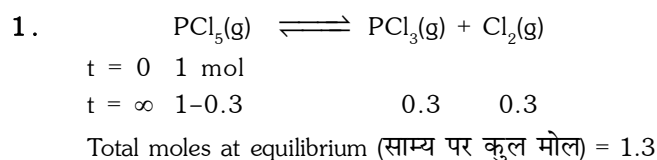


UNIT # 07 (PART - I)

CHEMICAL EQUILIBRIUM

EXERCISE # 1

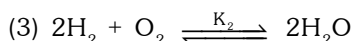
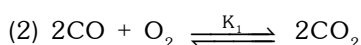
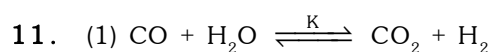


2. $K_c = \left[\frac{1}{1/8} \right]^2 = 64$

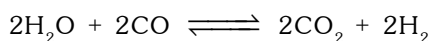
4. \therefore reaction is exothermic so an increasing temperature it shift to backward (अभिक्रिया उष्माक्षेपी है अतः ताप बढ़ने पर यह पश्च दिशा में जायेगी।)

7. $K_p = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{8^2}{4} = 16$

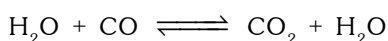
8. Greater value of K_c more is equilibrium favourable to products.
 (K_c का अधिक मान होने पर साम्य उत्पाद की ओर होगा।)



By subtraction (2) - (3) we get :

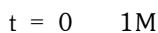
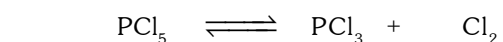


Dividing by (2) ;

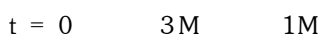


$K = \left(\frac{K_1}{K_2} \right)^{1/2}$

12. Changing concentration does not change K_c (सान्द्रता परिवर्तन पर K_c परिवर्तित नहीं होता है)

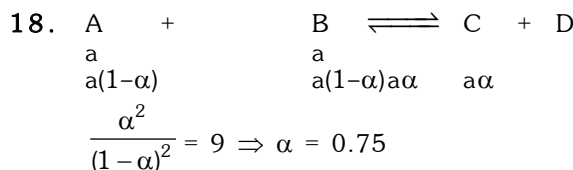


$K_c = \frac{0.4 \times 0.4}{0.6} = 0.267$

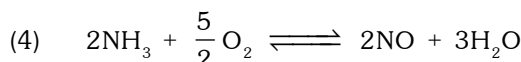
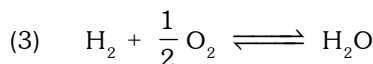
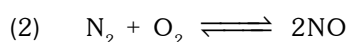
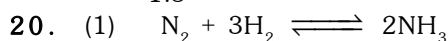


$K_c = \frac{\left(\frac{2}{3}\right)^2}{\left(\frac{8}{3}\right)\left(\frac{2}{3}\right)} = \frac{1}{4}$

15. Pure solids of added do not change state of equilibrium.
 (मिलाये गये ठोस साम्यवस्था को परिवर्तित नहीं करते हैं)

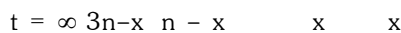
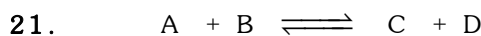


19. $K_c = \frac{1.5^2}{1.5^2} = 1$



(5) = (2) + 3(3) - (1)

i.e. $K_4 = \frac{K_2 K_3^3}{K_1}$

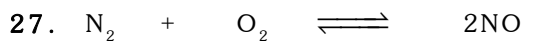
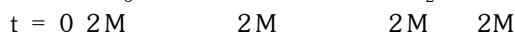


$n-x = x \rightarrow x = \frac{n}{2}$ i.e. $[D]_{\text{eq.}} = \frac{n}{2}$

22. $K_c = \frac{K_1}{K_2} = \frac{b+x}{\alpha-x}$

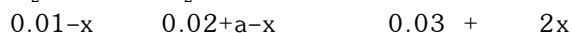
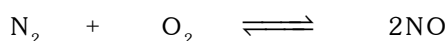
23. $K_p = K_c (RT)^1$ $K_c = \frac{0.03}{(0.0821 \cdot 700)^1}$

