THE VILLAGE
INTERNATIONAL SCHOOL
"We Nurture Dreams"

EQUILIBRIUM

Question 1. A liquid is in equilibrium with its vapours in a sealed container at a fixed temperature. The volume of the container is suddenly increased, (i) What is the initial effect of the change on the vapour pressure? (ii) How do the rates of evaporation and condensation change initially? (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?

Answer: (i) On increasing the volume of the container, the vapour pressure will initially decrease because the same amount of vapours are now distributed over a larger space.

(ii) On increasing the volume of the container, the rate of evaporation will increase initially because now more space is available. Since the amount of the vapours per unit volume decrease on increasing the volume, therefore, the rate of condensation will decrease initially.

(iii) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

Question 2. What is K_c for the following reaction in state of equilibrium?

Answer:

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

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.9\ M) \times (1.9\ M)}{(0.6\ M) \times (0.6\ M) \times (0.82\ M)}$$

$$= 12.229\ M^{-1} = \mathbf{12.229\ L\ mol^{-1}}$$

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

Given: $[SO_2] = 0.6\ M$; $[O_2] = 0.82\ M$; *and* $[SO_3] = 1.90\ M$

Question 3. Write the expression for the equilibrium constant for each of the following reactions

(i) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$

(ii) $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

(iii) $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

(iv) $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(v) $I_2(s) + 5F_2(g) \rightleftharpoons 2IF_5(l)$

Answer:

(i) $$K_c = \frac{[NO(g)]^2[Cl_2(g)]}{[NOCl(g)]^2}$$

(ii) $$K_c = \frac{[CuO(g)]^2[NO_2(g)]^4[O_2(g)]}{[Cu(NO_3)_2(s)]^2} = [NO_2(g)]^4[O_2(g)]$$

(iii) $$K_c = \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)][H_2O(l)]}$$

$$= \frac{[CH_3COOH(aq)][C_2H_5OH(aq)]}{[CH_3COOC_2H_5(aq)]}$$

(iv) $$K_c = \frac{[Fe(OH)_3(s)]}{[Fe^{3+}(aq)][OH^-(aq)]^3} = \frac{1}{[Fe^{3+}(aq)][OH^-(aq)]^3}$$

(v) $$K_c = \frac{[IF_5(l)]^2}{[I_2(s)][F_2(g)]^5} = \frac{[IF_5(l)]^2}{[F_2(g)]^5}$$

Question 4. Find the value of K_c for each of the following equilibria from the value of K

(a) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$; $K_p = 1.8 \times 10^{-2}$ *atm at 500 K*

(b) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$; $K_p = 167$ *atm at 1073 K.*

Answer:

K_p and K_c are related to each other as $K_p = K_c\ (RT)^{\Delta ng}$

The value of K_c can be calculated as follows:

(a) $2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2$

$K_p = 1.8 \times 10^{-2}$ atm,

$\Delta^{ng} = 3 - 2 = 1$; $R = 0.0821$ litre atm K^{-1} mol^{-1} ; $T = 500$ K

$$\therefore \quad K_c = \frac{K_p}{(RT)^{\Delta ng}} = \frac{(1.8 \times 10^{-2}\ \text{atm})}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 500\ \text{K})^1}$$

$$= \mathbf{4.4 \times 10^{-4}\ mol\ L^{-1}}$$

(b) $CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$

$K_p = 167$ atm, $\Delta^{ng} = 1$

$R = 0.0821$ liter atm K^{-1} mol^{-1} ; $T = 1073$ K

$$K_c = \frac{K_p}{(RT)^{\Delta ng}} = \frac{(167\ \text{atm})}{(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 1073\ \text{K})^1}$$

$$= \mathbf{1.9\ mol\ L^{-1}}$$

Question 5. What is meant by conjugate acid-base pair? Find the conjugate acid/base for the following species: HNO_2, CH^-, $HClO_4$, OH^-, CO_3^{2-}, S^{2-}
Answer: An acid-base pair which differs by a proton only ($HA \longrightarrow A^- + H^+$) is known as conjugate acid-base pair.
Conjugate acid:HCN,H_20,HCO_3^-,HS^-.
Conjugate base:NO_2^-,ClO_4^-,O_2^-

