

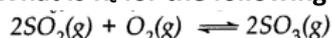
Q1. A liquid is in equilibrium with its vapours in a sealed container at a fixed temperature. The volume of the container is suddenly increased, (i) What is the initial effect of the change on the vapour pressure? (ii) How do the rates of evaporation and condensation change initially? (iii) What happens 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.

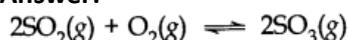
(iii) Finally, equilibrium will be restored when the rates of the forward and backward processes become equal. However, the vapour pressure will remain unchanged because it depends upon the temperature and not upon the volume of the container.

Q2. What is K_c for the following reaction in state of equilibrium?



Given: $[\text{SO}_2] = 0.6 \text{ M}$; $[\text{O}_2] = 0.82 \text{ M}$; and $[\text{SO}_3] = 1.90 \text{ M}$

Answer:



$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = \frac{(1.9 \text{ M}) \times (1.9 \text{ M})}{(0.6 \text{ M}) \times (0.6 \text{ M}) \times (0.82 \text{ M})}$$

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

Q3. Find the value of K_c for each of the following equilibria from the value of K

(a) $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2(\text{g})$; $K_p = 1.8 \times 10^{-2} \text{ atm}$ at 500 K

(b) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; $K_p = 167 \text{ atm}$ at 1073 K.

Answer:

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

The value of K_c can be calculated as follows:

(a) $2\text{NOCl}(\text{g}) \rightleftharpoons 2\text{NO}(\text{g}) + \text{Cl}_2$

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

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

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

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

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

$$K_p = 167 \text{ atm, } \Delta n_g = 1$$

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

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

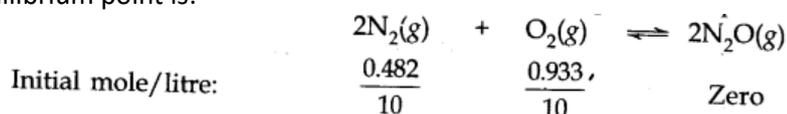
$$= 1.9 \text{ mol L}^{-1}$$

Q4. Reaction between nitrogen and oxygen takes place as follows:



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

Answer: Let x moles of $\text{N}_2(\text{g})$ take part in the reaction. According to the equation, $x/2$ moles of $\text{O}_2(\text{g})$ will react to form x moles of $\text{N}_2\text{O}(\text{g})$. The molar concentration per litre of different species before the reaction and at the equilibrium point is:



$$\text{Mole/litre at eqm. point: } \frac{0.482-x}{10} \quad \frac{0.933-\frac{x}{2}}{10} \quad \frac{x}{10}$$

The value of equilibrium constant (2.0×10^{-37}) is extremely small. This means that only small amounts of reactants have reacted. Therefore, x is extremely small and can be omitted as far as the reactants are concerned.

$$\text{Applying Law of Chemical Equilibrium } K_c = \frac{[\text{N}_2\text{O}(\text{g})]^2}{[\text{N}_2(\text{g})]^2[\text{O}_2(\text{g})]}$$

$$2.0 \times 10^{-37} = \frac{\left(\frac{x}{10}\right)^2}{\left(\frac{0.482}{10}\right)^2 \times \left(\frac{0.933}{10}\right)} = \frac{0.01 x^2}{2.1676 \times 10^{-4}}$$

$$x^2 = 43.352 \times 10^{-40} \quad \text{or} \quad x = 6.6 \times 10^{-20}$$

As x is extremely small, it can be neglected.

Thus, in the equilibrium mixture

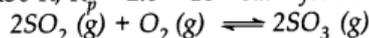
$$\text{Molar conc. of N}_2 = \mathbf{0.0482 \text{ mol L}^{-1}}$$

$$\text{Molar conc. of O}_2 = \mathbf{0.0933 \text{ mol L}^{-1}}$$

$$\begin{aligned} \text{Molar conc. of N}_2\text{O} &= 0.1 \times x = 0.1 \times 6.6 \times 10^{-20} \text{ mol L}^{-1} \\ &= \mathbf{6.6 \times 10^{-21} \text{ mol L}^{-1}} \end{aligned}$$

Q5.

At 450 K, $K_p = 2.0 \times 10^{10} \text{ bar}^{-1}$ for the equilibrium reaction:



What is K_c at this temperature?