25. $K_c = \frac{0.33}{0.67} \cdot \frac{0.33}{0.67} = \frac{1}{4}$



$K_c = \frac{0.03^2}{0.01 \cdot 0.02} = 4.5$

Let a moles of O_2 be added (माना O_2 के a मोल मिलाये गये हैं)

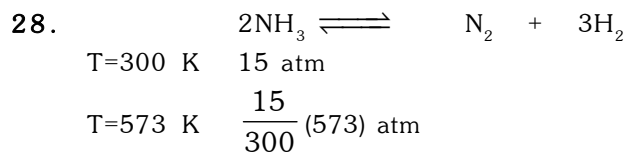


$0.03+2x = 0.04$

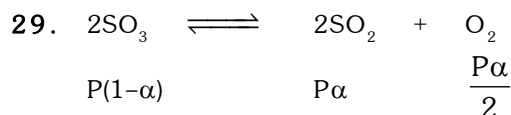
$\Rightarrow x = 0.005$

i.e., $4.5 = \frac{(0.04)^2}{(0.015+a)(0.005)}$

Moles of O_2
 added = a $100 = \frac{101}{18}$



$$\frac{15}{300} (573) [1 + \alpha] = 40.11 \Rightarrow \alpha = 0.4$$



$$P \left[1 + \frac{\alpha}{2} \right] = P_0$$

$$K_p = \frac{(P^2 \alpha^2) \left(P \frac{\alpha}{2} \right)}{P^2 (1-\alpha)^2} = \frac{P_0 \alpha^3}{(2+\alpha)(1-\alpha)^2}$$

32. By adding inert gas at constant pressure reaction shifts to increase number of gaseous molecules \therefore to left.

(नियत दाब पर अक्रिय गैस मिलाने पर अभिक्रिया गैसीय अणु की बढ़ी हुयी संख्या की ओर प्रतिस्थापित होती हैं)

37. Slope of plot (ग्राफ का ढाल) $= \frac{-\Delta H^\circ}{2.303R} = 1$

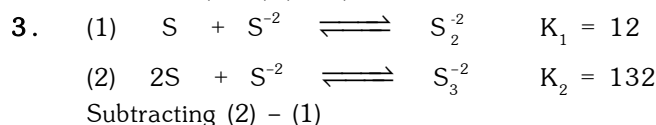
$$\Rightarrow \Delta H = -2.303 \times 2 = -4.606 \text{ cal.}$$

CHEMICAL EQUILIBRIUM

EXERCISE # 2

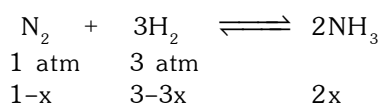
1. Greater value of K_c more is extent (K_c का मान अधिक तो मात्रा अधिक)
 (I) $K_c = 0.01$, (II) $K_c = 1$, (III) $K_c = 10^4$

2. $K_c = 9 = \frac{(2/V)^2}{(2/V)^3 (2/V)}$; $V = 6 \text{ L}$



$$\Rightarrow \text{S} + \text{S}_2^{-2} \rightleftharpoons \text{S}_3^{-2} \quad K_3 = \frac{132}{12} = 11$$

4. $K_p = K_c (0.0821 T)^1$
 $T = \frac{1}{0.0821} = 12 - 19 \text{ K}$

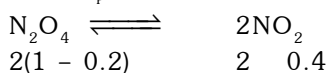


$$\Rightarrow 4 - 2x = 3 \Rightarrow x = \frac{1}{2}$$

$$K_p = \frac{(1)^2}{(1/2)(3/2)^3}$$

6. For dissociation of NH_3 (NH_3 के वियोजन के लिए)

$$K_p^1 = \frac{1}{K_p} = 0.5 \quad 1.5^3$$



Total pressure (कुल दाब) $= 1.6 + 0.8 = 2.4 \text{ atm}$

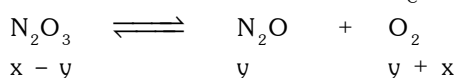
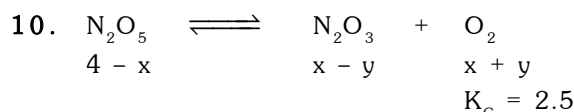
7. $\frac{(VD)_i}{(VD)_f} = \frac{n_i}{n_f}$



