
$$K_b \cdot K_a = [H^+][OH^-] = 1 \times 10^{-14}$$

$\therefore$
$$K_b = \frac{1 \times 10^{-14}}{K_a} = \frac{1 \times 10^{-14}}{5.55 \times 10^{-4}} = 1.8 \times 10^{-5}$$

S2. Conjugate bases of HF, HCOOH and HCN are F– HCOO– and CN–, respectively.

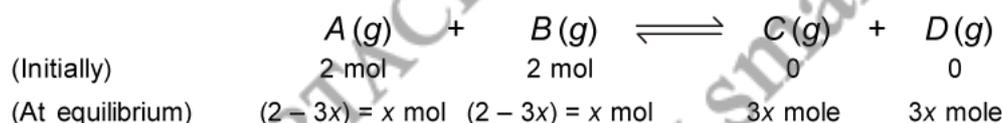If Ka is he ionisation constant of a weak acid (HA) and Kb is the ionisation constant of its conjugate base (A–), then

$$K_a K_b = K_w = 1 \times 10^{-14}$$

$$K_b(F^-) = \frac{K_w}{K_a(HF)} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11}$$

$$K_b(HCOO^-) = \frac{K_w}{K_a(HCOOH)} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.56 \times 10^{-11}$$

$$K_b(CN^-) = \frac{K_w}{K_a(HCN)} = \frac{1 \times 10^{-14}}{4.8 \times 10^{-9}} = 2.08 \times 10^{-6}.$$

S3.

	$A(g)$	+	$B(g)$	$\rightleftharpoons$	$C(g)$	+	$D(g)$
(Initially)	2 mol		2 mol		0		0
(At equilibrium)	$(2-3x) = x$ mol		$(2-3x) = x$ mol		$3x$ mole		$3x$ mole

$\Rightarrow$
$$2 - 3x = x$$

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

$$K_C = \frac{[C][D]}{[A][B]} = \frac{\left(\frac{3x}{V}\right)^2}{\left(\frac{2-3x}{V}\right)^2} = \frac{9 \times \left(\frac{1}{2}\right)^2}{4 - 12 \times \frac{1}{2} + 9 \times \left(\frac{1}{2}\right)^2}$$

$$K_C = 9.$$

S4. Number of moles of H_2SO_4 in 10 mL solution

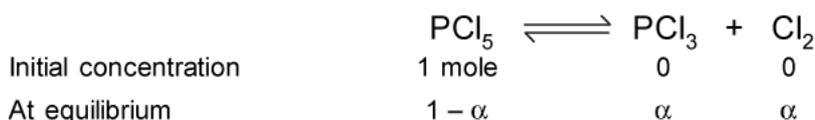$$= \frac{10 \times 0.01}{1000} = 0.0001 \text{ moles}$$

Number of moles of $Ca(OH)_2$ in 10 mL solution

$$= \frac{10 \times 0.01}{1000} = 0.0001 \text{ moles}$$

As both H_2SO_4 and $Ca(OH)_2$ are dibasic and present in equal quantity hence, they will completely neutralise each other

$\therefore$ pH = 7.0

S5. Let α is the degree of dissociation,

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial concentration	1 mole	0	0
At equilibrium	$1 - \alpha$	α	α

$\therefore$ Total number of moles at equilibrium

$$= 1 - \alpha + \alpha + \alpha = 1 + \alpha$$

If p is the total pressure at equilibrium, then partial pressures will be.

$$p_{PCl_3} = \frac{\alpha}{1+\alpha}p, \quad p_{Cl_2} = \frac{\alpha}{1+\alpha}p, \quad p_{PCl_5} = \frac{1-\alpha}{1+\alpha}p$$

$\therefore$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{\alpha}{1+\alpha}p\right) \times \left(\frac{\alpha}{1+\alpha}p\right)}{\left(\frac{1-\alpha}{1+\alpha}\right)p} = \frac{\alpha^2}{1-\alpha^2}p$$

As dissociation is 50% therefore, $\alpha = 0.5$ and $K_p = 1.6$ atm, thus,

$$1.6 = \frac{(0.5)^2}{1-(0.5)^2} \times p = 1.6 = \frac{0.25}{0.75} \times p$$

$\Rightarrow$

$$p = \frac{0.75 \times 1.6}{0.25} = 4.8 \text{ atm}$$

S6.

