CHEMICAL EQUILIBRIUM

Question 1

When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?

(i) $H_2(g) + S(s) \rightleftharpoons H_2S;\ K_c = 7.8 \times 10^5$
(ii) $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g);\ K_c = 7.4 \times 10^{-26}$

Solution

(i) Contain mostly products (With $K_c > 10^3$, the K_c value is large).
(ii) Contain mostly reactants (With $K_c < 10^3$, the K_c value is small).

Question 2

Anhydrous calcium chloride often used as a desiccant. In the presence of excess of $CaCl_2$, the amount of the water taken up is governed by

$K_p = 6.4 \times 10^{85} atm^{-6}$ for the following reaction at room temperature: $CaCl_2 + 6H_2O(g) \rightleftharpoons CaCl_2.6H_2O(s)$

What is the equilibrium vapour pressure of water in a vessel that contains $CaCl_2(s)$?

Solution

K_p expression for the given reaction equation is given by;

$$K_p = \frac{1}{\left(P_{H_2O}\right)^6}$$

Substituting;

$$6.4 \times 10^{85} atm^{-6} = \frac{1}{\left(P_{H_2O}\right)^6}$$

From which;

$$P_{H_2O} = \sqrt[6]{\frac{1}{6.4 \times 10^{85}\text{atm}^{-6}}} = 5 \times 10^{-15}\text{atm}$$

The equilibrium vapour pressure is 5×10^{-15}atm.

Question 3

Which of the following reactions yield appreciable equilibrium concentration of both reactants and products?

(i) $2Cu(s) + O_2(g) \rightleftharpoons 2CuO(s);\ K_c = 4 \times 10^{45}$
(ii) $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq);\ K_c = 7.5 \times 10^{-3}$
(iii) $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g); K_c = 2 \times 10^{-19}$

Solution

(ii) (K_c value is medium with value lying between of $10^{-3}$and 10^3).

Question 4

The vapour pressure of water at 25°C is 0.0313atm. Calculate the value of K_p and K_c at 25°C for the following equilibrium:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Solution

Vapour pressure is commonly given as equilibrium vapour pressure at given temperature.

So the vapour pressure of water at equilibrium is 0.0313atm

But from the equation of water vapourisation;

$$K_p = P_{H_2O} = 0.0313\text{atm}$$

The value of K_p is 0.0313atm.

Using;

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

Where;

$$\Delta \mathrm{n} = 1 - 0 = 1, \mathrm{R} = 0.082\mathrm{atmLmol^{-1}K^{-1}}, \mathrm{T} = 298\mathrm{K}$$

Substituting;

$$0.0313\mathrm{atm} = \mathrm{K_c}(0.082\mathrm{atmLmol^{-1}K^{-1}} \times 298\mathrm{K})^1$$

From which;

$$\mathrm{K_c} = 1.28 \times 10^{-3}\mathrm{mol/L}$$

The value of $\mathrm{K_c}$ is $1.28 \times 10^{-3}\mathrm{mol/L}$

Question 5

Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(\mathrm{K_c} = \frac{\mathrm{K_f}}{\mathrm{K_b}}\right)$. It is undeniable fact that the magnitude of both rate constants increases with an increase in temperature. However for some reactions, magnitude of the equilibrium constant is found to decrease as the temperature increases; explain how is this possible?

Solution

According to Arrhenius equation $\left(\mathrm{k} = \mathrm{Ae}^{\frac{-\mathrm{Ea}}{\mathrm{RT}}}\right)$; an increase in magnitude of rate constant at given temperature rise becomes high as the activation energy ($\mathrm{E_a}$) becomes high too. For exothermic reactions, the activation energy of backward reaction is higher than that of forward reaction making the increase in $\mathrm{K_b}$ value greater than that of $\mathrm{K_f}$ value at the given temperature rise and hence the $\mathrm{K_c}$ value decreases as the temperature increases

Question 6

2.00g of phosphorous pentachloride are allowed to reach equilibrium at 200°C in a vessel of $1\mathrm{dm^3}$ capacity. If the equilibrium constant of the reaction: $\mathrm{PCl_5} \rightleftharpoons \mathrm{PCl_3} + \mathrm{Cl_2}$ is $0.008\ \mathrm{moldm^{-3}}$ at this temperature and in the conditions stated, calculate the percentage dissociation of the phosphorous pentachloride at equilibrium.

Solution.

Initially: Number of moles of $PCl_5 = \frac{2}{208.5}\text{mol} = 0.00959\text{mol}$

Equation for the reaction: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

At equilibrium $0.00959 - x \quad x \quad x$

$$K_c = \frac{\left(\frac{x}{v}\right)\left(\frac{x}{v}\right)}{\left(\frac{0.00959 - x}{v}\right)} = \frac{x^2}{(0.00959 - x)v}$$

$x^2 + 0.008x - 0.00007672 = 0 \quad \text{or} \quad x = 0.005629$

Degree of dissociation of PCl_5:

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}}$$

$$= \frac{0.005629}{0.00959} = 0.587 \quad \text{or } 58.7\%$$

Hence degree of dissociation of PCl_5 is 58.7%

Question 7

Writing most common equilibrium constant expression for the reaction,

$A + B \rightleftharpoons C + D$ if:

(i) A, B, C and D are gases.

(ii) A, B, C and D are solutions.

(iii) A and C are solid while B and D are gases.

(iv) C is solid and A, B and D are solutions.

Solution

(i) $K_p = \frac{(P_C)(P_D)}{(P_A)(P_B)}$

For gases, the most common form of the equilibrium constant expression, is the equilibrium constant in terms of partial pressure.

(ii) $K_c = \frac{[C][D]}{[A][B]}$

(iii) $K_c = \frac{(P_D)}{(P_B)}$

(iv) $K_c = \frac{[D]}{[A][B]}$

Question 8

At certain temperature, $K_c = 4$ for the following reaction:

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g)$$

A 1.0L reaction vessel contained 0.045mol of $F_2(g)$ at equilibrium. What was initial amount of HF in the reaction vessel? (Assume initially there were HF only in the vessel).

Solution

Reaction equation;

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g)$$

Initial number of moles	h	0	0
Number of moles at equilibrium	$h - 2x$	x	x

Then;

$$K_c = \frac{[H_2][F_2]}{[HF]^2} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{h-x}{V}\right)^2} = \frac{x^2}{(h-2x)^2}$$

Substituting;

$$4 = \frac{(0.045)^2}{(h - 2 \times 0.045)^2}$$

Then;

$$\sqrt{4} = \sqrt{\frac{(0.045)^2}{(h - 2 \times 0.045)^2}};\ 2 = \frac{0.045}{h - 0.09}$$

From which; $h = 0.1125\text{mol}$

The initial amount of HF was 0.1125mol

Question 9

Write the equilibrium constant expression (K_c) for each of the following reactions:

(i) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$
(ii) $Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{2+}(aq)$
(iii) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$
(iv) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$
(v) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

Solution

(i) $K_c = \frac{[CO]^2}{[CO_2]}$

(Here C(s) is omitted because it is pure solid).

(ii) $K_c = \frac{[Hg_2^{2+}]}{[Hg^{2+}]}$

(Here Hg (l) is omitted because it is pure liquid).

(iii) $K_c = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$

(iv) $K_c = [O_2]^3$

(v) $K_c = \frac{[H_3O^+][F^-]}{[HF]}$

Question 10

20g Of $CaCO_3(s)$ were placed in a closed vessel, heated and maintained at 727°C under equilibrium:

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

And it is found that 75% of $CaCO_3$ was decomposed if the volume of the container was 15L, calculate the value of K_p.

Solution

Mass of $CaCO_3$ decomposed $= \frac{75}{100} \times 20g = 15g$

But from the mole ratio of the given reaction equation, 100g (1mol) of decomposed $CaCO_3$, gives 44g (1mol) of $CO_2(g)$;

Thus 15g of decomposed $CaCO_3$ gives $\frac{15\times44}{100}g = 6.6g$ of $CO_2(g)$

From ideal gas equation;

$$PV = nRT$$

From which;

$$P = \frac{nRT}{V} = \frac{mRT}{M_rV}$$

It follows that;

$$P_{CO_2} = \frac{6.6 \times 0.082 \times 1000}{44 \times 15} atm = 0.82atm$$

But from the given reaction equation;

$$K_p = P_{CO_2} = 0.82atm$$

The value of K_p is 0.82atm

Question 11

In which scenarios the following factors do not affect position of chemical equilibrium?

(i) Temperature
(ii) Concentration
(iii) Pressure
(iv) Catalyst

Solution

(i) When a reaction has (almost) zero heat of the reaction.

(ii) No scenario.

(iii) **First scenario:** When the reaction does not involve gas.

Second scenario: When reaction (even if it is involving gases) is not accompanied with change of number of gas particles.

(iv) Any scenario.

Question 12

When 2.98 moles of I_2 and 8.10 moles of H_2 are heated at constant volume at 444°C until equilibrium, 5.64moles of HI are formed. If we start with 5.3 moles of I_2 and 7.94 moles of H_2, how much HI is present at equilibrium at the same temperature?

$$I_2 \quad + \quad H_2 \quad \rightleftharpoons \quad 2HI$$

Solution

At equilibrium $\qquad 2.98 - x \quad 8.1 - x \qquad 2x$

$$K_c = \frac{[HI]^2}{[H_2\ ][I_2]} = \frac{4x^2}{(2.98 - x)(\ 8.1 - x)}$$

But $2x = 5.64$ (Amount of HI at equilibrium); $x = 2.82$

Substituting the value of *x* to above K_c expression gives $K_c = 37.65$

If we start with 5.3 moles of I_2 and 7.94 moles of H_2

$$I_2 \quad + \quad H_2 \quad \rightleftharpoons \quad 2HI$$

At equilibrium $\qquad 5.3 - x \quad 7.94 - x \qquad 2x$

Then;

$$37.65 = \frac{4x^2}{(5.3 - x)(\ 7.94 - x)}$$

Solving above equating gives;

$x = 4.62\text{mol}$ and $2x = 2 \times 4.62\text{ mol} = 9.24\text{mol}$

Hence number of moles of HI formed is 9.24moles

Question 13

Apply Arrhenius equation, $k = Ae^{-E_a/RT}$ to the forward and backward reactions, and show that a catalyst increases the rates of both reactions by the same factor.

Solution

(a) Let:

E_{afu} and E_{abu} be activation energy for uncatalysed forward and backward reaction respectively.

E_{afc} and E_{abc} be activation energy for catalysed forward and backward reaction respectively.

K_{fu} and K_{bu} be the rate constants for uncatalysed forward and backward reaction respectively.

K_{fc} and K_{bc} be the rate constant for catalysed forward and backward reaction respectively.

For uncatalysed reaction:

From Arrhenius equation; $\left(K = Ae^{-E_a/RT}\right)$

$K_{fu} = Ae^{-E_{afu}/RT}$ and $K_{bu} = Ae^{-E_{abu}/RT}$

For catalysed reaction:

From the Arrhenius equation;

$K_{fc} = Ae^{-E_{afc}/RT}$ and $K_{bc} = Ae^{-E_{abc}/RT}$

Then, the increasing factor for forward reaction rate;

$$\frac{R_{catalysed}}{R_{uncatlysed}} = \frac{K_{fc}}{K_{fu}} = \frac{Ae^{-E_{afc}/RT}}{Ae^{-E_{afu}/RT}} = e^{\frac{E_{afu}-E_{afc}}{RT}}$$

And the increasing factor for backward reaction rate;

$$\frac{R_{catalysed}}{R_{uncatlysed}} = \frac{K_{bc}}{K_{bu}} = \frac{Ae^{-E_{abc}/RT}}{Ae^{-E_{abu}/RT}} = e^{\frac{E_{abu}-E_{abc}}{RT}}$$

But;

$$E_{afu} - E_{afc} = E_{abu} - E_{abc} = \Delta E_a$$

Thus;

The forward reaction factor $=$ The backward reaction factor $= e^{\frac{\Delta E_a}{RT}}$

Hence the catalyst increases the rates of both forward and backward reactions by the same factor.

Question 14

Use the relation between the equilibrium constant and the forward and reverse rate constants, to show that a catalyst does not affect the value of the equilibrium constant.

Solution

Let: K_{cu} and K_{cc} be equilibrium constant for uncatalysed and catalysed reaction respectively.

Then using;

$$K_c = \frac{K_f}{K_b} = \frac{Ae^{-E_{af}/RT}}{Ae^{-E_{ab}/RT}} = e^{\frac{-(E_{af}-E_{ab})}{RT}}$$

But;

$$-(E_{af} - E_{ab}) = -\Delta H; \text{where } \Delta H \text{ is the heat of reaction}$$

Thus;

$$K_c = e^{\frac{-\Delta H}{RT}}$$

For uncatalysed reaction;

$$K_{cu} = e^{\frac{-H_u}{RT}}$$

For catalysed reaction;

$$K_{cc} = e^{-H_c/RT}$$

Then finding the ratio of K_c values for catalysed and uncatalysed reaction

$$\frac{K_{cu}}{K_{cc}} = \frac{e^{-H_u/RT}}{e^{-H_u/RT}} = e^{\left(\frac{H_c-H_u}{RT}\right)}$$

But $H_c = H_u$ and therefore; $H_c - H_u = 0$

Thus;

$$\frac{\mathrm{K_{cu}}}{\mathrm{K_{cc}}} = e^{0} = 1$$

Hence $\mathrm{K_{cu}} = \mathrm{K_{cc}}$ (catalyst does not change value of equilibrium constant).

Question 15

Write the chemical equation that has the following homogeneous equilibrium constant expression; $\mathrm{K_c} = \frac{[\mathrm{CO}]^2[\mathrm{O_2}]}{[\mathrm{CO_2}]^2}$

Solution

Reagent on the numerator of $\mathrm{K_c}$ expression appears as product in the equation while reagents in the denominator of the expression appear as reactant. That is $\mathrm{CO_2} \rightleftharpoons \mathrm{CO} + \mathrm{O_2}$

Powers in the concentration of each reagent are stoichiometric coefficients of the respective reagents in the equation: That is $2\mathrm{CO_2} \rightleftharpoons 2\mathrm{CO} + \mathrm{O_2}$
Hence the chemical equation corresponding to the given equilibrium constant expression is; $2\mathrm{CO_2} \rightleftharpoons 2\mathrm{CO} + \mathrm{O_2}$

Question 16

The equilibrium constant for the reaction is 9.40 at 900℃

$$\mathrm{S_2(g)} + \mathrm{C(s)} \rightleftharpoons \mathrm{CS_2(g)}$$

Calculate the pressure of two gases at equilibrium, when 1.42atm of $\mathrm{S_2}$ and excess of $\mathrm{C}(s)$ come to equilibrium.

Solution

Reaction equation:

$$\mathrm{S_2(g)} + \mathrm{C(s)} \rightleftharpoons \mathrm{CS_2(g)}$$

Initial pressure	1.42	0
Pressure at equilibrium	$1.42 - \mathrm{x}$	x

$$K_p = \frac{P_{CS_2}}{P_{S_2}} = \frac{x}{1.42 - x} = 9.4$$

Solving the above equation gives $x = 1.28\text{atm}$

Hence:

The partial pressure of CS_2 is 1.28atm

The partial pressure of S_2 is $1.42 - x = 1.42\text{atm} - 1.28\text{atm} = 0.14\text{atm}$

Question 17

Does adding amount of a component in a system of chemical equilibrium always shift equilibrium position? Give an explanation to justify your answer.