$t = 0 \quad a$

$t = \infty \quad a(1-\alpha) \quad 2a\alpha$

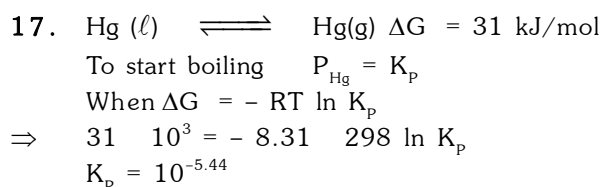
$$\frac{46}{30} = \frac{a(1+\alpha)}{a} \Rightarrow \alpha = 0.533$$



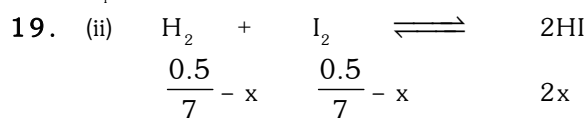
$$x+y = 2.5$$

$$\frac{(x+y)(x-y)}{4-x} = 2.5$$

solving $y = 0.334 \text{ M}$



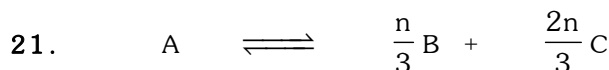
18. $\Delta_r G = -33 \times 10^3 + 8.314 \times 298 \ln \frac{(0.02)^2}{3^3 \times 1}$
 $\Delta_r G = -60.5 \text{ kJ/mol}$



$$\frac{(2x)^2}{\left(\frac{0.5}{7} - x \right)^2} = 49$$

Total pressure (कुल दाब) $P_T = \frac{0.5}{7} \times 0.0821 \times 700$

(iv) Partial pressure (आंशिक दाब) of
 $\text{HI} = (2x) (0.0821) \times 700 = 6.385 \text{ atm}$



$t=0 \quad a$

$t=\infty \quad a(1-\alpha) \quad a\alpha(n/3) \quad a\alpha(2n/3)$

$$\frac{D}{d} = \frac{a[1-\alpha+n\alpha]}{a} \quad \alpha = \frac{D-d}{d(n-1)}$$

23. Adding inert gas at constant volume does not affect state of equilibrium
(नियत आयतन पर अक्रिय गैस के योग पर साम्यावस्था प्रभावित नहीं होती है)

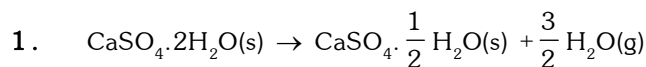
26. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ as the reaction is exothermic so more NH_3 will be obtained at lower temperature.

($N_2 + 3H_2 \rightleftharpoons 2NH_3$ क्योंकि अभिक्रिया उष्माक्षेपी है अतः निम्न ताप पर अधिक NH_3 प्राप्त होगी।)

CHEMICAL EQUILIBRIUM

EXERCISE # 3

COMPREHENSION # 1



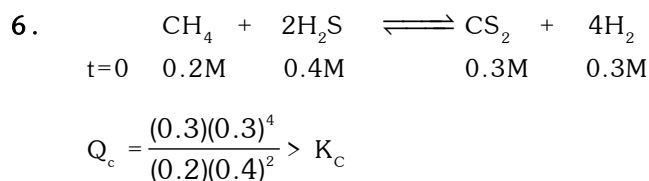
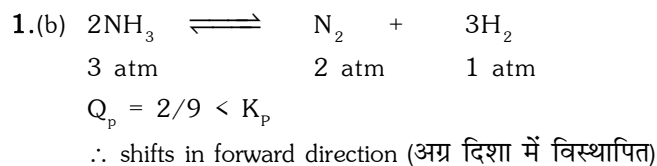
$$\Delta H = \frac{3}{2} (-241.8) + (-1575) - (-2021)$$

$$\text{For 1 kg } CaSO_4 \cdot 2H_2O = \frac{\Delta H}{172} \quad 100 = 484 \text{ kJ}$$