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

$$Q_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$
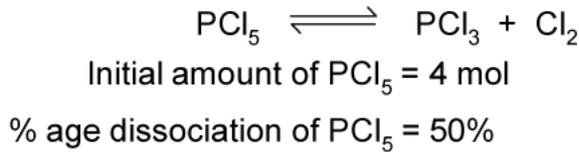
Given, $[NH_3] = \frac{8.13}{20} M = 0.4065 \text{ M}$

$$[N_2] = \frac{1.57}{20} M = 0.0785 \text{ M}, \quad [H_2] = \frac{1.92}{20} M = 0.096 \text{ M}$$

$$Q_C = \frac{[0.4065\ M]^2}{[0.0785\ M][0.096\ M]^3} = 2.379 \times 10^3\ M^{-2}$$

As $Q_C \neq K_C$, so the reaction mixture is not in equilibrium.

As $Q_C > K_C$, it indicates that the reaction will proceed in the direction of reactants.

S7. (a) PCl_5 dissociates as:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial amount of PCl_5 = 4 mol

% age dissociation of PCl_5 = 50%

∴ PCl_5 dissociated at equilibrium = $\dfrac{50}{100} \times 4 = 2$ mol

∴   Amounts of PCl_5, PCl_3 and Cl_2 at equilibrium will be

$$PCl_5 = 4 - 2 = 2\ \text{mol}$$

$$PCl_3 = 2\ \text{mol}$$

$$Cl_2 = 2\ \text{mol} \quad [\because\ 1\ \text{mole of } PCl_5\ \text{on dissociation gives}$$
$$1\ \text{mole of } PCl_3\ \text{and 1 mole of } Cl_2]$$

As the volume of the container is 4 dm3, therefore, the concentrations at equilibrium will be

$$[PCl_5] = \frac{2}{4}\ \text{mol dm}^{-3}, \quad [PCl_3] = \frac{2}{4}\ \text{mol dm}^{-3}, \quad [Cl_2] = \frac{2}{4}\ \text{mol dm}^{-3}$$

Applying the law of equilibrium to the dissociation equilibrium, we get

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{2/4 \times 2/4}{2/4} = 0.5\ \text{mol dm}^{-3}.$$

(b) Addition of inert gas at constant pressure shifts the equilibrium toards the larger under ofmoles, that is more dissociation of PCl_5 will occur.

S8. α-(D)-glucose $\rightleftharpoons$ β-(D)-glucose.

 1 – x

$$K_c = \frac{[\beta\text{-}(D)\text{-glucose}]}{[\alpha\text{-}(D)\text{-glucose}]} = \frac{x}{1-x} = 1.8$$

$$x = 1.8 - 1.8x \quad \Rightarrow \quad 2.8x = 1.8$$

$$x = \frac{1.8}{2.8} = 0.642$$

α-(D)-glucose = (1 – x) = 1 – 0.642 = 0.358

Percentage of α-(D)-glucose = 0.358 × 100 = 35.8%.

S9. pH of solution A = 6. Hence, $[H^+] = 10^{-6}\ \text{mol L}^{-1}$

pH of solution B = 4. Hence, $[H^+] = 10^{-4}\ \text{mol L}^{-1}$

On mixing 1 L of each solution, molar concentration of total H^+ is halved.

$$\text{Total } [H^+] = \frac{10^{-6} + 10^{-4}}{2} = \frac{10^{-4}[10^{-2} + 1]}{2}$$

$$[H^+] = \frac{1.01 \times 10^{-4}}{2} = 5.05 \times 10^{-5} \text{ mol L}^{-1}$$

$$[H^+] = 5.0 \times 10^{-5} \text{ mol L}^{-1}$$

$$pH = -\log [H^+]$$

$$pH = -\log (5.0 \times 10^{-5})$$

$$pH = -[\log 5 + (-5 \log 10)]$$

$$pH = 5 - \log 5 = 5 - 0.6990 = 4.3$$

Thus, the pH of resulting solution is 4.3.