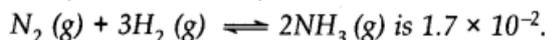
Answer:

$$K_p = K_c (RT)^{\Delta n_g} \quad \text{or} \quad K_c = \frac{K_p}{(RT)^{\Delta n_g}} = K_p (RT)^{-\Delta n_g}$$

$$K_p = 2.0 \times 10^{10} \text{ bar}^{-1}; R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}; T = 450 \text{ K}; \Delta n_g = 2 - 3 = -1$$

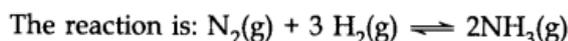
$$\begin{aligned} K_c &= (2.0 \times 10^{10} \text{ bar}^{-1}) \times [(0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}) \times (450 \text{ K})]^{-(-1)} \\ &= \mathbf{7.47 \times 10^{11} \text{ mol}^{-1} \text{ L} = 7.47 \times 10^{11} \text{ M}^{-1}} \end{aligned}$$

Q6. A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 and 8.13 mol 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



Is this reaction at equilibrium? If not, what is the direction of net reaction?

Answer:



$$\begin{aligned} \text{Concentration quotient } (Q_c) &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(8.13/20 \text{ mol L}^{-1})^2}{(1.57/20 \text{ mol L}^{-1}) \times (1.92/20 \text{ mol L}^{-1})^3} \\ &= \mathbf{2.38 \times 10^3} \end{aligned}$$

The equilibrium constant (K_c) for the reaction = 1.7×10^{-2}

As $Q_c \neq K_c$; this means that the reaction is not in a state of equilibrium.

Q7. If 1 mole of H_2O and 1 mole of CO are taken in a 10 litre vessel and heated to 725 K, at equilibrium point 40 percent of water (by mass) reacts with carbon monoxide according to equation.



Calculate the equilibrium constant for the reaction.

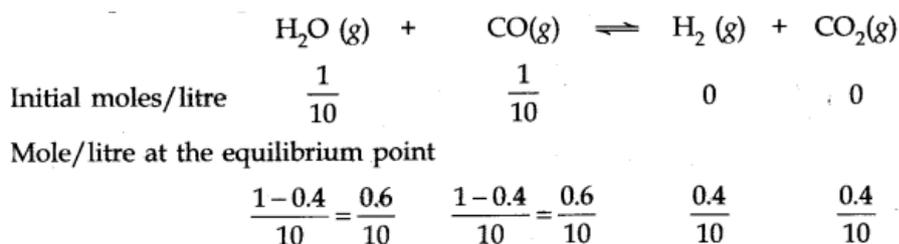
Answer: Number of moles of water originally present = 1 mol

Percentage of water reacted = 40%

Number of moles of water reacted = $1 \times 40/100 = 0.4 \text{ mol}$

Number of moles of water left = $(1 - 0.4) = 0.6 \text{ mole}$ According to the equation, 0.4 mole of water will react with 0.4 mole of carbon monoxide to form 0.4 mole of hydrogen and 0.4 mole of carbon dioxide.

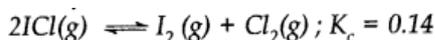
follows:



Applying law of chemical equilibrium,

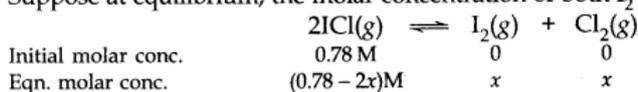
$$\begin{aligned} \text{Equilibrium constant } (K_c) &= \frac{[\text{H}_2(\text{g})][\text{CO}_2(\text{g})]}{[\text{H}_2\text{O}(\text{g})][\text{CO}(\text{g})]} = \frac{\left(\frac{0.4}{10} \text{ mol L}^{-1}\right) \times \left(\frac{0.4}{10} \text{ mol L}^{-1}\right)}{\left(\frac{0.6}{10} \text{ mol L}^{-1}\right) \times \left(\frac{0.6}{10} \text{ mol L}^{-1}\right)} \\ &= \frac{0.16}{0.36} = \mathbf{0.44} \end{aligned}$$

Q8. What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M?



Answer:

Suppose at equilibrium, the molar concentration of both $\text{I}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ is $x \text{ mol L}^{-1}$.



$$K_c = \frac{[\text{I}_2(\text{g})][\text{Cl}_2(\text{g})]}{[\text{ICl}(\text{g})]^2} = \frac{(x) \times (x)}{(0.78 - 2x)^2}$$

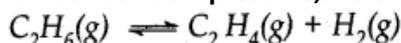
$$\frac{x}{(0.78 - 2x)} = (0.14)^{1/2} = 0.374 \quad \text{or} \quad x = 0.374 (0.78 - 2x)$$

$$x = 0.292 - 0.748x \quad \text{or} \quad 1.748x = 0.292; x = \frac{0.292}{1.748} = 0.167$$

$$[\text{ICl}] = (0.78 - 2 \times 0.167) = (0.78 - 0.334) = \mathbf{0.446 \text{ M}}$$

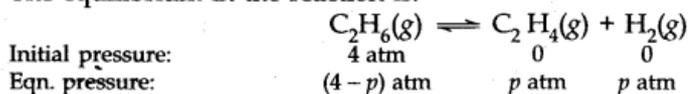
$$[\text{I}_2] = 0.167 \text{ M}; [\text{Cl}_2] = \mathbf{0.167 \text{ M}}$$

Q9. $K = 0.04 \text{ atm}$ at 898 K for the equilibrium shown below. What is the equilibrium concentration of C_2H_6 when it is placed in a flask at 4 atm pressure, and allowed to come to equilibrium.