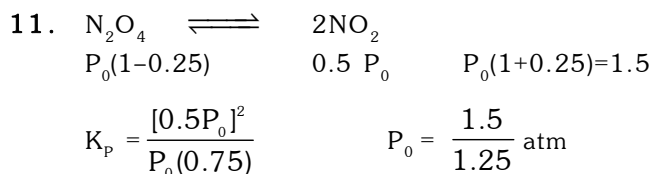
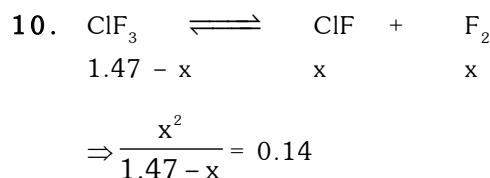
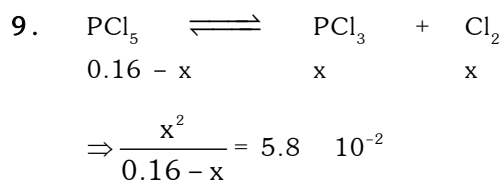
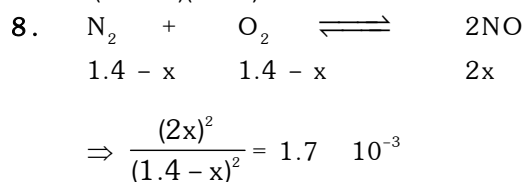
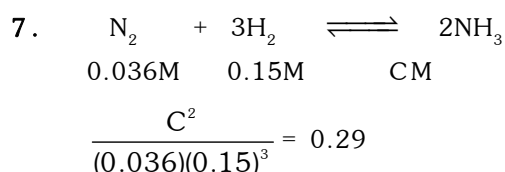
2. $\Delta S = \frac{3}{2} (188.6) + 130.5 - 194$
 $\Delta G = \Delta H - (298) \Delta S = -8.314 \quad 298 \ln (P_{H_2O})^{3/2}$
 $\Rightarrow P_{H_2O} = 8.1 \quad 10^{-3} \text{ bar}$

CHEMICAL EQUILIBRIUM

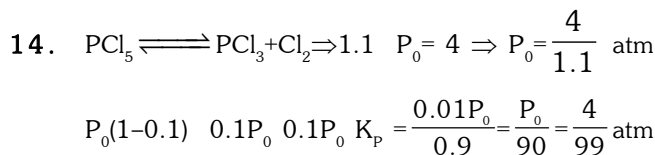
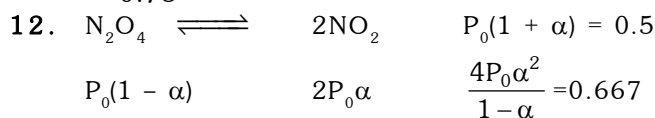
EXERCISE # 4[A]



\therefore shifts backward (पश्च विस्थापित)



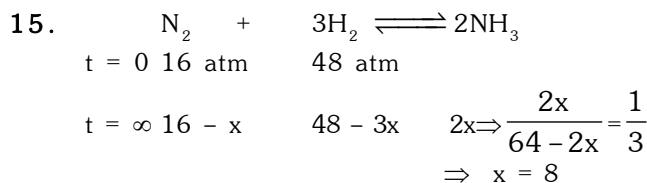
$$= \frac{0.25}{0.75} \quad \frac{1.5}{1.25}$$