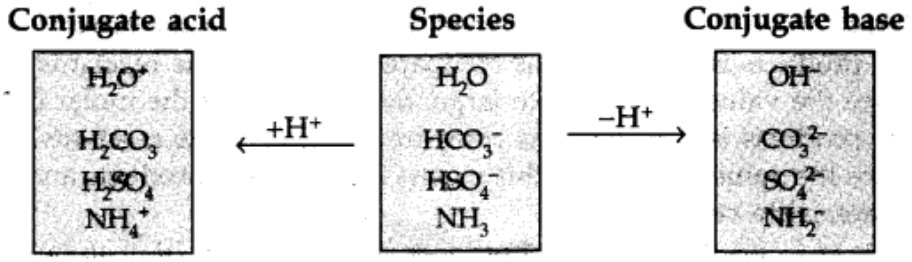
Question 6 . Which of the following are Lewis Acids?
H_2O,BF_3, H^+ and NH^{4+},
Answer: BF_3, H^+ ions are Lewis acids.

Question 7. What will be the conjugate bases for the Bronsted acids?HF, H_2S0_4 and H_2C0_3?

Answer: Conjugate bases: F^-, HSO^-_4 , HCO^-_3.

Question 8. Write the conjugate acids for the following Bronsted bases:
NH_2, NH_3 and $HCOO^-$
Answer: NH_3, NH_4^+ and HCOOH

Question 9.The species H_20, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acid and base. For each case, give the corresponding conjugate acid and base.
Answer:



Question 10. Classify the following species into Lewis acids and Lewis bases and show how these can act as Lewis acid/Lewis base?
(a) OH^- ions (b) F^- (c) H^+ (d) BCl_3
Answer: (a) OH^- ions can demate an electron pair and act as Lewis base.
(b) F^- ions can donate an electron pair and act'as Lewis base.
(c) H^+ ions can accept an electron pair and act as Lewis acid.
(d) BCl_3 can accept an electron pair since Boron atom is electron deficient. It is a Lewis acid.

Question 11 The concentration of hydrogen ions in a sample of soft drink is 3.8×10^{-3} M. What is the pH value?
Answer: $pH = -\log [H^+] = -\log (3.8 \times 10^{-3}) = -\log 3.8 + 3 = 3 - 0.5798 = 2.4202 = 2.42$

Question 12. The following concentration were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500 K.$[N_2(g)]$ = 1.5 x 10^{-2} M $[H_2(g)]$ = 3.0 x 10^{-2} M $[NH_3]$ = 1.2 x 10^{-2} M. Calculate equilibrium constant.

Answer:

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

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{[1.2 \times 10^{-2} M]^2}{[1.5 \times 10^{-2} M][3.0 \times 10^{-2} M]^3}$$

$$= \mathbf{3.55 \times 10^{-2} M}$$

Question 13. The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Answer: pH = – log $[H^+]$ or log $[H^+]$ = – pH = – 3.76 = 4.24

.-. $[H^+]$ = Antilog 4.24 = 1.738 x 10^{-4} = 1.74 x 10-4 M

Question 14. Write the equilibrium constant (K_c) expression for the following reactions.

(i) $Cu^{2+}(aq) + 2\,Ag\,(s) \rightleftharpoons Cu(s) + 2Ag^+\,(aq)$

(ii) $4HCl\,(g) + O_2(g) \rightleftharpoons 2Cl_2\,(g) + 2H_2O(g)$

Answer:

(i) $$K_c = \frac{[Ag^+(aq)]^2}{[Cu^{2+}(aq)]}$$

(ii) $$K_c = \frac{[Cl_2(g)]^2[H_2O(g)]^2}{[HCl(g)]^4[O_2(g)]}$$

Question 15. Given the equilibrium N_2O_4 (g) ——->$2NO_2$ (g) K=0.15 atm at 298 K

(a) What is K_p using pressure in torr?

(b) What is K_c using units of moles per litre.