S10.
$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\therefore \qquad pOH = pK_b + \log \frac{[NH_4Cl]}{[NH_4OH]}$$

$$[NH_4OH] = 0.40 \text{ mol L}^{-1}$$

$$[NH_4Cl] = 0.50 \text{ mol L}^{-1}$$

$$pK_b = -\log K_b = -\log (1.81 \times 10^{-5})$$

$$= 5 - 0.2577 = 4.7423$$

From Eq. (i)

$$pOH = 5.7423 + \log \frac{0.5}{0.4}$$

$$= 4.7423 + \log 1.25$$

$$= 4.7423 + 0.0969 = 4.8392$$

$$\therefore \qquad pH = 14 - pOH = 14 - 4.8392 = 9.1608 = 9.161.$$

S11.
$$CH_2(Br)COOH \rightleftharpoons CH_2(Br)COO^- + H^+$$

Initial conc.	C	0	0
Final conc.	$C - C\alpha$	$C\alpha$	$C\alpha$
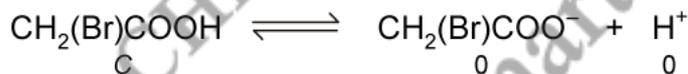
$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \qquad [\text{Where, } \alpha = \text{degree of dissociation}]$$
$$[\text{For weak acid, } (1-\alpha) = 1]$$

$$pK_a = -\log K_a \Rightarrow -\log (1.74 \times 10^{-3})$$
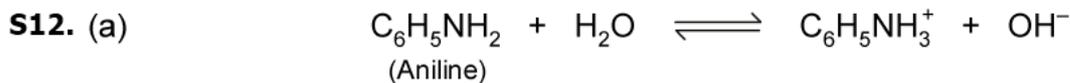
$$\Rightarrow \qquad = 3 - 0.2405 = 2.75$$

$$[H^+] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2} \text{ M}$$

$$pH = -\log [H^+]$$

$$\Rightarrow \qquad = -\log (1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$$

S12. (a)
$$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$$
(Aniline)

$$k_b = \frac{[C_6H_5NH_3^+][HO^-]}{[C_6H_5NH_2]}$$

As, $\quad [C_6H_5NH_3^+] = [OH^-]$

$\therefore \quad k_b = \frac{[HO^-]^2}{[C_6H_5NH_2]}$

$[OH^-] = \sqrt{k_b\,[C_6H_5NH_2]}$

$= \sqrt{(427 \times 10^{-10})(10^{-3})} = 6.534 \times 10^{-7}\,M$

$pOH = -\log(6.534 \times 10^{-7}) = 7 - 0.8152 = 6.18$

$\therefore \quad pH = 14 - 6.18 = 7.82$

(b) Also, $\quad C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$

Initial conc. $\qquad 0 \qquad\qquad\qquad\qquad 0 \qquad\quad 0$

At equilibrium, $\quad c - c\alpha \qquad\qquad\qquad c\alpha \qquad\quad c\alpha$
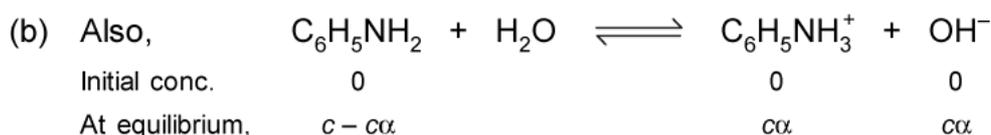
$$k_b = \frac{c\alpha \cdot c\alpha}{c\,(1-\alpha)} = \frac{c^2\alpha^2}{c\,(1-\alpha)} = \frac{c\alpha^2}{c\,(1-\alpha)}$$

As $\alpha <<< 1$, thus, $(1 - \alpha) \approx 1$

$\therefore \quad k_b = c\alpha^2$

$\Rightarrow \quad \alpha = \sqrt{k_b/c} = \sqrt{\dfrac{4.27 \times 10^{-10}}{10^{-3}}}$

$\alpha = 6.53 \times 10^{-4}$.