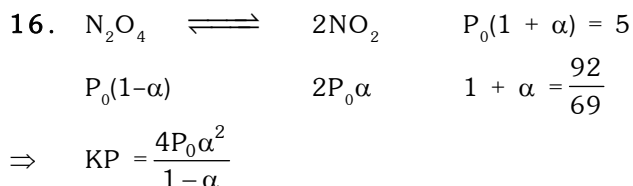
For 20% dissociation (20% वियोजन के लिए)

$$P_0^1 (1 - 0.2) \quad 0.2P_0^1 \quad 0.2P_0^1 \Rightarrow 1.2 P_0^1 = P_T$$

$$\frac{0.04P_0^1}{0.8} = \frac{4}{99}$$



$$K_p = \frac{16^2}{8(24)^3}$$



$$17. \quad \text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$$

$$t=0 \quad a \text{ mol} \quad \frac{a(1+\alpha)}{a} = \frac{46}{30} \Rightarrow \alpha = \frac{8}{15}$$

$$t=\infty \quad a(1-\alpha) \quad 2a\alpha$$

$$19. \quad \text{NH}_2\text{COONH}_4(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$$

Initial equilibrium $2P \quad P$

$\Rightarrow K_p = 4P^3, P_T = 3P$

Final equilibrium $3P \quad P^1$

$$\Rightarrow (3P)^2 P^1 = 4P^3 \Rightarrow P^1 = \frac{4P}{9}$$

$$\text{Ratio (अनुपात)} \quad \frac{P_{T^1}}{P_T} = \frac{31}{27} \quad P_{T^1} = 3P + \frac{4P}{9} = \frac{31P}{9}$$

$$20. \quad \text{Let } n \text{ moles each of } \text{CO}_2 \text{ \& } \text{CaO} \text{ be formed}$$

(माना CO_2 व CaO प्रत्येक के n मोल बने हैं)

$$0.04 \quad 0.821 = n(0.0821) \quad (1000)$$

$$21. \quad (P_{\text{H}_2\text{O}})^6 = 6.4 \quad 10^{85}$$

$$22. \quad \text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$

$t = 0 \quad 0.2 \text{ mol}$

$t = \infty \quad 0.2 \quad (1-0.75)0.2 \quad 0.75 \quad 0.2 \quad 0.75$

$$K_p = P_{\text{CO}_2} \Rightarrow K_p(15) = (0.2 - 0.75) (0.0821) (1000)$$

$$30. \quad \text{At equilibrium} \quad [A] = 0.3 \text{ M} [B] = 0.6 \text{ M}$$

Initially $[A] = 0.6 \text{ M}$

$$(i) \quad \text{A} \rightleftharpoons n\text{B}$$

$t = 0 \quad 0.6$

$t = \infty \quad 0.3 \quad 0.6 = 0.3n \Rightarrow n = 2$

$$(ii) \quad K_c = \frac{0.6^2}{0.3}$$

$$(iii) \quad \text{Initial rate} = \frac{\Delta[A]}{\Delta t} = \frac{0.6 - 0.3}{1} = 0.1 \text{ M hr}^{-1}$$

$$32. \quad \text{At } 300 \text{ K} \quad ; \quad K_1 = \frac{2 \times 10^{-2}}{4 \times 10^{-3}} = 5$$

$$\text{At } 400 \text{ K} \quad ; \quad K_2 = \frac{4 \times 10^{-2}}{16 \times 10^{-4}} = 25$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{400} \right]$$

$$36. \quad K_p = 0.313 \text{ atm} \quad K_c = \frac{0.313}{(0.0821 \times 298)^1}$$

$$39. \quad \text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$$

$1.2 - x \quad x \quad x$

$$\frac{x^2}{1.2 - x} = 3 \quad 10^{-2}$$

$$41. \quad \alpha^- \rightleftharpoons \beta^-$$

$a(1 - 0.6) \quad 0.6 a$

$$K_c = \frac{0.6}{0.4} = 1.5$$

$$\Delta G = -8.314 \quad 298 \ln 1.5 \text{ J/mol}$$

$$43. \quad 0$$

$$44. \quad \text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$$

$P_0(1-\alpha) \quad P_0\alpha \quad P_0\alpha$

$$1.78 = \frac{P_0\alpha^2}{1-\alpha}$$

$$P_0(1 + \alpha) = 1$$

$$M_{\text{avg}} = \frac{208.5}{1 + \alpha}$$

$$d_{\text{mix}} = \frac{\left[1 \times \frac{208.5}{1 + \alpha} \right]}{0.0821 \times 523}$$