Answer:

(a) $$K_p = \frac{(760 \text{ torr}) \times (0.15 \text{ atm})}{(1 \text{ atm})}$$

$$= \mathbf{1.14 \times 10^2 \text{ torr}}$$

(b)

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

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

$$= \frac{(0.15 \text{ atm})}{\left(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}\right)^{2-1}}$$

$$= \mathbf{6.13 \times 10^{-3} \text{ mol L}^{-1}}$$

Question 16. In the reaction A + B———> C + D, what will happen to the equilibrium if concentration of A is increased?
(b) The equilibrium constant for a reaction is 2×10^{-23} at 25°C and 2×10^{-2} at 50°C. Is the reaction endothermic or exothermic?
(c) Mention at least three ways by which the concentration of $S0_3$ can be increased in the following reaction in a state of equilibrium.
Answer: (a) The reaction will shift in the forward direction.
(b) Endothermic
(c) (i) lowering the temperature (ii) increasing pressure.
(iii) increasing concentration of oxygen.

Question 17. (i) Define Le Chatelier's principle.
(ii) Following reactions occur in a Blast furnace.
$Fe_20_3(s) + 3CO(g) \text{———–>} 2Fe(s) + 3CO_2(g)$
use Le chatelier's principle to predict the direction of reaction when equilibrium mixture is disturbed by
(a) adding Fe_20_3 (b) removing CO_2 .
(c) removing CO.
Answer: (a) When a system under equilibrium is subjected to a change in temperature, pressure or concentration, then the equilibrium shifts in such a direction so as to undo the effect of the change.
(ii) (a) On adding $Fe_20_3(s)$, the equilibrium will remain unaffected.
(b) By removing CO_2 (g), the equilibrium will be shifted in the forward direction.
(c) By removing CO(g), the equilibrium will be shifted in the backward direction

Question 18. (i) Point out the differences between ionic product and solubility product.
(ii) The solubility of AgCl in water at 298 K is 1.06×10^{-5} mole per litre. Calculate its solubility product at this temperature.
Answer: (i)

Ionic Product	*Solubility Product*
(*a*) It is applicable to all types of solutions. (*b*) Its value changes with the change in concentration of the ions.	(*a*) It is applicable to the saturated solutions. (*b*) It has a definite value for an electrolyte at a constant temperature.

(*ii*) The solubility equilibrium in the saturated solution is

$$AgCl\ (s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

The solubility of AgCl is 1.06×10^{-5} mole per litre.

$$[Ag^+(aq)] = 1.06 \times 10^{-5} \text{ mol } L^{-1}$$

$$[Cl^-(aq)] = 1.06 \times 10^{-5} \text{ mol } L^{-1}$$

$$K_{sp} = [Ag^+(aq)]\,[Cl^-(aq)]$$

$$= (1.06 \times 10^{-5} \text{ mol } L^{-1}) \times (1.06 \times 10^{-5} \text{ mol } L^{-1})$$

$$= \mathbf{1.12 \times 10^{-2} \text{ mol}^2 \text{ L}^{-2}}$$

Question 19.. At certain temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated at temperature remaining constant.

Answer: Calculation of K_p

$$\underset{1}{PCl_5(g)} \rightleftharpoons \underset{0}{PCl_3(g)} + \underset{0}{Cl_2(g)}$$

$$\underset{(1-\alpha)}{} \qquad \underset{\alpha}{} \qquad \underset{\alpha}{}$$

Total no. of moles in the equilibrium mixture $= 1 - \alpha + \alpha + \alpha$

$= (1 + \alpha)$ mol.

Let the total pressure of equilibrium mixture = p atm

Partial pressure of PCl_5

$$p_{PCl_5} = \frac{1-\alpha}{1+\alpha} \times p \text{ atm}$$

Partial pressure of $PCl_3 = \frac{\alpha}{1+\alpha} \times p$ atm

Partial pressure of Cl_2

$$p_{Cl_2} = \frac{\alpha}{(1+\alpha)} \times p \text{ atm}$$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}}$$

$$= \frac{\left(\frac{\alpha}{1+\alpha} p \text{ atm}\right) \times \left(\frac{\alpha}{1+\alpha} p \text{ atm}\right)}{\frac{1-\alpha}{1+\alpha} p \text{ atm}} = \frac{\alpha^2 p}{1-\alpha^2} \text{ atm}$$

$$P = 4 \text{ atm and } \alpha = 10\% = \frac{10}{100} = 0.1$$

$$K_p = \frac{(0.1) \times (0.1) \times (4 \text{ atm})}{1-(0.1)^2}$$

$$= \frac{0.04}{0.99} = 0.04 \text{ atm.}$$

Calculation of P under new condition

$$\alpha = 0.2, K_p = 0.04 \text{ atm}$$

$$K_p = \frac{\alpha^2 p}{1-\alpha^2} \text{ or } p = \frac{K_p(1-\alpha^2)}{\alpha^2}$$

$$= \frac{(0.04 \text{ atm})[(1-(0.2)^2]}{(0.2)^2} = \frac{0.04 \text{ atm} \times 0.96}{0.04}$$

$$= \mathbf{0.96 \text{ atm.}}$$

Question 20. The equilibrium expression, $K_c = [C0_2]$ represents the reaction.