S13. (a) We know that, $\quad \Delta G = \Delta G° + RT \ln Q$

where, $\quad \Delta G$ = change in free energy as the reaction proceeds

$\Delta Q°$ = reaction quotient

R = gas constant

T = Temperature (in K)

(b) As, $\quad \Delta G° = -RT \ln K$

$\therefore \quad \Delta G = -RT \ln K + RT \ln Q \quad = \quad \Delta G = RT \ln \dfrac{Q}{K}$

If $Q < K$, ΔG will be negative, then reaction will proceed in the forward direction. If $Q = K$, $\Delta G = 0$, reaction is in equilibrium and there is not net raction occurs.

(c)
$$K_C = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

If pressure is increased, volume decreases. Let pressure be doubled, volume will be halved. Hence, molar concentrations will be doubled.
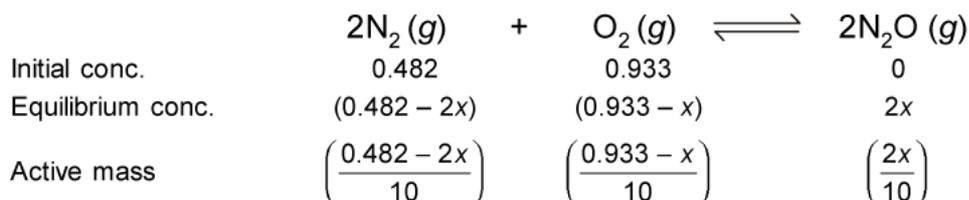
As, $$Q_C = \frac{(2[CH_4])(2[H_2O])}{(2[CO])(2[H_2])^3} = \frac{1}{4}\frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{1}{4}K_C$$

Thus, Q_C is less than K_C. Hence, to re-establish the equilibrium, Q_C will tend to increase, *i.e.*, equilibrium will shift in the forward direction.

S14. (a) Find the equilibrium concentration of reactants and products in the given equation be assuming $2x$ moles of N_2 and x moles of O_2 are disappeared and $2x$ moles of N_2O are appeared.

(b) Find the value of x and determine the concentration of reaction mixture.

Given reaction is

	$2N_2\,(g)$	+	$O_2\,(g)$	$\rightleftharpoons$	$2N_2O\,(g)$
Initial conc.	0.482		0.933		0
Equilibrium conc.	$(0.482 - 2x)$		$(0.933 - x)$		$2x$
Active mass	$\left(\dfrac{0.482 - 2x}{10}\right)$		$\left(\dfrac{0.933 - x}{10}\right)$		$\left(\dfrac{2x}{10}\right)$

$$K_C = 2.0 \times 10^{-37}$$

K_C is very-very small, which means negligible amounts of N_2 and O_2 react.

$$\therefore \qquad [N_2]_{eq} = \frac{0.482 - 2x}{10} = \frac{0.482}{10} = 0.0482$$

Similarly, $$[O_2]_{eq} = \frac{0.933 - x}{10} = \frac{0.933}{10} = 0.0933$$

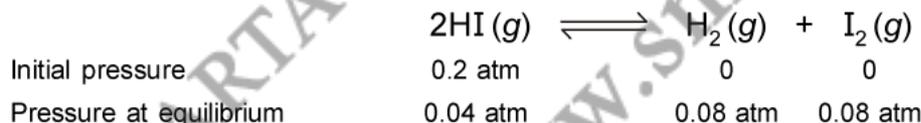$$\therefore \qquad K_C = \frac{[N_2O]^2}{[N_2]^2[O_2]}$$

$$K_C = 2.0 \times 10^{-37} = \frac{[4x^2/100]}{(0.0482)^2(0.0933)}$$

or $$x^2 = 10.837 \times 10^{-40} \quad \text{or} \quad x = 3.292 \times 10^{-20}$$

$$[N_2O] = \frac{2x}{10} = \frac{2 \times 3.292 \times 10^{-20}}{10} = 6.58 \times 10^{-21} \text{ mol L}^{-1}.$$