$$46. \quad n\text{A} \rightleftharpoons \text{A}_n$$

$1 - x \quad \frac{x}{n}$

$$\frac{PV}{RT} = 1 - x + \frac{x}{n}$$

$$K_c = \frac{\frac{x}{nv}}{\left[\frac{1-x}{V} \right]^n} = \frac{xV^{n-1}}{n(1-x)^n}$$

$$K_c \approx \frac{xV^{n-1}}{n(1-nx)}$$

$$\Rightarrow nK_c - nK_c x = xV^{n-1}$$

$$\Rightarrow x = \frac{nK_c}{V^{n-1}}$$

$$\text{i.e.} \quad \frac{PV}{RT} = 1 - \frac{nK_c}{V^{n-1}} + \frac{K_c}{V^{n-1}}$$

$$\frac{PV}{RT} = \left[1 - \frac{(n-1)K_c}{V^{n-1}} \right]$$

$$47. \quad \text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$$

$1 - x \quad x \quad x - y$

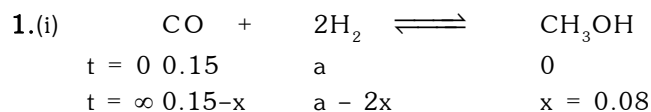
$$\text{C}(\text{g}) \rightleftharpoons \text{D}(\text{g}) + \text{E}(\text{g})$$

$x - y \quad y \quad y$

$$1 - x + x + x - y + 2y = 2$$

$$\Rightarrow x + y = 1$$

$$\frac{x-y}{x} = \frac{1}{5} \Rightarrow 5x - 5y = x; \quad \frac{x}{y} = \frac{5}{4}$$



Total moles finally (अन्त में कुल मोल)

$$= 0.15 + a - 2(0.08)$$

$$= a - 0.01$$

$$\Rightarrow 8.5 (2.5) = (a - 0.01) (0.0821) (750)$$

$$a = 0.355$$

Hence at equilibrium (अतः साम्य पर), $[\text{CO}] = 0.07\text{M}$,

$[\text{H}_2] = 0.195\text{ M}$ $[\text{CH}_3\text{OH}] = 0.08$

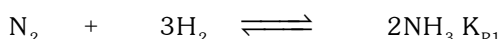
$$\therefore K_c = \frac{0.08 / 2.5}{\left(\frac{0.195}{2.5}\right)^2 \left(\frac{0.07}{2.5}\right)}$$

(ii) Total moles (कुल मोल) = 0.15 + 0.355 = 0.505

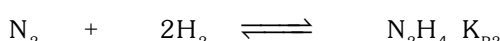
$$P(2.5) = (0.505) (0.0821) 750$$

$$P = 12.43\text{ atm}$$

2. Let initial pressure of N_2 be 9P and of H_2 be 13P (माना N_2 का प्रारम्भिक दाब 9P व H_2 का 13P है।)



$$9P - X - Y \quad 13P - 3X - 2Y \quad 2X$$



$$9P - X - Y \quad 13P - 3X - 2Y \quad Y$$

$$9P - X - Y + 13P - 3X - 2Y + 2X + Y = 7P_0 \quad \dots (1)$$

$$2X = P_0 \quad \dots (2)$$

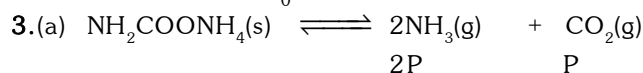
$$13P - 3X - 2Y = 2P_0 \quad \dots (3)$$

$$\text{Solving } x = P_0/2 \quad Y = 3P_0/2 \quad P = P_0/2$$

$$K_{P1} = \frac{(P_0)^2}{(4.5P_0 - 0.5P_0 - 1.5P_0)(6.5P_0 - 1.5P_0 - 3P_0)^3}$$

$$= \frac{P_0^2}{(2.5P_0)(8P_0^3)} = \frac{1}{20P_0^2}$$

$$\text{and } K_{P2} = \frac{3}{20P_0^2}$$



$$3P = 0.116$$

$$K_p = 4P^3 = 4\left(\frac{0.116}{3}\right)^3$$

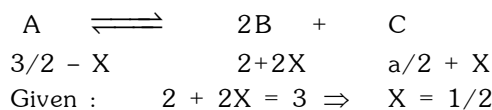
4. Let equilibrium concentration of C be a M.