Solution

No.

Explanation:

Adding the amount of certain component in the chemical equilibrium will only shift the equilibrium position if it either changes concentration of reagents present in the equilibrium or changes their partial pressures.

Adding pure liquid or solid in the chemical equilibrium does not change the equilibrium position because they neither change the concentration nor appear in the equilibrium constant expression.

Also adding a gas like noble gas which does not react with gases (reagents) present in the equilibrium does not shift equilibrium position because the gas does not affect partial pressures of gases present in the equilibrium.

Question 18

Given the following information:

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)\ K_c = 6.8 \times 10^{-4}$

$H_2C_2O_4(aq) \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq) \quad K_c = 3.8 \times 10^{-6}$

Determine the value of K_c for the reverse reaction;

$2HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2F^-(aq) + H_2C_2O_4(aq)$

Solution

Given that

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) K_{C_1} = 6.8 \times 10^{-4} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (i)$

$H_2C_2O_4(aq) \rightleftharpoons 2H^+(aq) + C_2O_4^{2-}(aq) K_{C_2} = 3.8 \times 10^{-6} \ldots\ldots\ldots.. (ii)$

Taking 2(i) gives

$2HF(aq) \rightleftharpoons 2H^+(aq) + 2F^-(aq); K_{C_3} = \left(K_{C_1}\right)^2 \ldots\ldots\ldots\ldots..\ldots\ldots.. (iii)$

Revering (ii) gives;

$2H^+(aq) + C_2O_4^{2-}(aq) \rightleftharpoons H_2C_2O_4(aq);\ K_{C_4} = \frac{1}{K_{C_2}} \ldots\ldots\ldots\ldots.\ldots\ldots (iv)$

Taking (iii) + (iv) gives;

$2HF(aq) + 2H^+(aq) + C_2O_4^{2-} \rightleftharpoons 2H^+(aq) + 2F^-(aq) + H_2C_2O_4(aq)$

Or $2HF(aq) + C_2O_4^{2-}(aq) \rightleftharpoons 2F^-(aq) + H_2C_2O_4(aq);\ K_C = K_{C_3} \times K_{C_4}$

The required $K_c = \left(K_{C_1}\right)^2 \times \frac{1}{K_{C_2}} = (6.8 \times 10^{-4})^2 \times \frac{1}{3.8\times10^{-6}} = 0.1217$

Hence the K_c of the given reaction is 0.1217

Question 19

Alcohol reacts in reversible reaction with acid to form ester and water:

i.e. Alcohol + Acid $\rightleftharpoons$ Ester + water

When 1 mole of ethanol (ethyl alcohol) reacts with 1 mole ethanoic acid until equilibrium at certain temperature, 0.333 mole of each alcohol and acid and 0.666 mole of each ester and water will be present; calculate the amount of ester when:

(a) 3 moles of ethanol are mixed with 1 mole of ethanoic acid

(b) 92g of ethanol (r.m.m = 46) are mixed with 60g of ethanol acid (r.m.m = 60)

(c) 1 mole of ethanol is mixed with 1 mole of acid in presence of 1 mole of water.

Solution

$$K_c = \frac{[\text{Ester}][\text{Water}]}{[\text{Alcohol}][\text{Acid}]}$$

Where $[\quad] = \frac{n}{V}$

$$K_c = \frac{\left(\frac{0.666}{V}\right)\left(\frac{0.666}{V}\right)}{\left(\frac{0.333}{V}\right)\left(\frac{0.333}{V}\right)} = \frac{(0.666)^2}{(0.333)^2} = 4$$

(a)	Alcohol +	Acid	⇌	Ester +	Water
Initially	3	1		0	0
At equilibrium	$3-x$	$1-x$		x	x

$$K_c = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{3-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 4x + 3}$$

Since K_c does not depend on original amount of reagents present in the system then;

$$4 = \frac{x^2}{x^2 - 4x + 3};\ 4x^2 - 16x + 12 = x^2;$$

$$3x^2 - 16x + 12 = 0$$

$x = 0.9$ ($x = 4.43$ is not practical answer because it exceed the initial amount of alcohol and acid).

Hence the amount of ester is 0.9moles.

(b) Using $n = \frac{m}{M_r}$

Number of moles of ethanol = $\frac{92\text{g}}{46\text{gmol}^{-1}} = 2\text{mol}$

Number of moles of ethanoic acid = $\frac{60\text{g}}{60\text{gmol}^{-1}} = 1\text{mol}$

	Alcohol +	Acid	$\rightleftharpoons$	Ester +	Water
Initially	2	1		0	0
At equilibrium	$2-x$	$1-x$		x	x

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2-3x+2} = 4$$

Then: $3x^2 - 12x + 8 = 0$; $x = 0.8$

Amount of ester present at equilibrium is 0.8moles.

(c)

	Alcohol +	Acid	$\rightleftharpoons$	Ester +	Water
Initially	1	1		0	1
At equilibrium	$1-x$	$1-x$		x	$1+x$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{1+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2+x}{x^2-2x+1} = 4$$

Then; $4x^2 - 8x + 4 = x^2 + x$

Or $3x^2 - 9x + 4 = 0$; $x = 0.54$

Hence the amount of ester is 0.54moles.

Question 20

(a) Consider the equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\theta = +58kJ/mol$

In which direction will equilibrium shift when?

(i) N_2O_4 is added
(ii) NO_2 is removed
(iii) The total pressure is increased by addition of $N_2(g)$
(iv) The volume is increased
(v) The temperature is decreased

In each case give clear reason to support your answer.

Solution

(a)

(i) The equilibrium shifts to the right.

Reason

The system will adjust to decrease the concentration of the added N_2O_4 by shifting to the NO_2 side.

(ii) The equilibrium shifts to the right.

Reason

The system will adjust to the removal of NO_2 by shifting to the side that produces more NO_2.

(iii) No shift to the position of the equilibrium.

Reason

Although adding N_2 will increase the total pressure of the system, N_2 is not involved in the reaction. The partial pressures of NO_2 and N_2O_4 are therefore unchanged and hence there is no shift to the position of the equilibrium.

(iv) The equilibrium shifts to the right.

Reason

If the volume is increase, the pressure of the system is decreased in accordance to Boyle's law and therefore the equilibrium will shift in the direction that has more gas molecules.

(v) The equilibrium shifts to the left.

Reason

The reaction is endothermic, so we can imagine heat as a reagent on the reactant side of the question. Decreasing the temperature, will shift the equilibrium in the direction that produces heat, that is in the N_2O_4 side.

Question 21

1 mole of dinitrogen tetraoxide was allowed to dissociate to nitrogen dioxide gas in a flask of certain volume at 500K. At equilibrium 1 mole of nitrogen dioxide was found to be present. If the equilibrium constant for the reaction is 0.4molL^{-1}. Calculate the volume of the flask.

Solution

The reaction equation;

	$N_2O_4\,(g)$ $\rightleftharpoons$	$2NO_2(g)$
Initially	1	0
At equilibrium	$1-\ x$	2x

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)} = \frac{4x^2}{(1-x)V}$$

But at equilibrium 1mole of nitrogen dioxide was found to be present;

So $2x\ =\ 1$ or $x\ =\ 0.5$

Then;

$$K_c = 0.4\text{molL}^{-1} = \frac{4 \times 0.5^2\text{mol}^2}{V(1-0.5)\text{mol}}$$

From which; $V\ = 5L$

The volume of the flask is 5L

Question 22

The equilibrium constant expression for a gas reaction is,

$$K_c = \frac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$$

Write the balanced chemical equation corresponding to this expression.

Solution

$$4NO(g) + 6H_2O(g) \rightleftharpoons 4NH_3(g) +\ 5O_2(g)$$

Question 23

The value of K_c for the reaction:

Solution

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ at 750°C is 0.771. If 1 mole of hydrogen gas and 1 mole of carbon dioxide are mixed in 1 Litre container at 750°C; what are concentrations of all substances at equilibrium?

The reaction equation;

	H_2 (g) +	CO_2 (g) ⇌	H_2O (g) +	CO (g)
Initially	1	1	0	0
At equilibrium	1 – x	1 – x	x	x

$$K_c = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 2x + 1} = 0.771$$

Then, $0.229x^2 + 1.54x - 0.771 = 0; x = 0.4675$

Using [ ] = $\frac{n}{V}$

$[H_2O] = \frac{0.4675}{1} M = 0.4675M$

$[CO] = \frac{0.4675}{1} M = 0.4675M$

$[H_2] = \frac{(1-0.4675)}{1} M = 0.5325M$

$[CO_2] = \frac{(1-0.4675)}{1} M = 0.5325M$

Question 24

The following equation represents a reversible decomposition:

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

Under what condition(s) will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

Solution

The amount of $CaCO_3$ must be so small that even after its complete decomposition it produces small amount of CO_2 with partial pressure which is less than K_p.

Question 25

12g of acetic acid is heated with 18.6g of ethanol in $1dm^3$ flask at 298K. At equilibrium the amount of acetic acid which remains unreacted was found to be 1.8g. Calculate the equilibrium constant.

Solution

Initially: Number of moles of acetic acid = $\frac{12g}{60gmol^{-1}} = 0.2mol$

Number of moles ethanol = $\frac{18.6g}{46gmol^{-1}} = 0.4mol$

At equilibrium: Number of moles acetic acid = $\frac{1.8g}{60gmol^{-1}} = 0.03mol$

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Initially	0.2	0.4	0	0
At equilibrium	$0.2 - x$	$0.4 - x$	x	x

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.2-x}{V}\right)\left(\frac{0.4-x}{V}\right)} = \frac{x^2}{x^2 - 0.6x + 0.08}$$

But at equilibrium, number of moles of CH_3COOH is 0.03mol

Then $0.2 - x = 0.03$ or $x = 0.17$

Then; $K_c = \frac{0.17^2}{0.17^2 - (0.6 \times 0.17) + 0.08} = 4.1884$

Thus the equilibrium constant is 4.1884

Question 26

The following reaction occurs when a burner on a gas stove is lit:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

Solution

No.

Explanation

For the equilibrium to be established the reversible reaction must take place in a closed system. But in this case, the system is not closed as products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

Question 27

1 mole of hydrogen gas and 1 mole of iodine are mixed together in 1dm^3 flask and the reaction was allowed to establish the equilibrium at 473K. Calculate the percentage of HI if the equilibrium constant is 4.

Solution

	H_2 (g) +	I_2 (g)	⇌ $2HI$ (g)
Initially	1	1	0
At equilibrium	$1 - x$	$1 - x$	$2x$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{4x^2}{x^2 - 2x + 1} = 4$$

Then: $4x^2 = 4x^2 - 8x + 4$

From which; $8x = 4$ or $x = 0.5$

At equilibrium; $n_T = 1 - x + 1 - x + 2x = 2$

And $n_{HI} = 2x = 2 \times 0.5 = 1$

Then $\%HI = \frac{n_{HI}}{n_T} \times 100\% = \frac{1}{2} \times 100\% = 50\%$

Hence the percentage of HI is 50%

Question 28

A necessary step in the manufacture of sulphuric acid is the formation of sulphur trioxide, SO_3, from sulphur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

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

(i) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(ii) Is the reaction endothermic or exothermic?

Solution

(i) Decrease (Because the equilibrium amount is higher at lower temperature).

(ii) Exothermic

Question 29

6.22cm^3 of the gas G_2 was mixed with 5.6 cm^3 of the L_2 gas in 1dm^3 flask at 25°C. At equilibrium 9.66cm^3 of GL were found in the flask. Calculate the equilibrium constant.

The reaction equation is $G_2\ (g)\ +\ L_2\ (g)\ \rightleftharpoons\ 2GL\ (g)$

Solution

For gases: Mole ratio = volume ratio (This fact is derived from Avogadro's law).

Then the volume of each gas at equilibrium can be deduced as follows:

	$G_2\ (g)$	$+\ L_2\ (g)$	$\rightleftharpoons\ 2GL\ (g)$
Initially:	6.22	5.6	0
At equilibrium:	6.22 – x	5.6 – x	2x

Then; $K_c = \frac{[GL]^2}{[G_2][L_2]} = \frac{\left(\frac{n_{GL}}{V}\right)^2}{\left(\frac{n_{G2}}{V}\right)\left(\frac{n_{L2}}{V}\right)}$ where V is the volume of the flask

Then $K_c = \frac{(n_{GL})^2}{n_{G_2} \times n_{L_2}} = \frac{n_{GL}}{n_{G_2}} \times \frac{n_{GL}}{n_{L_2}}$

But $\frac{n_{GL}}{n_{G_2}} = \frac{V_{GL}}{V_{G_2}}$ and $\frac{n_{GL}}{n_{L_2}} = \frac{V_{GL}}{V_{L_2}}$ (From Avogadro's law)

Thus $K_c = \frac{V_{GL}}{V_{G_2}} \times \frac{V_{GL}}{V_{L_2}} = \frac{(2x)^2}{(6.22-x)(5.6-x)} = \frac{4x^2}{(6.22-x)(5.6-x)}$

But at equilibrium, 9.66 cm^3 of GL were found to be present in the flask.

Thus; $2x = 9.66$ or $x = 4.83$

Then $K_c = \frac{4\times4.83^2}{(6.22-4.83)(5.6-4.83)} = 87.2$

Hence the equilibrium constant is 87.2

Question 30

The equilibrium constant,K_c, for the reaction of hydrogen with iodine is 57 at 700K and the reaction is endothermic.

$$H_2(g) \quad + \quad I_2(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2HI(g); \quad K_c = 57 \text{ at } 700K$$

(a) Is the rate constant, K_f for the formation of HI larger or smaller than the rate constant, K_r for the decomposition of HI?

(b) The value of K_r at 700 is $1.16 \times 10^{-3}M^{-1}S^{-1}$. What is the value k_f at the same temperature?

(c) How are the values of k_f, k_r and K_c affected by the addition of a catalyst?

(d) How are the values of k_f, k_r and K_c affected by an increase in temperature?

Solution

(a) Because $K_c = \frac{k_f}{k_r} = 57$, the rate constant for the formation of HI (forward reaction) is larger than the rate constant for the decomposition of HI (reverse reaction) by a factor of 57.

(b) $K_c = \frac{k_f}{k_r}$

Substituting;

$$57 = \frac{k_f}{1.16 \times 10^{-3}M^{-1}S^{-1}}$$

From which $K_f = 6.61 \times 10^{-2}M^{-1}s^{-1}$

(c) A catalyst lowers the activation energy barrier for the forward and reverse reactions by the same amount, thus increasing the rate constants k_f and k_r by the same factor. Because equilibrium constant, K_c equals to the ratio of k_f to k_r the value of K_c is unaffected by addition of catalyst.

(d) Because the reaction is endothermic, the activation energy for the forward reaction is greater than activation energy for the reverse reaction. Consequently, as the temperature increases, k_f increases more than k_r, and therefore $K_c = \frac{K_f}{K_r}$ increases, consistent with Le – Chatelier's principle.

Question 31

For the reaction: $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)$

(a) Calculate the mole percentage of ammonia in the equilibrium mixture formed at 400°C and 3×10^7 Pa pressure when gaseous hydrogen and nitrogen are mixed in 3:1 mole ratio and there is 61% conversion of nitrogen to ammonia.

(b) Calculate the value of K_p in (a) above.