S15. (a)
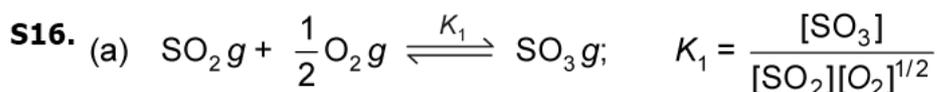
	$2HI\,(g)$	$\rightleftharpoons$	$H_2\,(g)$	+	$I_2\,(g)$
Initial pressure	0.2 atm		0		0
Pressure at equilibrium	0.04 atm		0.08 atm		0.08 atm

(Decrease in pressure of HI = 0.2 – 0.04 = 0.16 atm, so equilibrium pressure of $H_2 = \dfrac{0.16}{2}$ = 0.08 atm, and of $I_2 = \dfrac{0.16}{2}$ = 0.08 atm as two moles of HI on dissociation give 1 mol of H_2 and 1 mol of I_2)

$$K_p = \frac{p_{H_2} \times p_{I_2}}{p_{HI}^2} = \frac{0.08 \times 0.08}{(0.04)^2} = 4.0$$

(b) The conjugate acid should have one extra proton in each case and therefore, the corresponding conjugate acids are NH_3, NH_4^+ and $HCOOH$, respectively.

S16. (a) $SO_2\,g + \dfrac{1}{2}O_2\,g \xrightleftharpoons{K_1} SO_3\,g;$ $\quad K_1 = \dfrac{[SO_3]}{[SO_2][O_2]^{1/2}}$

$2SO_2\,g + O_2\,g \xrightleftharpoons{K_2} 2SO_3\,g;$ $\quad K_1 = \dfrac{[SO_3]^2}{[SO_2]^2\,[O_2]}$

Hence $\qquad\qquad\qquad\qquad K_1^2 = K_2$

(b) Given that, $\qquad\qquad K_a = 1.74 \times 10^{-5}$

Concentration of $CH_3COOH = 0.01\ \text{mol dm}^{-3}$

$$[H^+] = \sqrt{K_a \cdot C} = \sqrt{1.74 \times 10^{-5} \times 0.01} = 4.17 \times 10^{-4}$$
$$pH = -\log[H^+] = -\log[4.17 \times 10^{-4}] = 3.4$$

S17. Thinking process:

(a) Since, the percentage by mass is given, so calculate the number of moles of CO and CO_2 to calculate their mole fractions.

(b) Then, calculate the partial pressures of CO and CO_2 by using the formula $p_A = \chi_A \cdot p_{total}$.

(c) Calculate the value K_p by using the formula, $K_p = \dfrac{p_{CO}^2}{p_{CO_2}}$ and K_C by using the formula, $K_p = K_C(RT)^{\Delta n_g}$.

90.55% CO by mass means 90.55 g CO and 9.45 g CO_2 are present in 100 g mixture.

Number of moles of CO, $\qquad n_{CO} = \dfrac{90.55}{28} = 3.234\ \text{mol}$ (Molar mass of CO = 28 g mol^{-1})
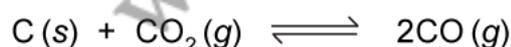
Number of moles of CO_2, $\qquad n_{CO_2} = \dfrac{9.45}{44} = 0.215\ \text{mol}$ (Molar mass of CO_2 = 44 g mol^{-1})

Partial pressure of CO, $\qquad p_{CO} = \chi_{CO} \cdot p_{total}$ $\left(\chi_{CO} = \dfrac{3.234}{3.234 + 0.215} = 0.938\right)$

$p_{CO} = 0.938 \times 1\ \text{atm} = 0.938\ \text{atm}$

Similarly, $\qquad\qquad p_{CO_2} = \chi_{CO_2} \cdot p_{total}$ $\left(\chi_{CO_2} = \dfrac{0.215}{3.234 + 0.215} = 0.062\right)$

$p_{CO_2} = 0.062 \times 1\ \text{atm} = 0.062\ \text{atm}$
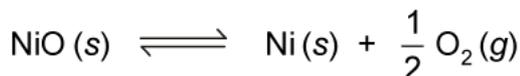
$$C\,(s) + CO_2\,(g) \rightleftharpoons 2CO\,(g)$$