Answer:

The equilibrium in the reaction is:



$$K_p = \frac{p_{\text{C}_2\text{H}_4} \times p_{\text{H}_2}}{p_{\text{C}_2\text{H}_6}} \quad \text{or} \quad 0.04 = \frac{p^2}{(4 - p)}$$

$$p^2 = 0.04(4 - p) \quad \text{or} \quad p^2 + 0.04p - 0.16 = 0$$

$$p = \frac{(-0.04) \pm \sqrt{0.0016 - 4(-0.16)}}{2}$$

$$= \frac{(-0.04) \pm 0.8}{2} = \frac{0.76}{2} = 0.38$$

Equilibrium pressure or concentration of $\text{C}_2\text{H}_6 = (4 - 0.38) = \mathbf{3.62 \text{ atm}}$.

Q10. A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was reached, the concentration of PCl_5 was found to be $0.5 \times 10^{-1} \text{ mol L}^{-1}$. If K_c is 8.3×10^{-3} what are the concentrations of PCl_3 and

Cl₂ at equilibrium?

Answer: Let the initial molar concentration of PCl₅ per litre = x mol

Molar concentration of PCl₅ at equilibrium = 0.05 mol

∴ Moles of PCl₅ decomposed = (x - 0.05) mol

Moles of PCl₃ formed = (x - 0.05) mol

Moles of Cl₂ formed = (x - 0.05) mol

The molar conc./litre of reactants and products before the reaction and at the equilibrium point are:

	PCl ₅	⇌	PCl ₃	+	Cl ₂
Initial moles/litre	x		0		0
Moles/litre at eqm. point	0.05		(x - 0.05)		(x - 0.05)
Equilibrium constant (K _c) = 8.3 × 10 ⁻³	= 0.0083				

Applying Law of chemical equilibrium,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}; \quad 0.0083 = \frac{(x - 0.05) \times (x - 0.05)}{0.05}$$

$$(x - 0.05)^2 = 0.0083 \times 0.05 = 4.15 \times 10^{-4}$$

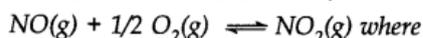
$$(x - 0.05) = (4.15 \times 10^{-4})^{1/2} = 2.037 \times 10^{-2} = 0.02 \text{ moles}$$

$$x = 0.05 + 0.02 = 0.07 \text{ mol}$$

The molar concentration per litre of PCl₃ at eqm. = 0.07 - 0.05 = **0.02 mol**

The molar concentration per litre of Cl₂ at eqm. = 0.07 - 0.05 = **0.02 mol**.

Q11. Calculate (a) ΔG° and (b) the equilibrium constant for the formation of NO₂ from NO and O₂ at 298 K



$$\Delta_f G^\ominus (\text{NO}_2) = 52.0 \text{ kJ/mol}, \quad \Delta_f G^\ominus (\text{NO}) = 87.0 \text{ kJ/mol}, \quad \Delta_f G^\ominus (\text{O}_2) = 0 \text{ kJ/mol},$$

Answer:

Step I. Calculation of ΔG°

$$\begin{aligned} \Delta G^\ominus &= \Delta_f G^\ominus (\text{NO}_2) - [\Delta_f G^\ominus (1/2 \text{O}_2)] \\ &= 52.0 - (87 + 0) = -35 \text{ kJ mol}^{-1} \end{aligned}$$

Step II. Calculation of K_c

$$\Delta G^\ominus = -2.303 RT \log K_c$$

$$\log K_c = -\frac{\Delta G^\ominus}{2.303 RT} = -\frac{(-35 \times 10^3 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ kJ mol}^{-1}) \times (298 \text{ K})} = 6.134$$

$$K_c = \text{Antilog } 6.134 = \mathbf{1.36 \times 10^6}$$

Q12. Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H₂. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction.



If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam so that P_{CO} = P_{H₂O} = 4.0 bar, what will be the partial pressure of H₂ at equilibrium? K_p = 0.1 at 400°C.