Solution

For 'a' moles of N_2 there are 3a moles of H_2, i.e. $n_{H_2}:n_{N_2} = 3:1$ (Given)

	$N_2\ (g)$	$+\ 3H_2\ (g)$	$\rightleftharpoons 2NH_3\ (g)$
Initially	a	3a	0
At equilibrium	$a - x$	$3a - 3x$	$2x$

At equilibrium: $n_T = (a - x) + (3a - 3x) + 2x = 4a - 2x$

$$\%NH_3 = \frac{n_{NH_3}}{n_T} \times 100\% = \left(\frac{2x}{4a - 2x}\right) \times 100\%$$

But $x = \frac{61a}{100} = 0.61a$

Then; $\%NH_3 = \frac{2\times0.61a}{4a-(2\times0.61a)} \times 100\% = \frac{1.22a}{2.78a} \times 100\% = 43.88\%$

(a) Percentage of ammonia is 43. 88%

$$P_{N_2} = X_{N_2}P_T = \left(\frac{a - x}{4a - 2x}\right) P_T$$

$$P_{H_2} = X_{H_2}P_T = \left(\frac{3a - 3x}{4a - 2x}\right) P_T$$

$$P_{NH_3} = X_{NH_3}P_T = \left(\frac{2x}{4a-2x}\right) P_T$$

Substituting x = 0.61a in each of the above expression for partial pressure:

$$P_{N_2} = \frac{0.39a}{2.78a} P_T = 0.14P_T$$

$$P_{H_2} = \frac{1.17a}{2.78a} P_T = 0.42P_T$$

$$P_{NH_3} = \frac{1.22a}{2.78a} P_T = 0.4388P_T$$

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{H_2}\right)^3\left(P_{N_2}\right)} = \frac{(0.4388P_T)^2}{(0.42P_T)^3(0.14P_T)} = \frac{18.56}{{P_T}^2}$$

But $P_T = 3 \times 10^7$ Pa

$$K_p = \frac{18.56}{(3 \times 10^7 Pa)^2} = 2.062 \times 10^{-14} Pa^{-2}$$

Hence K_p is $2.062 \times 10^{-14} Pa^{-2}$

Question 32

Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6H_2(g) \rightleftharpoons 4PH_3(g) \quad \Delta H = +110\text{kJ/mol}$$

Solution

1. Adding amount of P_4
2. Adding amount of H_2
3. Increasing temperature
4. Increasing pressure

Question 33

1.28 moles of dinitrogen tetraoxide (N_2O_4) was allowed to dissociate into nitrogen dioxide (NO_2) in a 5 litres vessel at 298K. At equilibrium 75% was found to be undissociated and the total pressure was 15 atm. What would be the degree of dissociation of N_2O_4 if the total pressure of the mixture was 10 atm?

Solution

Degree of dissociation is (100 – 75) % = 25%

	N_2O_4 (g) $\rightleftharpoons$	$2NO_2$ (g)
Initially	1.28	0
At equilibrium	$1.28 - x$	$2x$

Then $K_p = \dfrac{(P_{NO_2})^2}{(P_{N_2O_4})} = \dfrac{(X_{NO_2}P_T)^2}{X_{N_2O_4}P_T} = \dfrac{X_{NO_2}{}^2 P_T}{X_{N_2O_4}}$

But $n_T = (1.28 - x) + 2x = 1.28 + x$

So $X_{NO_2} = \frac{2x}{1.28+x}$

And $X_{N_2O_4} = \frac{1.28-x}{1.28+x}$

Then $K_p = \dfrac{\left(\dfrac{2x}{1.28 + x}\right)^2 P_T}{\left(\dfrac{1.28 - x}{1.28 + x}\right)} = \dfrac{4x^2 P_T}{1.28^2 - x^2}$

$$\text{Thus } K_p = \frac{4x^2 P_T}{1.6384 - x^2}$$

$$\text{But } x = \frac{25}{100} \times 1.28\text{moles} = 0.32\text{moles}$$

$$\text{And } P_T = 15\text{atm}$$

$$\text{Therefore: } K_p = \frac{4 \times 0.32^2 \times 15\text{atm}}{1.6384 - 0.32^2} = 4\text{atm}$$

If the total pressure, P_T is changed to 10atm, the value of K_p remains the same (K_p is only temperature dependent like K_c)

$$\text{Thus } K_p = 4 = \frac{10 \times 4x^2}{1.6384 - x^2} \quad \text{Or} \quad 40x^2 = 4 \times 1.6384 - 4x^2$$

$$\text{Or } 44x^2 = 4 \times 1.6384 = 6.5536$$

$$x = \sqrt{\frac{6.5536}{44}} = 0.386$$

$$\text{Degree of dissociation}, \alpha = \frac{\text{Number of moles dissociated}}{\text{Number of moles before dissociation}}$$

$$= \frac{0.386}{1.28} = 0.3 \text{ or } 30\%$$

Alternative solution:

Since the equilibrium constant does depend on initial amount of reagents present in the system, for simplifying the work we may assume 1 mole as initial amount of N_2O_4 instead of the given 1.28 moles.

It should be understood that:

When the initial amount is 1mole, numerical value of number of moles dissociated is equal to the numerical value for the degree of the dissociation, α

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

Initially	1	0
At equilibrium	1 – α	2α

$$\text{Then } K_p = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O_4}} = \frac{\left(X_{NO_2}P_T\right)^2}{X_{N_2O_4}P_T} = \frac{{X_{NO_2}}^2 P_T}{X_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}\right)^2 P_T}{\left(\frac{1-\alpha}{1+\alpha}\right)} = \boldsymbol{\frac{4\alpha^2 P_T}{1-\alpha^2}}$$

But $\alpha = \frac{25}{100} = 0.25$ and $P_T = 15\text{atm}$

$$\text{Then } K_p = \frac{4 \times 0.25^2 \times 15}{1 - 0.25^2}\text{atm} = 4\text{atm}$$

When $P_T = 10\text{atm}$

$4 = \frac{4\alpha^2 P_T}{1-\alpha^2} = \frac{10 \times 4\alpha^2}{1-\alpha^2} = \frac{40\alpha^2}{1-\alpha^2}$ or $44\alpha^2 = 4$ or $\alpha = 0.3$

Hence the degree of dissociation is 0.3 or 30%.

Question 34

0.8 moles of PCl_5 was allowed to dissociate to PCl_3 and Cl_2 in 5dm^3 vessels at 250°C. At equilibrium 60% of PCl_5 was found to dissociate completely and the total pressure was measured to be 30mmHg. Calculate:

(i) Equilibrium constant, K_p

(ii) What would be the total pressure if the degree of dissociation of PCl_5 was 35%?

Solution

Since the equilibrium constant does not depend on the initial amount of reagents present in the system, for simplifying the work we may assume the initial amount to be 1 mole instead of the given 0.8 moles.

Equilibrium for the reaction is:

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_5(g)$	$+\ Cl_2(g)$
Initially	1		0	0
At equilibrium	$1 - \alpha$		α	α

$$n_T = (1 - \alpha) + 2\alpha = 1 + \alpha.$$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{(X_{PCl_3}P_T)(X_{Cl_2}P_T)}{(X_{PCl_5}P_T)} = \frac{\left(\frac{\alpha}{1+\alpha}\right)P_T\left(\frac{\alpha}{1+\alpha}\right)P_T}{\left(\frac{1-\alpha}{1+\alpha}\right)P_T}$$

$$= \frac{\alpha^2 P_T}{1 - \alpha^2}$$

(i) When $\alpha = \frac{60}{100} = 0.6$

$$K_p = \frac{0.6^2 \times 30\text{mmHg}}{1 - 0.6^2} = 16.875\text{mmHg}$$

(ii) When $\alpha = \frac{35}{100} = 0.35$

Substituting the value of α to the above K_p expression;

$$16.875 = \frac{0.35^2 P_T}{1 - 0.35^2}$$

From which $P_T = 120.88\text{mmHg}$

Thus the total pressure would be 120.88mmHg.

Question 35

For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Comment on the magnitude of equilibrium constant(K_c) for this reaction?

Solution

100% yield implies that the magnitude of equilibrium constant is **infinitely large**.

Question 36

The reactions between carbon monoxide and hydrogen proceed according to the following equation:

$$CO\ (g)\ +\ 2H_2\ (g) \rightleftharpoons\ CH_3\,OH\ (g)$$

A dm^3 flask maintained at 700K, contain 0.1mole of carbon monoxide and suitable catalyst. When hydrogen is introduced into the flask until the equilibrium, the total pressure reaches 7atm and 0.06 moles of methanol is formed. Calculate the equilibrium constant, K_P.

Solution

Reaction equation;

	$CO\ (g) +$	$2H_2\ (g)$	$\rightleftharpoons$	$CH_3\,OH\ (g)$
Initially	0.1	a		0
At equilibrium	$0.1 - x$	$a - 2x$		x

$$n_T = (0.1 - x) + (a - 2x) + x = 0.1 - 2x + a$$

By Dalton's law of partial pressure; $P_T = P_{CO} + P_{H_2} + P_{CH_3OH}$

$$= \left(n_{CO} + n_{H_2} + n_{CH_3OH}\right)\frac{RT}{V}$$

Then $\frac{P_T V}{RT} = \left(n_{CO} + n_{H_2} + n_{CH_3OH}\right) = n_T$

So $\frac{7\times1}{0.082\times700} = 0.1 - 2x + a$

But $x = 0.06$

Then $0.122 = 0.1 - (2 \times 0.06) + a = n_T$ or $a = 0.142$

Thus the initial amount of H_2 was 0.142moles.

$$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} = \frac{X_{CH_3OH}P_T}{(X_{CO}P_T)(X_{H_2}P_T)^2} = \frac{\frac{n_{CH_3OH}}{n_T}P_T}{\left(\frac{n_{CO}}{n_T}P_T\right)\left(\frac{n_{H_2}}{n_T}P_T\right)^2}$$

$$= \frac{n_{CH_3OH} \times {n_T}^2}{n_{CO} \times {n_{H_2}}^2 \times {P_T}^2}$$

But $n_{CH_3OH} = x = 0.06$ moles

$n_{CO} = 0.1 - x = 0.1 - 0.06 = 0.04$moles

$n_{H_2} = a - 2x = 0.142 - (2 \times 0.06) = 0.022$mole

$n_T = 0.122$moles

And $n_T = 7$atm

Substituting $K_p = \frac{0.06 \times 0.122^2}{0.04 \times 0.022^2 \times (7\text{atm})^2} = 0.94\text{atm}^{-2}$

Alternative solution:

	$CO\ (g) +$	$2H_2\ (g)$	$\rightleftharpoons$	$CH_3\ OH\ (g)$
Initially	0.1			0
At equilibrium	$0.1 - x$			x

But $x = 0.06$moles

Then:

$n_{CO} = 0.1 - x = (0.1 - 0.06)$moles $= 0.04$moles

$$P_{CO} = \frac{n_{CO}RT}{V} = \frac{0.04 \times 0.082 \times 700\text{atm}}{1} = 2.296\text{atm}$$

$$P_{CH_3OH} = \frac{n_{CH_3OH}RT}{V} = \frac{0.06 \times 0.082 \times 700}{1} = 3.444\text{atm}$$

At equilibrium: $P_T = P_{CO} + P_{H_2} + P_{CH_3OH}$ (From Dalton's law of partial pressure)

$$7\text{atm} = 2.296\text{atm} + P_{H_2} + 3.444\text{atm}; \quad P_{H_2} = 1.26\text{atm}$$

$$K_p = \frac{P_{CH_3OH}}{(P_{CO})(P_{H_2})^2} = \frac{3.444\text{atm}}{(2.296\text{atm})(1.26\text{atm})^2} = 0.94\text{atm}^{-2}$$

Hence the equilibrium constant, K_p is 0.94atm^{-2}

Question 37

Ammonium hydrogen sulphide is allowed to dissociate into ammonia and hydrogen sulphide at 500K. At equilibrium the total pressure was measured to be 0.6atm. Calculate:

(i) The partial pressure of each

(ii) The equilibrium constant, K_p.

Solution

	$NH_4HS\,(s)$	$\rightleftharpoons$	$NH_3(g)$	$+$	$H_2S\,(g)$
Initially	a		0		0
At equilibrium	a – x		x		x

That is at equilibrium $n_{NH_3} = n_{H_2S}$ and hence $P_{H_2S} = P_{NH_3} = P$

$$\left(\begin{array}{c} \text{As } P_{H_2S} = \dfrac{n_{H_2S}RT}{V} \text{ and } P_{NH_3} = \dfrac{n_{NH_3}RT}{V}; \\ \text{so if } n_{H_2S} = n_{NH_3} \text{ then their respective partial pressures must be equal} \end{array} \right)$$

$$P_T = P_{NH_3} + P_{H_2S} = P + P = 2P; \text{thus } P = \frac{P_T}{2} = \frac{0.6\text{atm}}{2} = 0.3\text{atm}$$

Hence the partial pressure of NH_3 is 0.3atm and the partial pressure of H_2S is 0.3atm.

(ii) $K_p = P_{NH_3} \times P_{H_2S} = 0.3\text{atm} \times 0.3\text{atm} = 0.09\text{atm}^2$

Hence the equilibrium constant, K_p is 0.09atm^2

Question 38

Giving at least one example in each case, define the following:

(i) Homogeneous chemical equilibrium
(ii) Heterogeneous chemical equilibrium

Solution

(i) Homogeneous chemical equilibrium is the system of chemical equilibrium where by all reagents involved in the system are in the same phase.

Example: The reaction between hydrogen gas and nitrogen gas to form ammonia gas according to the following equation:

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

(ii) Heterogeneous chemical equilibrium is the system of chemical equilibrium where by reagents involved in the system are in different phase.

Example: The decomposition of solid ammonium chloride to form ammonia gas and hydrogen chloride gas.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

Question 39

Given that; $NH_4HS\ (s) \rightleftharpoons NH_3(g) + H_2S\ (g)$ and equilibrium constant is 0.108atm^2. A sample of NH_4HS is introduced into evacuated flask where it dissociated and establishes the equilibrium. Calculate the total pressure exerted by the gases in the flask.

Solution

(a) $K_p = P_{NH_3} \times P_{H_2S}$

But $P_{NH_3} = P_{H_2S} = P$

Then $K_p = P \times P = P^2$

$P = \sqrt{K_p} = \sqrt{0.108\text{atm}^{-2}} = 0.33\text{atm}$

By Dalton's law of partial pressure;

$P_T = P_{NH_3} + P_{H_2S} = 0.33\text{atm} + 0.33\text{atm} = 0.66\text{atm}$

Hence the total pressure exerted by gases in the flask is 0.66atm

Question 40

In the equilibrium: N_2O_4 (g) ⇌ $2NO_2$ (g); 3.2g of dinitrogen tetraoxide occupy a volume of 1dm^3 at 1×10^5Pa, and 25°C. Calculate:

(a) The degree of dissociation,

(b) The equilibrium constant, K_p.