Applying law of chemical equilibrium,

$$K_p = \dfrac{p_{CO}^2}{p_{CO_2}} = 14.19, \quad \Delta n_g = 2 - 1 = 1$$

As,
$$K_p = K_C(RT)^{\Delta n_g}; \qquad K_C = \frac{K_p}{RT} \qquad\qquad [\because \Delta n_g = 1]$$

$\therefore$
$$K_C = \frac{14.19}{0.0821 \times 1127} = 0.15336 \approx 0.153.$$

S18.
$$NiO\,(s) \rightleftharpoons Ni\,(s) + \frac{1}{2}O_2\,(g)$$

$$K_p = p_{O_2}^{1/2}$$
$$\Delta G^\circ = 213 \text{ kJ} = 212000 \text{ J}$$

$$\Delta G = -2.303\,RT\log K_p$$
$$212000 = -2.303 \times 8.314 \times 298 \log K_p$$
$$\log K_p = -37.155$$
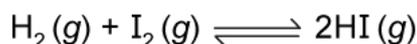$$K_p = 7 \times 10^{-38}$$

$$\sqrt{p_{O_2}} = 7 \times 10^{-38}$$
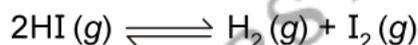
$$p_{O_2} = 4.9 \times 10^{-75} \text{ atm}$$

S19. (a) As we started the reaction with HI, so equilibrium constant for the dissoclation of HI ($2HI \rightleftharpoons H_2 + I_2$) is required. Thus, calculate the equilibrium constant for backward reaction

$$(K_c')\left((K_c') = \frac{1}{K_c}\right)$$

and then, calculata $[H_2]$ and $[I_2]$.
$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$
$$K_C = 54.8$$
$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

$$K_C' = \frac{1}{K_c} = \frac{1}{54.8}$$

$$K_C' = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{54.8}$$

Given, $[HI] = 0.5 \text{ mol L}^{-1}$

According to equation, $[H_2] = [I_2] = [x] \quad \Rightarrow \quad \frac{x \cdot x}{[0.5]^2} = \frac{1}{54.8}$

$$x_2 = \frac{[0.5]^2}{54.8} = 0.00456 \quad \Rightarrow \quad x = 0.0675\,M$$

$$[H_2] = [I_2] = x = 0.0675\,M$$

(b)
$$\Delta n_g = 3 - 2 = 1 \quad \Rightarrow \quad K_p = K_C(RT)^{\Delta n}$$
$\therefore$
$$K_p = K_C(RT)$$
$\Rightarrow$
$$K_p = 3.75 \times 10^{-6} \times 0.0831 \times 1000$$
$$= 3.11 \times 10^{-4}.$$

S20. For precipitation, ionic product > solubility product, so ionic product of each salt is calculated and compared it with solubility product.

$$[S^{2-}] = 1 \times 10^{-19} \, M$$

10 mL of S^{2-} is mixed with 5 mL of 0.04 M solution of different solubles, so that final volume of solution is 15 mL.

$$[S^{2-}]_{mix} = \frac{10 \times 10^{-19}}{15} = 6.67 \times 10^{-20} \, M$$

$$[M^{2+}] = \frac{5 \times 0.04}{15} = 1.33 \times 10^{-2} \, M$$

where,
$$[M^{2+}] = Fe^{2+}, \ Mn^{2+}, \ Zn^{2+} \ or \ Cd^{2+}$$

$$[M^{2+}][S^{2-}] = 1.33 \times 10^{-2} \times 6.67 \times 10^{-20}$$

i.e., ionic product of $[M^{2+}][S^{2-}] = 8.87 \times 10^{-22}$

Since, ionic product of $[M^{2+}][S^{2-}] > K_{sp}$ of ZnS and CdS.

So, these ($CdCl_2$ and $ZnCl_2$) are precipitated as CdS and ZnS.