(माना C की साम्य सांद्रता a M है)

$$K_c = \frac{(4^2)(a)}{3} = \frac{16a}{3} \quad \dots (1)$$

on doubling volume all concentration are halved and equilibrium shifts forward

(आयतन दुगुना करने पर सभी सांद्रता आधी हो जाती है तथा समय पीछे विस्थापित हो जाता है)



$$K_c = \frac{(3)^2 \left(\frac{a}{2} + \frac{1}{2}\right)}{\left(\frac{3}{2} - \frac{1}{2}\right)^2} \quad \dots (2)$$

$$\frac{16a}{3} = \frac{9(a+1)}{2}$$

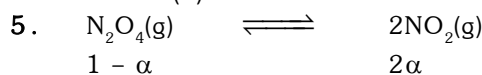
From (1) & (2),

$$\Rightarrow 32a = 27a + 27$$

$$\Rightarrow 5a = 27$$

$$a = 5.4$$

$$K_c = \frac{9(3.2)}{(1)} = 28.8$$



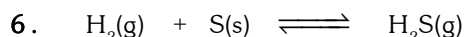
Average molar mass, M_{average} ($M_{\text{औसत}}$ औसत मोलर

$$\text{द्रव्यमान}) = \frac{1.8 \quad 0.0821 \quad 346}{1} = 51.1$$

$$\frac{92}{51.1} = 1 + \alpha \Rightarrow \alpha = 0.8$$

$$P_{\text{N}_2\text{O}_4} = \left(\frac{1-\alpha}{1+\alpha}\right) (I) \quad P_{\text{N}_2} = \left(\frac{2\alpha}{1+\alpha}\right) (II)$$

$$K_p = \frac{4\alpha^2/(1+\alpha)^2}{1-\alpha/1+\alpha} = \frac{4\alpha^2}{1-\alpha^2} ; K_c = K_p(RT)^{-1}$$

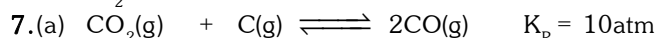


$$0.2 - x \quad x$$

$$K_p = K_c = 6.8 \quad 10^{-2}$$

$$\frac{x}{0.2 - x} = 6.8 \quad 10^{-2} \Rightarrow x = 0.012$$

$$P_{\text{H}_2\text{S}} = (x) RT = 0.012 (0.0821) (363)$$



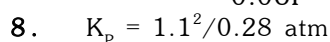
$P_0 - x$	$2x$
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$$\frac{4x^2}{P_0 - x} = 10 \text{ \& } P_0 + x = 4$$

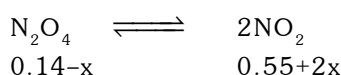
(b) Let total pressure be P atm (माना कुल दाब P atm है)

$$P_{\text{CO}_2} = 0.06 P \quad P_{\text{CO}_2} = 0.94 P$$

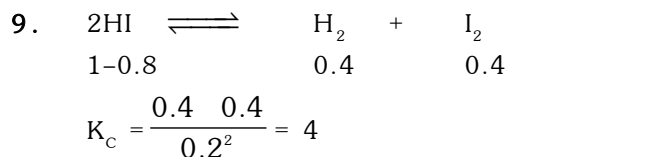
$$K_p = 10 = \frac{(0.94P)^2}{0.06P} \Rightarrow P = 0.08\text{ atm}$$



On doubling volume (आयतन दुगुना करने पर)

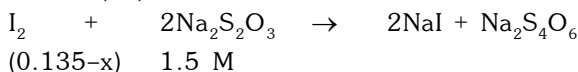


$$\frac{(0.55 + 2x)^2}{0.14 - x} = \frac{1.1^2}{0.28}$$



Let x mol of H_2 & I_2 react (माना H_2 व I_2 के x मोल क्रिया करते हैं)