Solution

Number of moles of $N_2O_4 = \frac{m}{M_r} = \frac{3.2}{92} = 0.035\text{moles}$

	N_2O_4 (g)	⇌	$2NO_2$ (g)
Initially	0.035		0
At equilibrium	0.035 – x		2x

$n_T = 0.035 - x + 2x = 0.035 + x$

By Dalton's law of partial pressure:

$$P_T = P_{N_2O_4} + P_{NO_2} = \frac{n_{N_2O_4}RT}{V} + \frac{n_{NO_2}RT}{V} = \left(n_{N_2O_4} + n_{NO_2}\right)\frac{RT}{V}$$

But $n_{N_2O_4} + n_{NO_2} = n_T$

$$\text{Then } P_T = \frac{n_TRT}{V} \text{ or } n_T = \frac{P_TV}{RT} = \frac{10^5 \times 10^{-3}}{8.314 \times 298} = 0.04 = 0.035 + x$$

From which; x = (0.04 – 0.035) moles = 0.005moles

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Original number of moles before dissociation}}$$

$$= \frac{0.005}{0.035} = 0.14 \text{ or } 14\%$$

Hence the degree of dissociation is 0.14 or 14%

	N_2O_4 (g)	$\rightleftharpoons$	$2NO_2$ (g)
Initially	1		0
At equilibrium	$1 - \alpha$		2α

$$n_T = 1 - \alpha + 2\alpha = 1 + \alpha; \; K_p = \frac{\left(P_{NO_2}\right)^2}{\left(P_{N_2O_4}\right)} = \frac{\left(X_{NO_2}P_T\right)^2}{\left(X_{N_2O_4}P_T\right)} = \frac{X_{NO_2}{}^2 P_T}{X_{N_2O_4}}$$

Substituting values for mole fractions of NO_2 NO_2 and N_2O_4 to above K_p expression gives:

$$K_p = \frac{4\alpha^2 P_T}{1-\alpha^2} = \frac{4\times 0.14^2 \times 10^5}{1-0.14^2}\text{Pa} = 7.9967 \times 10^3 \text{Pa}$$

Hence the equilibrium constant, K_p is 7.9967×10^3Pa

Question 41

(a) The expression for an equilibrium constant, K_c, for a homogeneous equilibrium reaction is given below.

$$K_c = \frac{[A]^3[B]^2}{[C]^4[D]^3}$$

(i) Write an equation for the forward reaction.

(ii) Deduce the units of K_c

(iii) State what can be deduced from the fact that the value of K_c is larger when the equilibrium is established at a lower temperature.

Solution

(i) $4C + 3D \rightleftharpoons 3A + 2B$

(ii) $\text{Units of } K_c = \frac{(\text{Units of }[A])^3(\text{Units of }[B])^2}{(\text{Units of }([C])^4(\text{Units of }[D])^3}$

$$\text{Units of } K_c = \frac{(\text{moldm}^{-3})^3(\text{moldm}^{-3})^2}{(\text{moldm}^{-3})^4(\text{moldm}^{-3})^3} = (\text{moldm}^{-3})^{-3} = \mathbf{dm^9mol^{-3}}$$

The reaction is exothermic

Question 42

Consider the reaction: $N_2O_4(g) \rightleftharpoons 2NO_2(g); K_p = 0.131\text{atm}$

A flask initially contains $N_2O_4(g)$ at 1.00atm pressure. Calculate the pressures of $NO_2(g)$ and $N_2O_4(g)$ at equilibrium.

Solution

Since partial pressures of gases, varies directly proportional to the number of moles,

$$\text{mole ratio} = \text{pressure ratio}$$

Thus pressures can be treated like moles as follows;

	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
Pressure of each at $t = 0$	1	0
Pressure of each at equilibrium	$1 - x$	$2x$

Then $$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(2x)^2}{1-x} = \frac{4x^2}{1-x} = 0.131$$

From which $4x^2 + 0.131x - 0.131 = 0$

Solving above equation gives practical value of $x = 0.165$($x = -0.198$ is ignored because pressure value cannot be negative).

Hence at equilibrium;

Pressure of $N_2O_4 = 1 - x = 1 - 0.165\text{ atm} = 0.835\text{atm}$

Pressure of $NO_2 = 2x = 2 \times 0.165\text{ atm} = 0.33\text{ atm}$

Question 43

(a) The manufacture of sulphuric acid is carried out on a large scale in most industrialised countries because it is needed by many other industries. In most countries the raw material is sulphur. The process consists of three main stages: the burning of sulphur in air, the conversion of sulphur dioxide to sulphur trioxide and the formation of sulphuric acid. The equation for the conversion to sulphur trioxide is;

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

(i) The conversion to sulphur trioxide is favoured by low temperature. Is the reaction exothermic or endothermic? Explain.

(ii) Give the name of the catalyst used in this reaction. State the effect of the catalyst on the percentage yield at equilibrium of sulphur trioxide and on the rates of both forward and reverse reactions.

(iii) A typical operating temperature is 450 °C. State **one** advantage and **one** disadvantage of operating the process at a temperature $50°C$ lower.

Solution

Exothermic

Explanation

If the temperature is lowered the system must respond in accordance to Le-Chatelier's principle by producing heat (exothermic process) to compensate the amount of the heat lowered. Since the low temperature also favour the formation of sulphur trioxide, the conversion must be exothermic too.

(i) **Name:** Vanadium(V) oxide.

Effect on the yield: No effect.

Effect on the rate: It increases the rate of both forward and backward reaction by equal amount.

(ii) **Advantage:** High yield of sulphur trioxide is obtained.

Disadvantage: Slow rate of producing sulphur trioxide.

Question 44

A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.82L and heated to 1000K until equilibrium is reached.The equilibrium constant for the reaction $\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$ is $4 \times 10^{-2}\mathrm{atm}$ at this temperature. Calculate the mass of CaO present at equilibrium.

Solution

Given that; $\mathrm{CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)}$

From which;$\mathrm{K_p = P_{CO_2}}$

Thus $\mathrm{P_{CO_2}}$ at 1000K was $4 \times 10^{-2}\mathrm{atm} = \mathrm{K_p}$

From ideal gas equilibrium; $\mathrm{n = \frac{PV}{RT}}$

Thus number of moles of $\mathrm{CO_2}$ at equilibrium will be given by;

$$\mathrm{n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{4\times10^{-2}\times0.82}{0.082\times1000}}\ \text{ or } 4 \times 10^{-4}\mathrm{mol}$$

Since initially there were no $\mathrm{CO_2}$ in the container, number of moles of $\mathrm{CO_2}$ produced in the reaction will be equal to the number of moles of the $\mathrm{CO_2}$ at the equilibrium.

Thus $\mathrm{n_{CO_2}}$produced in the reaction,$= 4 \times 10^{-4}\mathrm{mol}$
From the stoichiometric of the reaction, mole ratio of $\mathrm{CO_2}$ to CaO is 1:1

Thus $\mathrm{n_{CO_2}}$produced=$\mathrm{n_{CaO}}$ produced$= 4 \times 10^{-4}\mathrm{mol}$
Using $\mathrm{m = nM_r}$; mass of $\mathrm{CaO} = 4 \times 10^{-4} \times 56$ or$0.0224\mathrm{g}$

Question 45

0.04 moles of $\mathrm{SO_3}$ was allowed to dissociate in 3 Litres vessel at 900K. At equilibrium the amount of $\mathrm{SO_3}$ present is found to be 0.0284 moles

(i) Derive the relationship between $\mathrm{K_c}$and $\mathrm{K_p}$

(ii) Calculate $\mathrm{K_c}$ and $\mathrm{K_p}$

Solution

Equation for the reaction is: $2SO_3\ (g) \rightleftharpoons 2SO_2\ (g) + O_2\ (g)$

$$K_p = \frac{\left(P_{SO_2}\right)^2\left(P_{O_2}\right)}{\left(P_{SO_3}\right)^2}$$

But from ideal gas equation: $PV = nRT$; $P = \left(\frac{n}{V}\right)RT$

But $\frac{n}{V} = [\quad]$; so $P = [\quad]RT$

$$\text{Then } K_p = \frac{([SO_2]RT)^2([O_2]RT)}{([SO_3]RT)^2} = \frac{[SO_2]^2[O_2]RT}{[SO_3]^2}$$

$$\text{But } \frac{[SO_2]^2[O_2]}{[SO_3]^2} = K_c$$

Hence $K_p = \quad K_cRT$

	$2SO_3\ (g)$	$\rightleftharpoons$	$2SO_2\ (g)$	$+\ O_2\ (g)$
Initially	0.04		0	0
At equilibrium	$0.04 - 2x$		$2x$	x

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{\left(\frac{2x}{V}\right)^2\left(\frac{x}{V}\right)}{\left(\frac{0.04-2x}{V}\right)^2}$$

But $0.04 - 2x = 0.0284 = 0.0058$

$$\text{Thus } K_c = \frac{4 \times 0.0058^3}{(0.04 - (2 \times 0.0058))^2 \times 3} = 3.225 \times 10^{-4}\text{moldm}^{-3}$$

But from (i); $K_p = K_c\ RT$

Where $R = 0.082$ and $900K$

Then $K_p = 3.225 \times 10 - 4 \times 0.0082 \times 900\text{atm} = 0.0238\text{atm}$

Hence $K_p = 0.0238\text{atm}$

Question 46

0.196g of nitrogen gas was reacted with 0.14g of hydrogen in 1 litre flask at 500K. At equilibrium the total pressure was found to be 10% less than the original pressure. Calculate:

(i) K_p for the reaction
(ii) Percentage volume of each gas

Solution

Using $n = \frac{m}{M_r}$

Number of moles of nitrogen gas $= \frac{0.196}{28}\text{moles} = 0.007\text{moles}$

Number of moles hydrogen gas $= \frac{0.14\text{moles}}{2} = 0.07\text{moles}$

	$N_2\,(g)$	$+\ 3H_2(g)$	$\rightleftharpoons\ 2NH_3\,(g)$
Initially	0.007	0.07	0
At equilibrium	$0.007 - x$	$0.07 - 3x$	$2x$

$$n_T = (0.007 - x) + (0.07 - 3x) + 2x$$
$$= 0.077 - 2x \text{ (At equilibrium)}$$

n_T before the reaction $= (0.007 + 0.07) = 0.077\text{moles}$

From ideals gas equation $P = \frac{nRT}{V}$

So before the reaction: $P_o = \frac{0.077RT}{V}$

At equilibrium $P_{eq} = \frac{(0.077-2x)RT}{V}$

But $P_{eq} = \frac{90}{100}P_o = 0.9P_o$

Then $\frac{0.9P_o}{P_o} = \frac{(0.077-2x)RT}{V} \div \frac{0.077RT}{V} = \frac{0.077-2x}{0.077} = 0.9$

$$0.077 - 2x = 0.077 \times 0.9$$

$$2x = 0.0077; \quad x = 0.00385.$$

From the equation for the reaction:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{0.007 - x}{V}\right)\left(\frac{0.07 - 3x}{V}\right)^3}$$

$$= \frac{V^2 \times 4x^2}{(0.007 - x)(0.07 - 3x)^3}$$

$$= \frac{1 \times 4 \times 0.00385^2}{(0.007 - 0.00385)\big(0.07 - (3 \times 0.00385)\big)^3} = 94.26\mathrm{dm^6mol^{-2}}$$

Using $K_p = K_c\,(RT)^{\,n-m}$

Where: n is the number of molecules in the products side = 2

m is the number of molecules in the reactants side = 4

$K_p = K_c\,(RT)^{\,2-4} = K_c\,(RT)^{\,-2}$

But $K_c = 94.26\ \mathrm{dm^6\ mol^{-2}}$, $R = 0.082$, $T = 500K$

Thus $K_p = 94.26 \times (0.082 \times 500)^{-2}\ \mathrm{atm^{-2}} = 0.056\mathrm{atm^{-2}}$

Hence the Kp for the reaction is $0.056\mathrm{atm^{-2}}$

(iii) At equilibrium:

$n_T = 0.077 - 2x = 0.077 - (2 \times 0.00385) = 0.0693\text{moles}$

Since volume ratio = mole ratio (The relationship is true only for gases according to Avogadro's law)

Then: $\%NH_3 = \frac{n_{NH_3}}{n_T} \times 100\% = \frac{2 \times 0.00385}{0.0693} \times 100\% = 11.11\%$

Thus the percentage of ammonia by volume is 11.11%

$$\%N_2 = \frac{n_{N_2}}{n_T} \times 100\% = \frac{(0.007 - x)}{n_T} \times 100\%$$

$$= \frac{(0.007 - 0.00385)}{0.0693} \times 100\% = 4.5\%$$

Hence the percentage by volume of N_2 is 4.5%

$$\%H_2 = \frac{n_{H_2}}{n_T} \times 100\% = \frac{(0.07 - 3x)}{n_T} \times 100\%$$

$$= \frac{\big(0.07 - (3 \times 0.00385)\big)}{0.0693} \times 100 = 84.34\%$$

Hence the percentage by volume of H_2 is 84.34%

Question 47

At 400℃ the value of K_c for the reaction:

$N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$ is $0.509\text{dm}^6\text{mol}^{-2}$.

If 2.5 moles of N_2, 7.5moles of H_2 were introduced into 2.5 Litres flask and in the pressure of catalyst allowed coming to equilibrium at 400℃.

(i) What would be the equilibrium concentration of each gas?
(ii) What is the value of K_P for the reaction?

Solution

	N_2 (g) +	$3H_2$(g) ⇌	$2NH_3$ (g)
Initially	2.5	7.5	0
At equilibrium	2.5 – x	7.5 – 3x	2x

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{2.5 - x}{V}\right)\left(\frac{7.5 - 3x}{V}\right)^3} = \frac{V^2 \times 4x^2}{(2.5 - x)\big(3(2.5 - x)\big)^3}$$

Thus $K_c = \frac{V^2 \times 4x^2}{27(2.5 - x)^4} = 0.509$

Then $\sqrt{\frac{V^2 \times 4x^2}{27(2.5 - x)^4}} = \sqrt{0.509}$; $\quad \frac{V \times 2x}{5.196(2.5 - x)^2} = 0.713$

Substituting V = 2.5L and simplifying above equation gives;

$3.7x^2 - 23.52x + 23.155 = 0$; $x = 1.22$

Using $[\quad] = \frac{n}{V}$

Thus at equilibrium:

$$[N_2] = \frac{2.5 - x}{V} = \frac{2.5 - 1.22}{2.5} = 0.512M$$

$$[H_2] = \frac{7.5 - 3x}{V} = \frac{7.5 - (3 \times 1.22)}{2.5} = 1.536M$$

$$[NH_3] = \frac{2x}{V} = \frac{2 \times 1.22}{2.5} = 0.976M$$

$K_p = K_c(RT)^{n-m}$ where $n = 2$ and $m = 4$

Then $K_p = 0.509 \times (0.082 \times 673)^{-2}atm^{-2} = 1.67 \times 10^{-4}atm^{-2}$

The K_p for the reaction is $1.67 \times 10^{-4}atm^{-2}$

Question 48

What is the chemical equilibrium?

Solution

Is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction. It is the state in which both reactants and products are simultaneously consumed and produced by the same speed such that their concentrations remain unchanged.

Question 49

What are necessary conditions for chemical equilibrium to be established?

Solution

Conditions which favour the formation of chemical equilibrium are:

1. The system (reaction) must be reversible.
2. The reaction should take place in a closed system, that is; no material is allowed to enter or to leave the system.

Question 50

A 1200°C, the following equilibrium is established between chlorine atoms and molecules;

$$Cl_2(g) \rightleftharpoons 2Cl(g)$$

The composition of the equilibrium mixture may be determined by measuring the rate of effusion of the mixture through a pin hole. It is found that at 1200°C and 1atm pressure; the mixture effuses 1.16 times as fast as krypton effuses under the same condition. Calculate the equilibrium constant, K_c.

Solution

Conditions which favour the formation of chemical equilibrium are:

The system (reaction) must be reversible.