S21.
$$Codeine + H_2O \rightleftharpoons CodH^+ + OH^-$$

Here, pH = 9.95

= pOH = 14 − 9.95 = 4.05 $\Rightarrow$ $-\log[OH^-] = 4.05$

or $[OH^-] = -antilog \, (4.05) = 8.913 \times 10^{-5} \, M$

$$K_b = \frac{[CodH^+][OH^-]}{[Cod]} = \frac{[OH^-]^2}{[Cod]} = \frac{(8.913 \times 10^{-5})^2}{(5 \times 10^{-3})} = 1.588 \times 10^{-6}$$

$$pK_b = -\log(1.588 \times 10^{-6}) = 6 - 0.1987 = 5.8$$

S22. (a)
$$2NaIO_3 + CuCrO_4 \longrightarrow Na_2CrO_4 + Cu(IO_3)_3$$

After mixing, $[NaIO_3] = [O_3^-] = \dfrac{2 \times 10^{-3}}{2} = 10^{-3} \, M$

$$[CuCrO_4] = [Cu^{2+}] = \frac{2 \times 10^{-3}}{2} = 10^{-3} \, M$$

Ionic product of $Cu(IO_3)_2 = [Cu^{2+}][IO_3]^2$
$$= (10^{-3})(10^{-3}) = 10^{-9}$$

As ionic product becomes less than K_{sp}, then no precipitation takes place.

(b) Given, $K_w = 9.55 \times 10^{-14}$

For water, $[H_3O^+] = [OH^-]$

$$K_w = [H_3O^+][OH^-]$$

or
$$K_w = [H_3O^+][H_3O^+]$$
$$K_w = [H_3O^+]^2$$

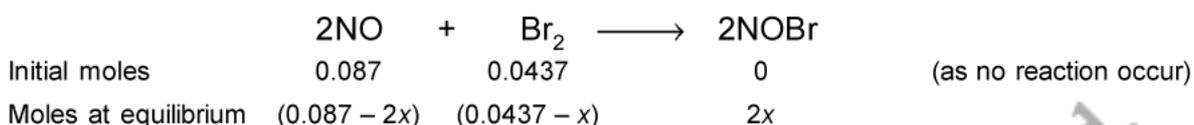$\Rightarrow$
$$[H_3O^+] = \sqrt{K_w} = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7} \text{ M}$$

$\therefore$
$$\text{pH} = -\log[H_3O^+] = -\log(3.09 \times 10^{-7})$$
$$= -(\log 3.09 + \log 10^{-7}) = -(0.49 - 7) = 6.51.$$

S23. We can calculate amount of NO and Br_2 in following steps:

Step I: Balanced reaction and the expected equilibrium amounts of reactants and products can be written as:

	2NO	+	Br_2	$\longrightarrow$	2NOBr	
Initial moles	0.087		0.0437		0	(as no reaction occur)
Moles at equilibrium	$(0.087 - 2x)$		$(0.0437 - x)$		$2x$	

[Here we multiply the value of x with the stoichiometric coefficient of the molecule.]

Step II: Comparision with the given information

Given, equilibrium moles of NOBr = 0.0518

$\therefore$
$$2x = 0.0518 \quad \Rightarrow \quad x = \frac{0.0518}{2} = 0.0259$$

Step III: Putting the value of x to obtain equilibrium concentration of other species, we get

Moles of NO at equilibrium = $(0.087 - 2x) = 0.087 - 0.0518 = 0.0252$

Moles of Br_2 at equilibrium = $(0.0437 - x) = 0.0437 - 0.0259 = 0.0178$

S24. Let S be the solubility of $Al(OH)_3$.
$$Al(OH)_3 \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$$
$$K_{sp} = [Al^{3+}][OH^-] = (S)(3S)^3 = 27S^4$$

$$S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{11}}{27} = 1 \times 10^{-12}$$

$$S = 1 \times 10^{-3} \text{ mol L}^{-1}$$

Molar mass of $Al(OH)_3$ is 78 g.

Therefore, solubility of $Al(OH)_3$ in gL^{-1}

$$= 1 \times 10^{-3} \times 78 \text{ gL}^{-1} = 78 \times 10^{-3} \text{ gL}^{-1}$$
$$= 7.8 \times 10^{-2} \text{ gL}^{-1}$$

Also, for calculating pH of the solution

We have,
$$[OH^-] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$$
$$\text{pOH} = 3 - \log 3 \qquad \qquad \text{... (i)}$$

$$pH = 14 - pOH \qquad \ldots (ii)$$

From Eq. (i), we get $\quad 11 + \log 3 = 11.4771.$