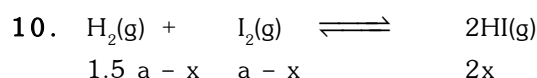
$$4 = \frac{(0.135-x)^2}{(2x)^2}$$



If V L of hypo are used (यदि हाइपो के V L प्रयुक्त हुए)

$$(0.135 - x) \cdot 2 = 1.5 \text{ V}$$

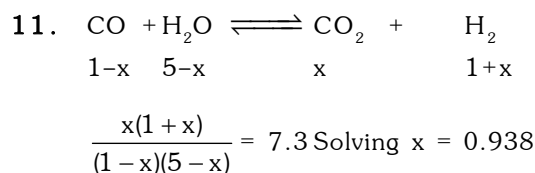
Let initially a mole I_2 & (1.5 a) mol H_2 be present (माना प्रारम्भ में a मोल I_2 व (1.5 a) मोल H_2 उपस्थित होते हैं)



$$\frac{a-x}{2x} = \frac{1}{18} \Rightarrow 9a - 9x = x$$

$$x = 9a/10$$

$$K_c = \frac{[2(9a/10)]^2}{\left(1.5a - \frac{9a}{10}\right)(a - 9a/10)} = \frac{81}{6} \cdot \frac{4}{1} = 54$$



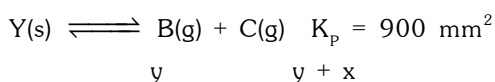
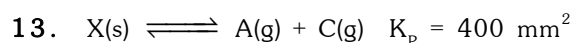
12.
$$\frac{r_{\text{mix}}}{r_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{avg.}}}} = 1.16$$

$$\text{Solving, } M_{\text{average}} = \frac{83.8}{1.16^2}$$

$$\frac{71}{M_{\text{avg.}}} = 1 + \alpha.$$

$$K_p = \frac{4\alpha^2}{1-\alpha^2}$$

$$\Rightarrow K_c = \frac{K_p}{(0.0821)(1473)} = 6.3 \cdot 10^{-4}$$



$$x(x+y) = 400$$

$$y(x+y) = 900$$

(b) Mole ratio of A & B (A व B का मोल अनुपात) = $\frac{x}{y} = \frac{4}{9}$

(c) Total pressure (कुल दाब) = $2(x+y)$

14.
$$M_{\text{average}} = \frac{12.8 \times 0.0821 \times 1000}{1.642} = 64$$



$$t = 0 \quad 1$$

$$t = \infty \quad 1-\alpha \quad \alpha \quad \alpha/2$$

$$\frac{80}{64} = 1 + \alpha/2 \Rightarrow \alpha = 0.5$$

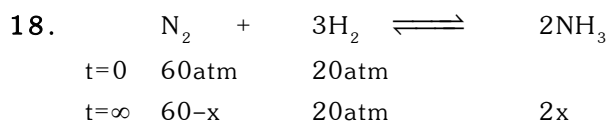
15. At 288 K,
$$M_{\text{avg.}} = \frac{3.62 \times 0.0821 \times 288}{1}$$

$$\frac{92}{M_{\text{avg.}}} = 1 + \alpha \Rightarrow K_{p1} = \frac{4\alpha^2}{1-\alpha^2}$$

Similarly at 348K,
$$M'_{\text{avg.}} = \frac{1.84 \times 0.0821 \times 348}{1}$$

$$\frac{92}{M'_{\text{avg}}} = 1 + \alpha' \Rightarrow K_{p2} = \frac{4\alpha'^2}{1-\alpha'^2}$$

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{288} - \frac{1}{348} \right]$$



$$\frac{2x}{80-2x} = \frac{1}{10} \Rightarrow 20x = 80 - 2x \Rightarrow x = \frac{80}{22}$$

$$\Rightarrow K_p = \frac{\left[2\left(\frac{80}{22}\right)\right]^2}{\left[60 - \frac{80}{22}\right]\left[20 - \frac{240}{22}\right]^3}$$

19.
$$-16.5 \cdot 10^3 = -8.314 \cdot 298 \cdot 2.303 \log K_1$$

$$K_2 = K_1^2$$

$$K_3 = \frac{1}{K_1}$$

let initial pressure of NO be p and of NO_2 be 2p