The reaction should take place in a closed system, that is; no material is allowed to enter or to leave the system.

If M_m and M_{Kr} represents molar mass of the mixture and krypton respectively,

And R_m and R_{Kr} represents rate of diffusion of the mixture and krypton respectively.

Then $\frac{R_{Kr}}{R_m} = \sqrt{\frac{M_m}{M_{Kr}}}$

Or $\quad M_m = M_{Kr}\left(\frac{Rkr}{Rm}\right)^2$

But $\frac{Rm}{Rkr} = 1.16 \quad$ or $\quad \frac{R_{Kr}}{R_m} = \frac{1}{1.16}$

Then $M_m = 84 \times \left(\frac{1}{1.16}\right)^2 = 62.4257 g/mol$

Considering the dissociation of Cl_2;

Van’t Hoff’s factor, $i = \frac{\text{Expected molar mass}}{\text{Observed molar mass}} = \frac{71}{62.4257} = 1.1374$

And degree of dissociation, $\alpha = \frac{i-1}{N-1} = \frac{1.1374-1}{2-1} = 0.1374$

It follows that: $Cl_2(g) \rightleftharpoons 2Cl(g)$

At equilibrium; $1-\alpha \qquad 2\alpha$

$$K_p = \frac{(P_{Cl})^2}{P_{Cl_2}} = \frac{(X_{Cl}P_T)^2}{X_{Cl_2}P_T} = \frac{(X_{Cl})^2\,P_T}{X_{Cl_2}}$$

But $X_{Cl} = \frac{n_{Cl}}{n_T} = \frac{2\alpha}{1+\alpha} = \frac{2\times0.1374}{1+0.1374} = 0.2416$

And $X_{Cl_2} = \frac{n_{Cl_2}}{n_T} = \frac{1-\alpha}{1+\alpha} = \frac{1-0.1374}{1+0.1374} = 0.7584$

Substituting $K_p = \frac{(0.2416)^2\times1atm}{0.7584} = 0.077atm$

Using; $K_c = K_p(RT)^{m-n} = 0.077 \times (0.82 \times 1473)^{-1}moldm^{-3}$

$= 6.37 \times 10^{-4}moldm^{-3}$

Hence the equilibrium constant,$K_c = 6.37 \times 10^{-4}moldm^{-3}$

Question 51

Sulphuric acid is manufactured by the contact process which makes use of the equilibrium reaction: $SO_2 + O_2 \rightleftharpoons 2SO_3$

(a) Heat is given out in the formation of sulphur trioxide. State what effect there would be on the equilibrium concentration of sulphur trioxide if:
   (i) The pressure were increased.
   (ii) The temperature were raised.

(b) At 450°C, K_c for hydrogen iodide synthesis is 50.5.You place 1×10^{-2}moles of hydrogen, 3×10^{-2} moles of iodine and 2×10^{-2}moles of hydrogen iodide in a 2 litres container at 450°C. In which direction the reaction, $H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$ proceed in order to reach the equilibrium

Solution

(a)

(i) Concentration of sulphur trioxide will be increased (the forward reaction proceed with reduction of volume, thus increasing pressure will shift the position of equilibrium to the right and hence the production of SO_3 will be increased).

(ii) Concentration of sulphur trioxide will be decreased (since heat is given out; the forward reaction is exothermic so increase in temperature shifts position of equilibrium to the left and hence the production of SO_3 will be decreased).

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2 \times 10^{-2}}{V}\right)^2}{\left(\frac{1 \times 10^{-2}}{V}\right)\left(\frac{3 \times 10^{-2}}{V}\right)} = 1.33$$

But $K_c = 50.5$; thus $Q_c < K_c$

Hence the reaction will proceed to the right hand side to reach the equilibrium.

Question 52

At 400°C, the three gases, hydrogen, iodine and hydrogen iodide exist together in equilibrium. The equation for the reaction is;

$$H_2 + I_2 \rightleftharpoons 2HI$$

What effect will an increase in pressure have on the position of equilibrium?

Solution

Increase in pressure has no effect on position of chemical equilibrium because the reaction does not accompany with change in volume of the reagents.

Question 53

The solution containing $0.2MFe^{2+}, 0.1MAg^{+}$ and $0.5MFe^{3+}$ were mixed together with silver and the reaction was left to establish the equilibrium. Calculate the percentage of each reagent at equilibrium if the equilibrium reaction is formed as follows:

$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$; Given that $K_c = 4$

Solution

Calculating Q_c so as to determine the position of chemical equilibrium,

$$Q_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]} = \frac{0.5}{0.2\times0.1} = 25$$

But $K_c = 4$

Thus $Q_c > K_c$ and hence the position of the chemical equilibrium shift to the left so as to establish the equilibrium (backward reaction is more favoured).

	$Fe^{2+}(aq)$ +	$Ag^{+}(aq)$ $\rightleftharpoons$	$Fe^{3+}(aq)$ + $Ag(s)$
Initially	0.2	0.1	0.5
At equilibrium	$0.2 + x$	$0.1 + x$	$0.5 - x$

$$K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]} = \frac{0.5 - x}{(0.2 + x)(0.1 + x)} = \frac{0.5 - x}{x^2 + 0.3x + 0.02} = 4$$

$4x^2 + 1.2x + 0.08 = 0.5 - x$

Or $4x^2 + 2.2x - 0.42 = 0$; $x = 0.15$

$n_{Fe^{2+}} = 0.2 + x = (0.2 + 0.15)$ moles $= 0.35$moles

$n_{Ag^{+}} = 0.1 + x = (0.1 + 0.15)$ moles $= 0.25$moles

$n_{Fe^{3+}} = 0.5 - x = (0.5 - 0.15)$ moles $= 0.35$moles

$n_T = (0.35 + 0.25 + 0.35)$ moles $= 0.95$moles

$$\%Fe^{2+} = \frac{n_{Fe^{2+}}}{n_T} \times 100\% = \frac{0.35}{0.95} \times 100\% = 36.842\%$$

$$\%Ag^{+} = \frac{n_{Ag^{+}}}{n_T} \times 100\% = \frac{0.25}{0.95} \times 100\% = 26.316\%$$

$$\%Fe^{3+} = \frac{n_{Fe^{3+}}}{n_T} \times 100\% = \frac{0.35}{0.95} \times 100\% = 36.842\%$$

Hence: Percentage of Fe^{2+} is 36.842%

Percentage of Ag^+ is 26.316%

Percentage of Fe^{3+} is 36.842%

Question 54

Nitrogen, hydrogen and oxygen undergo the reaction shown below:

Reaction 1: $^1/_2\, N_2(g) + {}^1/_2\, O_2(g) \rightleftharpoons NO(g) \qquad \Delta H_f^\theta = +91KJmol^{-1}$

Reaction 2: $^1/_2\, N_2(g) + 1\, {}^1/_2\, H_2(g) \rightleftharpoons NH_3(g) \quad \Delta H_f^\theta = -46KJmol^{-1}$

Reaction 3: $H_2(g) + {}^1/_2\, O_2(g) \rightleftharpoons H_2O(g) \qquad \Delta H_f^\theta = -242KJmol^{-1}$

Use this information in answering the question below:

(a) In which, if any, of the reaction above would the percentage yield of products at equilibrium increase if the temperature were to be raised? Explain your answer.

(b) In which, if any, of the reactions above would the percentage yield of products at equilibrium not increase if the pressure were to be raised? Explain your answer.

(c)
  (i) In which direction, if any would any equilibrium reaction move if $\Delta H = 0$ and the temperature were to be decreased?
  (ii) Predict for which of the reactions above the percentage yield of products at equilibrium would be most affected by a change in temperature. Explain your answer.

Solution

(a) Reaction 1

Explanation

The forward reaction is endothermic. So according to Le-Chatelier's principle, increase in temperature (which in turn increases heat at initial stage) will shift the position of equilibrium to the right hand side so as to absorb the added heat energy.

(b) Rection 1

Explanation

The reaction is not accompanied with change in number of moles of gas molecules which in turn means the reaction does neither increase nor decrease the pressure and hence pressure has no effect on the equilibrium.

(c)

(i) None

(ii) Reaction 3

Explanation

The reaction has greatest enthalpy change and hence more affected with the change in temperature

Question 55

The equation for the reaction by which ammonia is manufactured is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(a) What would be the effect on the equilibrium concentration of ammonia of

(i) Increasing the pressure

(ii) Increasing the nitrogen concentration

(b) The equilibrium concentration of ammonia increases as the temperature is lowered. Is heat evolved or absorbed when ammonia is formed?

(c) Why is a catalyst used in this reaction?

Solution

(a) (i) Concentration of ammonia will be increased

(ii) Concentration of ammonia will be increased

(b) Heat is evolved (low temperature favours forward reaction of exothermic reaction)

(c) High percentage yield of ammonia is ensured by employing low temperature; but at low temperature the rate of the production of the gas is very slow and hence catalyst must be employed to increase the rate of production of the ammonia gas by enabling the equilibrium to be reached earlier.

Question 56

In the Haber process for manufacture of ammonia, nitrogen and hydrogen react as shown in the equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H^{\theta} = -92\text{kJ/mol}$$

The table shows the percentage yield of ammonia, under different conditions of pressure and temperature when the reaction has reached dynamic equilibrium.

Temperature/ K	600	800	1000
% yield of ammonia at 10MPa	50	10	2
% yield of ammonia at 20MPa	60	16	4
%yield of ammonia at 50MPa	75	25	7

(a) Explain the meaning of the term **dynamic equilibrium**.

(b) Use Le-Chatelier's principle to explain why, at given temperature, the percentage yield of ammonia increases with an increase in overall pressure.

(c) Give reason why a high pressure of 50MPa is not normally used in the Haber process although it gives better yield?

(d) Many industrial ammonia plants operate at a **compromise temperature** of about 800K.

  (i) State and explain, by using Le-Chatelier's principle one advantage of using temperature lower than 800K

  (ii) State the major advantage of using a temperature higher than 800K

  (iii) Hence (from (i) and (ii) above) explain why 800K is referred as a **compromise temperature**.

Solution

(a) It is the balance of the rate of the two reactions (forward and reverse reaction) which are proceeding at the same time in opposite directions. It is an equilibrium involving the constant interchange of particles in motion in opposite directions of forward and reverse reaction.

(b) System of chemical equilibrium opposes the change. So increase in pressure shifts the position of chemical equilibrium to the side with fewer moles ($NH_3 -$ side) so as to decrease the pressure.

(c) Too expensive to generate such high pressure (50MPa) and therefore is not economic.

(d)

(i) Yield of ammonia increases

Explanation

The forward reaction is exothermic. So according to the Le-Chatelier's principle, the decrease in temperature will shift the position of equilibrium to the $NH_3 -$ side so as increase the temperature.

(ii) Increase the rate of producing NH_3.

(iii) Balance between **rate** of producing NH_3 and **yield** of NH_3 (This means good yield of NH_3 is obtained at reasonable rate).

Question 57

The reaction $N_2 + O_2 \rightleftharpoons 2NO$ is reversible and (from left to right) endothermic, all reagents being gaseous. If the system is in equilibrium which (at temperature which allows quite rapid reaction), what if any, will be the effect on the equilibrium of:

(a) Doubling the total pressure.

(b) Doubling the pressure of nitrogen.

(c) Lowering temperature slightly.

(d) Explain briefly why this reaction (when used industrially) was not catalysed? What alternative was available?

Solution

(a) Has no effect.

(b) Position of chemical equilibrium will shift to right because doubling the pressure of nitrogen gas, doubles its concentration so to lower the added concentration the equilibrium must shift to the right by producing more NO

(c) Position of equilibrium will shift to the left.

(d) Since the forward reaction is endothermic, the production of NO (forward reaction) is favoured by high temperature which also increases the rate of production of NO at the same time. So industrially, they employ high temperature.

Question 58

(a) Two solid allotropes A and B of densities 2.07 and 1.97gcm^{-3} respectively are in equilibrium according to ;

$$\text{A(s)} \rightleftharpoons 2\text{B(s)}\ \Delta\text{H} = +0.4\text{kJmol}^{-1}$$

What is the effect of pressure in above equilibrium?

Solution

Has no effect because pressure has no effect in reaction whose reagents are in solid phase which are always incompressible.

Question 59

An analysis of the gaseous phase ($\text{S}_2\text{(g)}$ and $\text{CS}_2\text{(g)}$) present at equilibrium at $1000°\text{C}$ in the reaction; $\text{C(s)} + \text{S}_2\text{(g)} \rightleftharpoons \text{CS}_2\text{(g)}$; shows it to be 13.71% C and 86.29% S, by mass. What is K_c for this reaction?

Solution

$$\text{Mass of C in 100g of gases} = 13.71\text{g}$$

$$\text{Number of moles of C atoms in CS}_2 = \frac{13.71\text{g}}{12\text{gmol}^{-1}} = 1.14\text{mol}$$

But 1mol of CS_2 contains 1mol of C; so number of moles of CS_2 is also 0.18mol

Also 1mol of CS_2 contains 2mol of S atoms; so number of moles of S atoms in $CS_2 = 2 \times 1.14\text{mol} = 2.28\text{mol}$

Mass of S in 100g of gases $= 86.29\text{g}$

Total number of moles of S atoms $= \dfrac{86.29\text{g}}{32\text{gmol}^{-1}} = 2.7\text{mol}$

Number of moles of S atoms in S_2

$= $ Total number of moles of S atoms $-$ Number of moles of S atoms in CS_2

$= (2.7 - 2.28)\text{mol} = 0.42\text{mol}$

Number of moles of S_2 molecules $= \dfrac{0.42\text{mol}}{2} = 0.21\text{mol}$

Then from $C(s) + S_2(g) \rightleftharpoons CS_2(g)$;

$$K_c = \frac{[n_{CS_2}]}{[n_{S_2}]} = \frac{\frac{n_{CS_2}}{V}}{\frac{n_{S_2}}{V}} = \frac{n_{CS_2}}{n_{S_2}} = \frac{1.14\text{mol}}{0.21\text{mol}} = 5.4$$

Question 60

(a) Consider the reaction:

$$X_2(g) + 3Y_2(g) \rightleftharpoons 2XY_3(g) \qquad \Delta H = -92\text{kJ/mol}$$

Is the production of XY_3 favoured by low or large volume of the flask? Explain.

Solution

(a) The production of the given gas is favoured by low volume of the flask.

Explanation

The reaction is accompanied with decrease of volume from the left to the right so the forward reaction (production of XY_3) is favoured by high pressure and from Boyle's law whereby pressure varies inversely proportional to the volume; high pressure is obtained when the volume of flask is low.

Question 61

Consider the following reaction: $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$

If nitrosyl bromine (NOBr) is 33.33% dissociated at $25°C$ and a total pressure is 0.28atm. Calculate K_p for the dissociation at this temperature.

Solution

Reaction equation:

	$2NOBr(g) \rightleftharpoons$	$2NO(g) +$	$Br_2(g)$
Initial pressure	P	0	0
Pressure at equilibrium	$P - 2x$	$2x$	x

Where $P_T = P - 2x + 2x + x = P + x = 0.28atm$

But $\frac{2x}{P} \times 100 = 33.33;\ x = 0.16665P$

Then $P + x = P + 0.16665P = 0.28atm;\ P = 0.24atm$

Thus at equilibrium:

$P_{NOBr} = P - 2x = 0.24atm - (2 \times 0.16665 \times 0.24)atm = 0.16atm$

$P_{NO} = 2x = 2 \times 0.16665 \times 0.24atm = 0.08atm$

$P_{Br_2} = x = 0.16665 \times 0.24atm = 0.04atm$

$$K_p = \frac{(P_{NO})^2 \times P_{Br_2}}{(P_{NOBr})^2} = \frac{(0.08atm)^2 \times 0.04atm}{(0.16atm)^2} = 0.01atm$$

The K_p is 0.01atm

Question 62

Study the gases equilibrium: $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)\ \Delta H^{\theta}(g) = kJ/mol$

(i) Write an expression for the equilibrium constant, $K_{p,}$ in terms of partial pressure.