Answer:

Let the partial pressure of hydrogen (H₂) at equilibrium point = p bar

	$\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$			
Initial pressure:	4.0 bar	4.0 bar	0	0
Eqm. pressure:	(4-p) bar	(4-p) bar	p bar	p bar

$$K_p = \frac{p_{\text{CO}_2} \times p_{\text{H}_2}}{p_{\text{CO}} \times p_{\text{H}_2\text{O}}} \quad \text{or} \quad 0.1 = \frac{(p \text{ bar}) \times (p \text{ bar})}{(4-p) \text{ bar} \times (4-p) \text{ bar}}$$

$$\frac{p^2}{(4-p)^2} = 0.1 \quad \text{or} \quad \frac{p}{(4-p)} = (0.1)^{1/2} = 0.316$$

$$p = 0.316(4-p) \quad \text{or} \quad p = 1.264 - 0.316p$$

$$1.316p = 1.264 \quad \text{or} \quad p = \frac{1.264}{1.316} = \mathbf{0.96 \text{ bar}}$$

Q13 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) BCl₃

Answer: (a) OH⁻ ions can donate 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) BCl₃ can accept an electron pair since Boron atom is electron deficient. It is a Lewis acid.

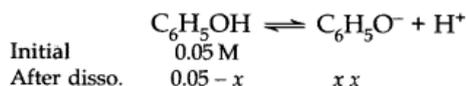
Q14. . The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it.

Answer: $\text{pH} = -\log [\text{H}^+]$ or $\log [\text{H}^+] = -\text{pH} = -3.76 = 4.24$

$$\therefore [\text{H}^+] = \text{Antilog } 4.24 = 1.738 \times 10^{-4} = 1.74 \times 10^{-4} \text{ M}$$

Q15. The ionization constant of phenol is 1.0×10^{-10} . What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01 M in sodium phenolate?

Answer:



$$\therefore K_a = \frac{x \times x}{0.05 - x} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad \frac{x^2}{0.05} = 1.0 \times 10^{-10}$$

$$\text{or } x^2 = 5 \times 10^{-12} \quad \text{or } x = 2.2 \times 10^{-6} \text{ M}$$

In presence of 0.01 C₆H₅ONa, suppose y is the amount of phenol dissociated, then at equilibrium

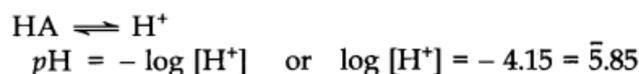
$$\begin{array}{l} [\text{C}_6\text{H}_5\text{OH}] = 0.05 - y \approx 0.05, \\ [\text{C}_6\text{H}_5\text{O}^-] = 0.01 + y \approx 0.01 \text{ M}, [\text{H}^+] = y \text{ M} \end{array}$$

$$\therefore K_a = \frac{(0.01)(y)}{0.05} = 1.0 \times 10^{-10} \text{ (Given)} \quad \text{or} \quad y = 5 \times 10^{-10}$$

$$\therefore \alpha = \frac{y}{c} = \frac{5 \times 10^{-10}}{5 \times 10^{-2}} = 10^{-8}$$

Q16. It has been found that the pH of a 0.01 M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its PK_a.

Answer:



$$\text{pH} = -\log [\text{H}^+] \quad \text{or} \quad \log [\text{H}^+] = -4.15 = \bar{5}.85$$

$$\therefore [\text{H}^+] = 7.08 \times 10^{-5} \text{ M} = 7.08 \times 10^{-5} \text{ M}$$

$$[\text{A}^-] = [\text{H}^+] = 7.08 \times 10^{-5} \text{ M}$$

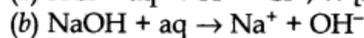
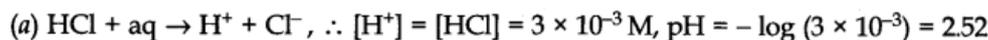
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(7.08 \times 10^{-5})(7.08 \times 10^{-5})}{10^{-2}} = 5.0 \times 10^{-7}$$

$$\text{p}K_a = -\log K_a = -\log (5.0 \times 10^{-7}) = 7 - 0.699 = 6.301$$

Q17. Assuming complete dissociation, calculate the pH of the following solutions:

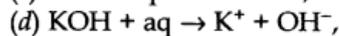
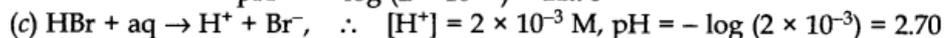
(a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH

Answer:



$$\therefore [\text{OH}^-] = 5 \times 10^{-3} \text{ M}, [\text{H}^+] = 10^{-14} / (5 \times 10^{-3}) = 2 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log (2 \times 10^{-12}) = 11.70$$



$$\therefore [\text{OH}^-] = 2 \times 10^{-3} \text{ M}, [\text{H}^+] = 10^{-14} / (2 \times 10^{-3}) = 5 \times 10^{-12}$$

$$\text{pH} = -\log (5 \times 10^{-12}) = 11.30$$

Q18 Calculate the pH of the following solutions:

(a) 2g of TIOH dissolved in water to give 2 litre of the solution

(b) 0.3 g of Ca(OH)₂ dissolved in water to give 500 mL of the solution

(c) 0.3 g of NaOH dissolved in water to give 200 mL of the solution

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.