(a) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$ (b) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(c) $CO(g) + \frac{1}{2} O_2(g) \rightleftharpoons CO_2(g)$ (d) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

Question 21. Hydrogen molecule (H_2) can be dissociated into hydrogen atoms (H). Which one of the following changes will not increase the number of atoms present at equilibrium?

(a) adding H atoms (b) increasing the temperature

(c) increasing the total pressure (d) increasing the volume of the container

Question 3. What is the expression for K_{eq}? for the reaction

$$2N_2O\,(g) + O_2\,(g) \rightleftharpoons 4NO\,(g)?$$

(a) $\frac{[N_2][O_2]}{[NO]}$ (b) $\frac{[NO]^4}{[N_2O]^2}$ (c) $\frac{[NO]^4}{[N_2O]^2[O_2]}$ (d) $\frac{[N_2O]^2[O_2]}{[NO]^4}$

Question 22. A catalyst will increase the rate of a chemical reaction by

(a) shifting the equilibrium to the right (b) shifting the equilibrium to the left (c) lowering the activation energy (d) increasing the activation energy

Question 5. What is the correct expression for the representation of the solubility product constant of $Ag_2\,Cr0_4$?

(a) $[Ag^+]^2\,[CrO_4^{2-}]$ (b) $[2Ag^+]\,[CrO_4^{2-}]$ (c) $[Ag^+]\,[CrO_4^{2-}]$ (d) $[2Ag^+]^2\,[CrO_4^{2-}]$

Question 23. For the equilibrium 2 NOCl(g)——-> 2NO(g) + Cl_2(g) the value of the equilibrium constant Kc is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

Answer: We know that $K_p = K_c(RT)^{\Delta n}$

For the above reaction, $\Delta n = (2 + 1) - 2 = 1$ $K_p = 3.75 \times 10'6\ (0.0831 \times 1069)$

$K_p = 0.033$.

Question 24. The values of Ksp of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble? Explain.

Answer:

$AgCN \rightleftharpoons Ag^+ + CN^-$

$Ksp = [Ag^+][CN^-] = 6 \times 10^{-17}$

$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

$Ksp = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$S_1^2 = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$

$(S_2)\ (2S_2)^2 = 2 \times 10^{-15}$, $S_2 = 0.58 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

Question 25.. The value of Kc for the reaction 2A——>B + C is 2 x 10^{-3}. At a given time, the composition of reaction mixture is [A] = [B] = [C] = 3 x 10^{-4} M. In which direction the reaction will proceed?

Answer: For the reaction the reaction quotient Q_c is given by Q_c = [B] [C]/[A]2 as [A] = [B] = [C] = 3 x 10-4 M Q_c = (3 x 10^{-4}) (3 x10^{-3})/(3 x 10) = 1

as $Q_c > K_c$, so, the reaction will proceed in the reverse direction.

Question 26.. PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K and having concentration 1.59M PCl_5 1.59M Cl_2 and 1.41M PCl_5. Calculate K_c for the reaction PCl_5———>PC_{13}+ Cl_2

Answer: The equilibrium constant Kc for the above reaction can be written as:

$$Kc = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{(1.59)^2}{1.41} = 1.79$$

Question 27.. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction:

$CH_4(g) + H_2O(g)$ ——> $CO(g) + 3\ H_2(g)$

(a) Write an expression for $K_p$for the above reaction.

(b) How will the values of K_p and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

Answer:

$$(a)\ K_p = \frac{[p_{CO}][p_{H_2}]^3}{[p_{CH_4}][p_{H_2O}]}$$

(b) (i) value of K_p will not change, equilibrium will shift in backward direction.

(ii) value of K_p will increase and reaction will proceed in forward direction.

(iii) no effect.

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