(ii) At 60°C, 1.00dm ^{3} of the gas weighed 2.585g under a pressure of $1.01 \times 10^5 \mathrm{N/m^2}$. Find the degree of dissociation of N_2O_4 and the value of K_p

Solution

(i) $K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$

(ii) From $M_r = \frac{mRT}{PV}$

Where: $m = 2.585\mathrm{g}, V = 1\mathrm{dm}^3 = 10^{-3}\,\mathrm{m}^3, R = 8.314,$

$P = 1.01 \times 10^5\ \mathrm{N/m^2};\ T = 60°\mathrm{C} = (60 + 273)\ \mathrm{K} = 333\mathrm{K}$

Then observed molar of the gas $= \frac{2.585\times 8.314\times 333}{1.01\times 10^5\times 10^{-3}}\mathrm{g/mol}$

$= 70.86\mathrm{g/mol}$

$i = \frac{\text{Expected molar mass of the gas}}{\text{observed molar mass of the gas}}$

But expected molar mass of N_2O_4 is 92g /mol

Thus $i = \frac{92}{70.86} = 1.3$

Using $\alpha = \frac{i-1}{N-1}$ where $N = 2$

$$\alpha = \frac{1.3 - 1}{2 - 1} = 0.3 \text{ or } 30\%$$

Hence degree of dissociation of N_2O_4 is 30%

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

At equilibrium $1 - \alpha$ $\qquad$ 2α

$n_T = (1 - \alpha) + 2\alpha = (1 + \alpha)\mathrm{moles}$

$$P_{N_2O_4} = \left(\frac{1-\alpha}{1+\alpha}\right)P_T = \left(\frac{1-0.3}{1+0.3}\right) \times 1.01 \times 10^5 = 5.44 \times 10^4 \mathrm{Nm^{-2}}$$

$$P_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right) P_T = \left(\frac{2 \times 0.3}{1+0.3}\right) \times 1.01 \times 10^5 = 4.66 \times 10^4 \text{Nm}^{-2}$$

Using K_p expression in (i) above:

$$K_p = \frac{(4.66\times10^4)^2}{5.44\times10^4} \text{Nm}^{-2} = 3.99 \times 10^4 \text{Nm}^{-2}$$

Question 63

On what factors, does the value of the equilibrium constant of reaction depend?

Solution

Depends on temperature only.

Question 64

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

$$C_{(g)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)}$$

Calculate K_c for this reaction at the above temperature.

Solution

Mass of CO in 100g of the mixture = 90.55g

Thus mass of CO_2 in the gaseous mixture = (100 – 90.55) g = 9.45g

Number of moles of CO $= \frac{90.55}{28} \text{mol} = 3.24\text{mol}$

Number of moles of CO_2 $= \frac{9.45}{44} \text{mol} = 0.215\text{mol}$

$$P_{co} = X_{co} P_T; \quad P_{CO} = \left(\frac{3.234}{3.234 + 0.215}\right) \times 1\text{atm} = 0.94 \text{ atm}$$

$P_{CO_2} = P_T - P_{CO}$ (From Dalton's law of partial pressure)

$P_{CO_2} = (1 - 0.94)$ atm = 0 .06atm

Then $K_p = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(0.94\text{atm})^2}{0.06\text{atm}} = 14.73\text{atm}$

Using $K_c = K_p (RT)^{m-n}$

Where:

m is the number of molecules in the reactant side = 1 (for gases only).

n is the number of molecules in the product side = 2.

Then; $K_c = 14.73 \times (0.082 \times 1127)^{1-2} \mathrm{moldm}^{-3} = 0.159 \mathrm{moldm}^{-3}$

Hence the equilibrium constant, $K_c = 0.159 \mathrm{moldm}^{-3}$

Question 65

What is meant by:

(i) A chemical equilibrium

(ii) The position of chemical equilibrium

Solution

(i) Is the state that occurs in the reversible reaction when the rate forward reaction is equal to the rate of backward reaction.

(ii) Is the direction to which the reversible reaction proceed so as to establish the equilibrium and therefore acting as the measure of relative concentrations of reacting substances at equilibrium.

Question 66

A 1:3 mixture by volume of nitrogen and hydrogen gases was made up and left to equilibrium at $1.01 \times 10^6 \mathrm{N/m^2}$ at 327°C. Calculate equilibrium constant, K_p given that the equilibrium partial pressure of ammonia is 15%

Solution

$$N_{2(g)} + H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Initially $(t = 0)$	1	3	0
At equilibrium	$1 - x$	$3 - 3x$	$2x$

And total number of moles of gases at equilibrium,

$n_T = (1 - x) + (3 - 3x) + 2x = (4 - 2x)\text{moles}$

But from Avogadro's law; Mole ratio $=$ volume ratio

Thus; percentage by volume of the gas $=$ percentage by moles

Then $\left(\frac{n_{NH_3}}{n_T}\right) = 0.15$ or $\frac{2x}{4-2x} = 0.15$ or $x = 0.26$

$$X_{H_2} = \frac{3-(3\times0.26)}{4-(2\times0.26)} = 0.64$$

$$X_{N_2} = \frac{1-0.26}{4-(2\times0.26)} = 0.21$$

$$K_P = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3} = \frac{\left(X_{NH_3}P_T\right)^2}{\left(X_{N_2}P_T\right)\left(X_{H_2}P_T\right)^3} = \frac{\left(X_{NH_3}\right)^2}{\left(X_{N_2}\right)\left(X_{H_2}\right)^3 P_T^2}$$

$$K_P = \frac{(0.15)^2}{0.21 \times (0.64)^3(1.01 \times 10^6)^2} = 4 \times 10^{-13}\text{Pa}^{-2}$$

Hence the equilibrium constant, K_p is $4 \times 10^{-13}\text{Pa}^{-2}$

Question 67

Consider the decomposition of phosphorous pentachloride:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Solution

(a) $K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})}$

But from $PV = nRT$ or $P = \frac{n}{V}RT$

Where $\frac{n}{V} = [\quad]$

Thus $P = [\quad]RT$

Then $P_{PCl_3} = [PCl_3]RT$

$P_{Cl_2} = [Cl_2]RT$

$$P_{PCl_5} = [PCl_5]RT$$

Substituting above results into K_p expression, gives:

$$K_p = \frac{([PCl_3]RT)([Cl_2]RT)}{([PCl_5]RT)} \quad \text{or} \quad K_p = \frac{[PCl_3][Cl_2](RT)}{[PCl_5]}$$

But $\frac{[PCl_3][Cl_2]}{[PCl_5]} = K_c$

Hence $K_P = K_c RT$

Question 68

Derive the expression relating K_c and K_p for the above reaction. For the Haber process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g): K_p = 1.45 \times 10^{-5} \text{ at } 500℃$$

In equilibrium mixture of the three gases at 500℃, the partial pressure of H_2 is 0.928atm and that of N_2 is 0.432atm.What is the partial pressure of NH_3 in the equilibrium mixture.

Solution

From the given reaction equation:

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3}$$

Substituting;

$$1.45 \times 10^{-5} = \frac{\left(P_{NH_3}\right)^2}{0.432\text{atm} \times (0.928\text{atm})^3}$$

From which; $P_{NH_3} = 2.24 \times 10^{-3}$atm

The partial pressure of ammonia is 2.24×10^{-3}atm.

Question 69

Deduce the relationship between K_c and K_p for the following gaseous equilibria:

(i) $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$

(ii) $NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$

Solution

using $K_p = K_c\,(RT)^{n-m}$

Where n is the total number of molecules in product side

m is the total number of molecules in the reactant side

(i) $n = 2$ and $m = 3$

Then $K_p = K_c\,(RT)^{2-3} = K_c\,(RT)^{-1}$

Hence $K_p = \frac{K_c}{RT}$

(ii) $n = 1$ and $m = \frac{3}{2}$

Then $K_p = K_c\,(RT)^{1-3/2} = K_c\,(RT)^{-1/2}$

Hence $K_p = \frac{K_c}{\sqrt{RT}}$

Question 70

Consider the following equilibrium: $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$

Orange yellow

What would you expect to see if:

(i) Dilute sodium hydroxide is added to the equilibrium mixture?

(ii) Dilute hydrochloric acid is added to the equilibrium mixture?

(iii) Calcium chloride is added to the equilibrium mixture?

Solution

(b)(i) Yellow colouration of CrO_4^{2-}

(Addition of NaOH is equivalent to removal of H^+ thus shifting the position of equilibrium to the right).

(ii) Orange colouration of $Cr_2O_7^{2-}$ (Addition of HCl(aq) shift the position of chemical equilibrium to the left).

(iii) Orange colouration of $Cr_2O_7^{2-}$ (Anhydrous $CaCl_2$ absorbs thus shifting position of chemical equilibrium to the left).

Question 71

Given the hypothetical chemical reaction:

$$K_2 + N_2 \rightleftharpoons 2KN \quad \Delta H = -20.1 Jmol^{-1}$$

Suggest the direction of equilibrium (with reasons) if

(i) Pressure is decreased

(ii) Temperature is raised

(iii) K_2 is introduced in the system

(iv) N_2 is removed from the system

(v) KN is introduced in the system

Solution

No effect on position of the chemical equilibrium

(ii) The position of equilibrium will shift to the left

(i) The position of the equilibrium will shift to the right

(ii) The position of the equilibrium will shift to the left

(iii) The position of the equilibrium will shift to the left

Question 72

Using hypothetical reaction above in 43(a) has the equilibrium constant, $K_c = 10$. What is its equilibrium constant in terms of partial pressures K_p at 25°C.

Solution

(i)(c) Using $K_p = K_c\,(RT)^{n-m}$

For given reaction $m = n = 2$

Thus $K_p = K_c\,(RT)^{2-2} = K_c\,(RT)^0 = 1$

Hence the equilibrium constant in terms of partial pressures, K_p is 10.

Question 73

At 311K Sulphur dioxide and oxygen combine in equilibrium reaction according to the equation: $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

0.1mole of oxygen and 0.2 mole of sulphur dioxide are introduced into a 0.2L flask and were allowed to react. If the equilibrium amount of oxygen and sulphur dioxide is 10% of the equilibrium mixtures calculate

(i) The equilibrium amount of oxygen, sulphur dioxide and sulphur trioxide

(ii) Calculate the total pressure of the system at equilibrium

Solution

$$O_{2(g)} + 2SO_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Initially	0 .1	0.2	0
At equilibrium	$0.1 - x$	$0.2 - 2x$	$2x$

At equilibrium $n_T = (0.1 - x) + (0.2 - 2x) + 2x = (0.3 - x)$ moles

But $\frac{(n_{O_2} + n_{SO_2})}{n_T} \times 100 = 10$

$\frac{(0.1-x)+(0.2-2x)}{0.3-x} = 0.1$ or $0.3 - 3x = 0.03 - 0.1x$ or $x = 0.093$ moles

Hence at equilibrium:

Amount of $O_2 = 0.1 - x = 0.0069$ moles

Amount of $SO_2 = 0.2 - 2x = 0.0138$ moles

Amount of $SO_3 = 2x = 0.1862$ moles

By Dalton’s law of partial pressure: $P_T = P_{O_2} + P_{SO_2} + P_{SO_3}$

$$P_T = \frac{n_{O_2}RT}{V} + \frac{n_{SO_2}RT}{V} + \frac{n_{SO_3}RT}{V}$$

$$P_T = (n_{O_2} + n_{SO_2} + n_{SO_3})\frac{RT}{V}$$

$$P_T = \frac{n_T RT}{V}$$

But of equilibrium $n_T = (0.3 - x) = 0.2069\text{moles}$

Then;

$$P_T = \frac{0.2069 \times 0.082 \times 311}{0.2}\text{atm} = 26.38\text{atm}$$

Hence the pressure of the system at equilibrium is 26.38 atm

Question 74

List down any five characteristics of chemical equilibrium.

Solution

1. At equilibrium state, the rates of forward and backward reactions are equal.
2. The observable properties such as pressure, concentration, colour, density, viscosity etc., of the system remain unchanged with time once the system has attained chemical equilibrium.
3. The chemical equilibrium is a dynamic equilibrium because both the forward and backward reactions continue to occur even through it appears static externally.
4. The chemical equilibrium can be reached by starting the reaction either from the reactants side or from the product side.
5. Both pressure and concentration affect the position of equilibrium but do not affect the equilibrium constant.
6. The temperature can affect both the position of equilibrium as well as the equilibrium constant.

7. A positive catalyst can increase the rates of both forward and backward reactions and thus helping the system to attain the equilibrium faster; but it does not affect the position of equilibrium and equilibrium constant.

Question 75

The reaction: $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$, is at equilibrium at temperature in which the equilibrium constant, K_c, is $375\ mol^{-1}dm^3$ The equilibrium amount of oxygen found in a 0.755litre containing this equilibrium mixture is 0.148 mol .What is the ratio of [NO] to$[NO_2]$ in this equilibrium mixture.

Solution

For given reaction: $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$

But at equilibrium: $[O_2] = \frac{0.148}{0.755}M = 0.196M$

And it is given that**,** $K_c = 375mol^{-1}dm^3$

Then $375 = \frac{[NO_2]^2}{[NO]^2 \times 0.196}$

$$\frac{[NO_2]^2}{[NO]^2} = 0.196 \times 375 = 73.5$$

$$\text{Or } \frac{[NO]^2}{[NO_2]^2} = \frac{1}{73.5} = 0.0136$$

$$\text{Or } \frac{[NO]}{[NO_2]} = \sqrt{0.0136} = 0.1166 = \frac{583}{5000}$$

Hence the ratio of $[NO]$ to $[NO_2]$ is $583:5000$

Question 76

(a) In the preparation of ethylethanoate shown in the equation below, concentrated H_2SO_4 is often added to the mixture:

$$C_2H_5OH + CH_3COOH \xrightarrow[\text{conc.}H_2SO_4]{} CH_3COOC_2H_5 + H_2O$$

(i) State two (2) functions of concentrated H_2SO_4 in the production of the compound.

(ii) What will be the effect of adding NaOH(aq) instead of conc. H_2SO_4 in the production of the compound.

Solution

(i)

1. Catalyses the reaction thus increasing the rate of production of the compound.
2. Dehydrate (remove) water which makes the reaction to be more forward thus increasing percentage yield of the compound (ethylethanoate).

(ii) No significant production of ethylethanoate will be observed (Alkaline solution like NaOH is good catalyst for reverse reaction in the production of carboxylic acid like ethanoic acid).

Question 77

(i) When 1.00mol/dm^3 of CH_3COOH were heated with 0.18mol of C_2H_5OH in a 1dm^3 closed vessel, 0.829mol of CH_3COOH remained at equilibrium. Calculate the value of K_c

(ii) What mass of ethylethanoate should be present in the equilibrium mixture formed under the same experimental conditions as 9(b)(i) above if 0.30moles of ethanol were heated with 0.20moles of ethanoic acid in 1.0dm^3 closed vessel?

Solution

(i) $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3C00C_2H_5 + H_2O$

Initially	0.18	1	0	0
At equilibrium	$0.18 - x$	$1 - x$	x	x

$$K_c = \frac{[CH_3C00C_2H_5][H_2O]}{[C_2H_5OH][CH_3COOH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.18 - x}{V}\right)\left(\frac{1 - x}{V}\right)} = \frac{x^2}{(0.18 - x)(1 - x)}$$

But $1 - x = 0.829$ (0.829 moles of CH_3COOH remained at equilibrium)

$x = 0.171$ moles

$$K_c = \frac{0.171^2}{(0.18 - 0.171)(1 - 0.171)} = 3.919$$

Hence

The value of K_c is 3.919

(ii) $$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initially	0.3	0.2	0	0
At equilibrium	$0.3 - x$	$0.2 - x$	x	x

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.3 - x}{V}\right)\left(\frac{0.2 - x}{V}\right)} = \frac{x^2}{(0.3 - x)(0.2 - x)} = 3.919$$

$$x^2 = 3.919x^2 - 1.9595x + 0.23514$$

$x = 0.156$ moles ($x = 0.515$ is not practical solution because it exceed initial amount of reactants present in the system).

Hence number of moles of ethylethanoate ($CH_3COOC_2H_5$) formed in a dm^3 was 0.156moles.

But molar mass of ethylethanoate = 88g /mole using $m = nM_r$

Mass of the ethylethanoate = $0.156 \times 88g = 13.728g$

Hence mass of ethylethanoate in $1dm^3$ of equilibrium mixture is 13.728g

Question 78

(a) Explain the meaning and significance of equilibrium constant.

Solution

(a) This is the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.

It is the fixed ratio which is obtained according to the equilibrium law.

For the reaction: $\mathrm{Aa} \;+\; \mathrm{bB} \rightleftharpoons \mathrm{cC} \;+ \mathrm{dD}$

Then $\quad \mathrm{Equilibrium\ constant}, \mathrm{K_c} = \frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$

Significance

The value of equilibrium constant $\mathrm{K_c}$ is important in predicting the extent of forward reaction or backward reaction of which a particular reaction proceeds. If $\mathrm{K_c}$ is too large then the reaction is more forward while small value of $\mathrm{K_c}$ implies that the reaction is more backward.

Question 79

When the solution containing $[\mathrm{Ag^+}] = 0.2\mathrm{M}$ was added to the flask containing ferrous solution of 0.100M, Ferric of 0.3M and solid silver; ferrous convert silver ions to solid and itself it undergo oxidation. What are ions concentrations when the equilibrium is established? Given that; equilibrium constant for the reaction is 2.98.

Solution

Equation for the reaction: $\mathrm{Fe^{2+}_{(aq)}} + \mathrm{Ag^{+}_{(aq)}} \rightleftharpoons \mathrm{Ag_{(s)}} + \mathrm{Fe^{3+}_{(aq)}}$

As we are given with all reagents at the beginning of the reaction; we must firstly find reaction quotient ($\mathrm{R_Q}$) so as to determine the direction to which the reaction proceed.

$$\mathrm{R_Q} = \frac{[\mathrm{Fe^{3+}}]}{[\mathrm{Fe^{2+}}][\mathrm{Ag^+}]} = \frac{0.3}{0.2\times0.1} = 15$$

But $\mathrm{K_c} = 2.98$

So $\mathrm{R_Q} > \mathrm{K_c}$ and hence the reaction **proceed backward** to establish the equilibrium.

	$\mathrm{Fe^{2+}_{(aq)}}$	$+ \mathrm{Ag^{+}_{(aq)}}$	$\rightleftharpoons \mathrm{Ag_{(s)}}$	$+ \mathrm{Fe^{3+}_{(aq)}}$
Initially	0.1	0.2		0.3
At equilibrium	0.1 + x	0.2 + x		0.3 − x

$$K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]}$$

Then $\frac{0.3 - x}{(0.2 + x) \times (0.1 + x)} = 2.98$

Or $2.98x^2 + 1.894x - 0.2404 = 0$ or $x = 0.10843$

Hence at equilibrium:

$[Fe^{3+}] = 0.19157M$

$[Ag^{+}] = 0.30843M$

$[Fe^{2+}] = 0.20843$

Question 80

(a) Derive the relationship between equilibrium constant (K_c) and rate constant for forward reaction (K_f) and backward reaction (K_b).

Solution

(a) Consider the following single bimolecular step reversible chemical reaction:

$$A + B \rightleftharpoons C + D$$

From which:

$$R_f = K_f [A] [B]$$
$$R_b = K_b [C] [D]$$

Where R_f and R_b are rates of forward and backward reaction respectively.

But at equilibrium; $R_f = R_b$

Then;

$$K_f [A] [B] = K_b [C] [D]$$

From which;

$$\frac{K_f}{K_b} = \frac{[C][D]}{[A][B]}$$

But;

$$\frac{[C][D]}{[A][B]} = K_c$$

Hence $K_c = \frac{K_f}{K_b}$

Question 81

23.8g of sulphur thiochloride ($SOCl_2$) were mixed with 19.2g of SO and 142g of Cl_2 in $1\,dm^3$ vessel at once and the reaction was allowed to establish equilibrium. Calculate the equilibrium composition of each gas if the equilibrium constant K_c for the reaction:

$SOCl_{2(g)} \rightleftharpoons SO_{(g)} + Cl_{2(g)}$ is 1.2M.

Solution

Initially:

Number of moles of $[SOCl_2] = \frac{23.8}{119} = 0.2$ moles

Number of moles of $[SO] = \frac{19.2}{48} = 0.4$ moles

Number of moles of $[Cl_2] = \frac{142}{71} = 2$ moles

Thus at the beginning of the reaction:

Using $[\quad] = \frac{n}{V}$ where $V = 1dm^3$

$[SOCl_2] = 0.2M$

$[SO] = 0.4M$

$[Cl_2] = 2M$

$$Q_c = \frac{[SO][Cl_2]}{[SOCl_2]} = \frac{0.4M \times 2M}{0.2M} = 4M$$

But $K_c = 1.2M$. So $Q_c > K_c$ and hence the reaction will proceed in reverse direction to establish the equilibrium**.**

$$SOCl_{2(g)} \rightleftharpoons SO_{(g)} + Cl_{2(g)}$$

Initially 0.2 0.4 2

At equilibrium: $0.2 + x \quad 0.4 - x \quad 2 - x$

$$K_c = \frac{[SO][Cl_2]}{[SOCl_2]}$$

Then $\frac{(0.4-x)(2-x)}{(0.2+x)} = 1.2$

At equilibrium $n_T = (0.2 + x) + (0.4 - x) + (2 - x) = 2.437\text{moles}$

Number of moles of $SOCl_2 = 0.2 + x = 0.363$ moles

Number of moles of $SO = 0.4 - x = 0.237$ moles

Number of moles of $Cl_2 = (2 - x) = 1.837$ moles

$$\%SOCl_2 = \frac{n_{SOCl_2}}{n_T} \times 100\% = \frac{0.363}{2.437} \times 100\% = 14.9\%$$

$$\%SO = \frac{n_{SO}}{n_T} \times 100\% = \frac{0.237}{2.437} \times 100\% = 9.7\%$$

$$\%Cl_2 = \frac{n_{Cl_2}}{n_T} \times 100\% = \frac{1.837}{2.437} \times 100\% = 75.4\%$$

Hence the equilibrium composition of each gas is $14.9\%, 97\%$ and 75.4% by volume for $SOCl_2$, SO, and Cl_2 respectively

Question 82

Explain why there is a constant pressure of carbon dioxide at a particular temperature over calcium carbonate undergoing thermal dissociation $CaCO_{3(s)} \rightleftharpoons CaO_{(S)} + CO_{2(g)}$ and why a current air is blown through a lime kiln during production of quick lime CaO

Solution

- Once equilibrium has been attained the concentration of carbon dioxide gas (CO_2) remain unchanged and hence the pressure become constant.

- The current of blown air displace $CO_2(g)$ from the line kiln thus removing the carbon dioxide and hence the position of chemical equilibrium will shift to the right by producing more quick lime CaO.

Question 83

When one mole ethanoic acid (acetic acid) is maintained at 25℃ with one mole of ethanol, one third of the ethanoic acid remains when equilibrium is attained. How much would have remained if three quarters of one mole of ethanol had been used instead of one mole at the same temperature?

Solution

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initially	1	1	0	0
At equilibrium	$1-x$	$1-x$	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\left({}^{x}/_{V}\right)\left({}^{x}/_{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{1-x}{V}\right)}$$

$$K_c = \frac{x^2}{x^2 - 2x + 1}$$

But

$1 - x = {}^{1}/_{3}$ or $x = {}^{2}/_{3}$ **(**One third of ethanoic acid remains at equilibrium).

Substituting $x = {}^{2}/_{3}$ in above equilibrium constant expression gives, $K_c = 4$.

If three quarters of one mole of ethanol is used:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Initially	1	${}^{3}/_{4}$	0	0
At equilibrium	$1-x$	${}^{3}/_{4} - x$	x	x

$$K_c = \frac{(^x/_V)(^x/_V)}{\left(\frac{^3/_4 - x}{V}\right)\left(\frac{1-x}{V}\right)} = \frac{x^2}{x^2 - 1.75x + 0.75} = 4 \quad \text{or } x = 0.57$$

And $1 - x = 1 - 0.57 = 0.43$ moles

Hence the amount of ethanoic acid which would remain is 0.43moles.

Question 84

The equilibrium constant for synthesis of hydrogen chloride, hydrogen bromide and hydrogen iodide are given below:

$H_2 + Cl_2 \rightleftharpoons HCl, \qquad K_c = 10^{17}$

$H_2 + Br_2 \rightleftharpoons HBr, \qquad K_c = 10^{9}$

$H_2 + I_2 \rightleftharpoons HI, \qquad K_c = 10$

(i) What do the values of K_c tell you about the extent of each reaction

(ii) Which of these reactions you would regard as complete conversion?

(iii) Predict the effect of increasing pressure on the above equilibrium

Solution

(i) If the reaction has greater value of K_c then the reaction is more forward. Thus the first reaction is most forward followed by the second reaction while the third reaction having lowest value of K_c is most backward (least forward).

(ii) First reaction which involve combination of H_2 and Cl_2 to form HCl.

(iii) Pressure has no effect on the given equilibrium because all reaction are not accompanied with change in volume of gases.

Question 85

(a) Ammonia is manufactured by passing hot nitrogen at high pressure over on iron catalyst .The equation of the reaction for this process is given as:
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

The equilibrium constant for the reaction is expressed as:

$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$. Name and state the law applied to get the expression K_c

Solution

Name of the law: Equilibrium law

It states that: This is the temperature dependent fixed ratio which is obtained as the quotient of the product of the equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients.

Question 86

If at 402°C, the reaction in (a) above has a K_p value of 2×10^{-14} Pa. calculate the pressure at which ammonia is 95% dissociated into its elements.

What will happen to the value of K_p if 0.5 mole of NH_3 is added to the equilibrium mixture at 402°C

Solution

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Initially	0	0	1
At equilibrium	3x	x	1 − 2x

n_T at equilibrium $3x + x + 1 - 2x = (1 + 2x)\text{moles}$

Where 2x is numerically equal to the degree of dissociation

$$K_p = \frac{\left(P_{NH_3}\right)^2}{\left(P_{H_2}\right)^3\left(P_{N_2}\right)} = \frac{\left(X_{NH_3}P_T\right)^2}{\left(X_{H_2}P_T\right)^3\left(X_{N_2}P_T\right)} = \frac{\left(X_{NH_3}\right)^2}{\left(X_{H_2}\right)^3\left(X_{N_2}\right)P_T^2}$$

But $2x = 0.95$ (95% NH_3 of dissociated into its elements)

$x = 0.475$

Then:

$$X_{NH_3} = \frac{1-2x}{1+2x} = 0.026$$

$$X_{H_2} = \frac{3x}{1+2x} = 0.731$$

$$X_{N_2} = \frac{x}{1+2x} = 0.244$$

Then $2 \times 10^{-14} = \frac{0.026^2}{0.731^3 \times 0.244 P_T^2}$ or $P_T = 5.955 \times 10^5 Pa$

Hence the pressure is $5.955 \times 10^5 Pa$

(ii) K_p will remain the same as the constant does not depend on the concentration of the reagents present in the system (like K_c, K_p is only temperature dependent).

Question 87

Nitrogen and oxygen combine at high temperatures with absorption of heat according to the equation: $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

The equilibrium constant for this reaction at 2680K and 1atm is 3.6×10^{-3} when equal volumes of nitrogen and oxygen are mixed at 2680K and 1atm and allowed to react until equilibrium is reached. Calculate the fraction

(i) Of the original nitrogen which is used in the reaction

(ii) By volume of nitric oxide in the mixture

Solution

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

	$N_{2(g)}$	$O_{2(g)}$	$2NO_{(g)}$
Initially	1	1	0
At equilibrium	$1-\alpha$	$1-\alpha$	2α

$$K_p = \frac{(P_{NO})^2}{(P_{O_2})(P_{N_2})} = \frac{(X_{NO}P_T)^2}{(X_{O_2}P_T)(X_{N_2}P_T)} = \frac{(X_{NO})^2}{(X_{O_2})(X_{N_2})}$$

But $n_T = (1-\alpha) + (1-\alpha) + 2\alpha = 2$ moles

Then $X_{NO} = \frac{2\alpha}{2} = \alpha$

$$X_{N_2} = X_{O_2} = \frac{1-\alpha}{2}$$

So $3.6 \times 10^{-3} = \frac{4\alpha^2}{(1-\alpha)^2} = \frac{4\alpha^2}{\alpha^2 - 2\alpha + 1}$

Or $3.9964\alpha^2 - 0.0072\alpha - 0.0036 = 0$ or $\alpha = 0.029$

Hence the fraction of original nitrogen which is used in the reaction is 0.029

The fraction by volume of nitric oxide in the mixture $= X_{NO} = \alpha = 0.029$

Hence the fraction of nitric oxide in the mixture is also 0.029

Question 88

At temperature close to 400°C, hydrogen iodide has a degree of dissociation of 20%. Calculate the composition of the equilibrium mixture produced if 1mole of hydrogen and 2.1mole of iodine react to equilibrium at this temperature.

Solution

	$2HI$	$\rightleftharpoons$	H_2	$+$	I_2
Initially	1		0		0
At equilibrium	$1-2\alpha$		α		α

Where 2α is numerically equal to the degree of dissociation

$$K_c = \frac{[H_2\ ][I_2]}{[HI]^2} = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\left(\frac{1-2\alpha}{V}\right)^2} = \frac{\alpha^2}{4\alpha^2 - 4\alpha + 1}$$

But $2\alpha = 0.2$ (Degree of dissociation is 20%)

So $\alpha = 0.1$

Substitute $\alpha = 0.1$ to above K_c expression gives, $K_c = 0.015625$

If moles of hydrogen and 2.1 mole of iodine react

$$\begin{array}{lccccc} & 2HI & \rightleftharpoons & H_2 & + & I_2 \\ \text{Initially} & 0 & & 1 & & 2.1 \\ \text{At equilibrium} & 2x & & 1-x & & 2.1-x \end{array}$$

$$K_c = \frac{(1-x)(2.1-x)}{(2x)^2}$$

But since temperature is kept constant, $K_c = 0.015625$ (remain unchanged).

$$\frac{(1-x)(2.1-x)}{(2x)^2} = 0.015625 \quad \text{or} \quad x = 0.95$$

Hence at equilibrium

Number of moles of HI $= 2x = 1.9$ moles

Number of moles of $H_2 = 1 - x = 0.05$ moles

Number of moles of $I_2 = 2.1 - x = 1.15$ moles

Question 89

Giving reasons argue for or against the statement that, “reactions with large equilibrium constants are very fast.”

Solution

No; reactions with large equilibrium constant are not necessary to be very fast.

Reason:

Equilibrium constant is the measure of relative concentration of reactants and products at equilibrium. So even slow reactions with greater concentration of products than that of reactants have large equilibrium constants.

Question 90

At 1 atmosphere, and 55℃ N_2O_4 is 50% dissociated. Calculate the equilibrium constant for this reaction in terms of pressure. Hence calculate the degree of dissociation of the gas at 55℃ and 10 atmosphere pressure.

Solution

	$N_2O_{4(g)} \rightleftharpoons$	$2NO_{2(g)}$
Initially	1	0
At equilibrium	$1-\alpha$	2α

Where α is numerically equal to the degree of dissociation.

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(X_{NO_2}P_T)^2}{(X_{N_2O_4}P_T)} = \frac{(X_{NO_2})^2 P_T}{(X_{N_2O_4})}$$

But $X_{NO_2} = \frac{2\alpha}{1+\alpha}$ Where $n_T = (1-\alpha) + 2\alpha = 1+\alpha$

And $X_{N_2O_4} = \frac{1-\alpha}{1+\alpha}$

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

When $\alpha = 0.5$ and $P_T = 1\text{atm}$

$$K_p = \frac{4 \times 0.5^2 \times 1}{1-0.5^2}\text{atm} = {}^4\!/_3\,\text{atm}$$

Hence the equilibrium constant in terms of pressure is ${}^4\!/_3$ atm

When the pressure, P_T is changed to 10atm

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

When $P_T = 10\text{atm}$

Since temperature is kept constant, K_p remain unchanged.

Then ${}^4\!/_3 = \frac{4\times10\alpha^2}{1-\alpha^2}$ or $\alpha = 0.18$ or 18%

Hence when the pressure is 10atm, degree of dissociation of the gas becomes 18%.

Question 91

At a certain temperature, the equilibrium pressures of steam and hydrogen in contact with iron and its black oxide Fe_3O_4 were found to be $1533Nm^{-2}$ (11.5mmHg) and $32190Nm^{-2}$(241.5 mmHg) respectively. Calculate:

(a) The pressure of hydrogen in equilibrium with 1066 Nm^{-2} (8mmHg) of steam pressure.

(b) The pressure of hydrogen and steam at a total pressure of 101300 Nm^{-2}(760mmHg) at this temperature. Equation for the reaction is $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(S)} + 4H_{2(g)}$

Solution

From the given equation of the reaction: $K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4} = \left(\frac{P_{H_2}}{P_{H_2O}}\right)^4$

But at equilibrium: $P_{H_2O} = 1533Nm^{-2}$, $P_{H_2} = 32190Nm^{-2}$

Then $K_p = \left(\frac{32190}{1533}\right)^4 = 21^4$

(a)When $P_{H_2O} = 1066Nm^{-2}$

$$\frac{P_{H_2}}{1066^4} = 21^4 \text{ or } P_{H_2} = 22386Nm^{-2}$$

Hence the pressure of hydrogen will be $22386Nm^{-2}$

(b) $K_p = \left(\frac{P_{H_2}}{P_{H_2O}}\right)^4$

By Dalton's law of partial pressures: $P_T = P_{H_2} + P_{H_2O}$

Then $P_{H_2} + P_{H_2O} = 101300$ or $P_{H_2O} = 101300 - P_{H_2}$

So $21^4 = \left(\frac{P_{H_2}}{101300 - P_{H_2}}\right)^4$

Thus $P_{H_2} = 96695 Nm^{-2}$ and $P_{H_2O} = 101300 - 96695 = 4605 Nm^{-2}$

Hence:

The pressure of hydrogen is $96695 Nm^{-2}$

The pressure of steam is $4605 Nm^{-2}$

Question 92

When bromine is dissolved in water, the following equilibrium is established:

$$Br_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + Br^-(aq) + HBrO(aq)$$

Yellow colourless

State and explain the effect on the colour of the solution of:

(a) Adding an acid
(b) Adding an alkali
(c) Adding solution of sodium bromide
(d) Adding a silver nitrate solution

Solution

(a) The solution will be yellow because addition of acid increase concentration of H^+ thus shifting the position of equilibrium to the left.
(b) The solution will be colourless because the alkaline solution neutralises an acid which is equivalent to removal of H^+ and hence the equilibrium will shift to right.
(c) The solution will be yellow because NaBr being strong ionic salt ionises completely yielding Br^-; so there is an increase in concentration of Br^-, the factor which shifts the position of chemical equilibrium to left.
(d) The solution will be colourless because the silver nitrate solution reacts with Br^- to give AgBr thus decreasing the concentration of Br^- and hence equilibrium shifts to the right.

Question 93

Explain the meaning and significance of reaction quotient (Q_c)

Solution

(a) Reaction quotient, Q_c is the ratio of product of concentration of products to that of reactants raised to power equal to their stoichiometric coefficients obtained in the course of the chemical reaction.

If: $aA + bB \rightleftharpoons cC + dD$

$$Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Where '[ ]' stands for molar concentration at **any time** in the course of the chemical reaction.

Significance

The quotient is useful in determination of the position of the chemical equilibrium (the direction to which the reaction proceed more so as to establish the equilibrium) by comparing its value with that of the equilibrium constant at given temperature.

- When $Q_c < K_c$, the position of the chemical equilibrium shifts to the right that is: forward reaction is more favoured.
- When $Q_c > K_c$, the position of the chemical equilibrium shifts to the left, that is; backward (reverse) reaction is more favoured.
- When $Q_c = K_c$, the reaction is at equilibrium.

Question 94

At certain temperature, and a pressure of 1 atmosphere, iodine vapour contains 40% by volume of iodine atoms. $I_2 \rightleftharpoons I + I$. At what total pressure (without temperature change) would this pressure reduced to 20?

Solution

Equation for the reaction: $I_2 \rightleftharpoons I + I$

Simplified equation after combining two I atoms is;

	$I_2 \rightleftharpoons$	$2I$
Initially	1	0
At equilibrium	$1-\alpha$	2α

$$K_p = \frac{(P_I)^2}{(P_{I_2})} = \frac{(X_I P_T)^2}{(X_{I_2} P_T)} = \frac{(X_I)^2 P_T}{(X_{I_2})}$$

$$X_I = \frac{2\alpha}{1+\alpha} \quad \text{and} \quad X_{I_2} = \frac{1-\alpha}{1+\alpha}$$

Then $K_p = \frac{4\alpha^2 P_T}{1-\alpha^2}$ But $\frac{2\alpha}{1+\alpha} = 0.4$ (iodine vapour contains 40% by volume of iodine atoms) or $\alpha = 0.25$

And it is given that $P_T = 1\text{atm}$

$$K_p = \frac{4 \times 0.25^2 \times 1}{1-0.25^2} = \frac{4}{15}\text{atm}$$

If the pressure is reduced to 20%

$\frac{2\alpha}{1+\alpha} = 0.2$ or $\alpha = \frac{1}{9}$

Substituting $\alpha = \frac{1}{9}$ and $K_p = \frac{4}{15}$

$$\frac{4}{15} = \frac{4\left(\frac{1}{9}\right)^2 P_T}{1-\left(\frac{1}{9}\right)^2} \quad \text{or} \quad P_T = 5.33\text{atm}$$

Thus the percentage will be reduced to the given amount when the total pressure is 5.33atm.

Question 95

State Van’t Hoff’s law of mobile as used to explain the effect of temperature in the equilibrium position.

Solution

Increase in temperature and decrease in temperature favour forward reaction for endothermic reaction and exothermic reaction respectively and vice versa.

Question 96

At a certain high temperature, the equilibrium constant of the reaction:

$$N_2 + O_2 \rightleftharpoons 2NO \ \text{ is } 8 \times 10^{-4}$$

Assuming air to be a mixture of four volumes of nitrogen with one volume of oxygen, calculate the percentage of nitrogen monoxide by volume in the gas produced by allowing air to reach equilibrium at this temperature.

Solution

$$\begin{array}{lccc} & N_2 + & O_2 \rightleftharpoons & 2NO \\ \text{Initially} & 4 & 1 & 0 \\ \text{At equilibrium} & 4 - x & 1 - x & 2x \end{array}$$

$$K_c = \frac{[NO]^2}{[\ N_2][O_2]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{4-x}{v}\right)\left(\frac{1-x}{v}\right)} = \frac{4x^2}{x^2 - 5x + 4} = 8 \times 10^{-4}$$

$$3.9992x^2 + 0.004x - 0.0032 = 0 \quad \text{or } x = 0.0278$$

$$\%NO = \frac{n_{NO}}{n_T} \times 100\% = \left(\frac{2x}{5}\right) \times 100\% = 1.112\%$$

Hence the percentage of nitrogen monoxide by volume is 1.112%

Question 97

The equilibrium constant of the reaction: $CO_2 + H_2 \rightleftharpoons CO + H_2O$ at 1000°C is 1.6. What is the percentage by volume of each gas in the equilibrium mixture at 1000°C produced from:

(a) A mixture of $50cm^3$ hydrogen and $50cm^3$ carbon dioxide.

(b) $25cm^3$ each of carbon dioxide and monoxide and $50cm^3$ of hydrogen.

Solution

From the given reaction equation: $K_c = \frac{[CO][H_2O]}{[CO_2][H_2]}$

Then $K_c = \frac{\left(\frac{n_{CO}}{V}\right)\left(\frac{n_{H_2O}}{V}\right)}{\left(\frac{n_{CO_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)} = \frac{n_{CO} \times n_{H_2O}}{n_{CO_2} \times n_{H_2}}$

But for gases; mole ratio $=$ volume ratio (from Avogadro's law)

Then: $K_c = \frac{V_{CO} \times V_{H_2O}}{V_{CO_2} \times V_{H_2}}$

Where V is the volume of each gas at equilibrium.

(a)	CO_2 +	$H_2 \rightleftharpoons$	CO +	H_2O
Initially	50	50	0	0
At equilibrium	$50 - x$	$50 - x$	x	x

Then $1.6 = \frac{x^2}{(50-x)^2} = \frac{x^2}{x^2 - 100x + 2500} = 1.6 \quad x = 27.9$

Total volume of gaseous mixture

$= (50 - x) + (50 - x) + x + x = 100cm^3$

Hence:

The percentage of $CO = x = 27.9\%$

The percentage of $H_2O = x = 27.9\%$

The percentage of $H_2 = 50 - x = 22.1\%$

The percentage of $CO_2 = 50 - x = 22.1\%$

(b)	CO_2 +	$H_2 \rightleftharpoons$	CO +	H_2O
Initially	25	50	25	0
At equilibrium	$25 - x$	$50 - x$	$25 + x$	x

$$1.6 = \frac{x(25+)}{(25 - x)(50 - x)} = \frac{x^2 + 25x}{x^2 - 75x + 1250}$$

$0.6x^2 - 145x + 2000 = 0$ or $x = 14.68$

Total volume of gaseous mixture at equilibrium is;

$(25 - x) + (50 - x) + (25 + x) + x = 100cm^3$

Hence:

The percentage of CO_2 is 10.32%

The percentage of H_2 is 35.32%

The percentage of CO is 39.68%

The percentage of H_2O is 14.68%

It should be understood that:

In above equilibrium constant expression, water is included in the expression although its normal physical state is liquid while normal physical state of other reactants are gases because the reaction is undertaken at 1000°C where water exists in gaseous state as a vapour (steam).

Question 98

When wine spoils, ethanol is oxidised to acetic acid as O_2 from the air reacts with the wine;

$$\underset{\text{Ethanol}}{CH_3CH_2OH(aq)} + O_2(aq) \rightleftharpoons \underset{\text{acetic acid}}{CH_3CO_2H(aq)} + H_2O(l)$$

The value of K_c for this reaction at 25°C is 1.2×10^{82}. Will much ethanol remain when the reaction has reached equilibrium? Explain.

Solution

No. There is almost no ethanol at all when the reaction is at equilibrium.

Explanation

K_c for the reaction very large suggesting that the reaction reach almost to completion. So ethanol being at reactant side will almost be completely consumed when the reaction has reached equilibrium.

Question 99

At $817°\text{C}$, K_p for the reaction between CO_2 and excess hot graphite to form $CO(g)$ is 10atm.

(i) What is the mole fraction of each gas at equilibrium at $817°\text{C}$ and the total pressure of 4atm?

(ii) At what total pressure, will the gas mixture contain 6% CO_2 by volume?

Solution

Reaction equation;

$$CO_2(g) + C(g) \rightleftharpoons 2CO(g)$$

From which;

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}}$$

But by Dalton's law of partial pressure;

$$P_T = 4 = P_{CO} + P_{CO_2}$$

From which;

$$P_{CO_2} = 4 - P_{CO}$$

Then;

$$K_p = 10 = \frac{(P_{CO})^2}{4 - P_{CO}};$$

$$(P_{CO})^2 + 10P_{CO} - 40 = 0$$

Solving the above quadratic equation with P_{CO} as the unknown gives;

$P_{CO} = 3\text{atm}$ and therefore $P_{CO_2} = 4 - P_{CO} = (4-3)\text{atm} = 1\text{atm}$

Then;

$$X_{CO} = \frac{P_{CO}}{P_T} = \frac{3\text{atm}}{4\text{atm}} = 0.75 \text{ and } X_{CO_2} = \frac{P_{CO_2}}{P_T} = \frac{1\text{atm}}{4\text{atm}} = 0.25$$

The mole fraction of CO is 0.75

The mole fraction of CO_2 is 0.25

(ii) For gases;

Volume ratio $=$ Mole ratio (Avogadro's law)

It follows that;

$$\frac{V_{CO_2}}{V_T} \times 100 = \frac{n_{CO_2}}{n_T} \times 100 = 6$$

But;

$$\frac{n_{CO_2}}{n_T} = X_{CO_2};\ \text{so}\ X_{CO_2} = 0.06\ \text{and}\ X_{CO} = 1 - X_{CO_2} = 1 - 0.06 = 0.94$$

Then;

$$K_p = 10 = \frac{(P_{CO})^2}{P_{CO_2}} = \frac{(X_{CO}P_T)^2}{X_{CO_2}P_T} = \frac{(X_{CO})^2 P_T}{X_{CO_2}} = \frac{(0.94)^2 P_T}{0.06}$$

From which the total pressure (P_T) is 0.68atm

Question 100

Why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

Solution

This is because, equilibrium constant is uniquely found by using concentration of reagents when the chemical system of the reversible reaction is at equilibrium while reaction quotient is found by using the concentrations at any time in the course of the reversible reaction

Question 101

When 2.94 moles of iodine and 8.1moles of hydrogen are heated at constant volume at 444°C until the equilibrium is established, 5.6moles of hydroiodic acid were formed. Calculate the equilibrium constant, K_c at 444°C .

Solution

$$\begin{array}{lccc} & I_2 + & H_2 & \rightleftharpoons & 2HI \\ \text{At equilibrium} & 2.94 - x & 8.1 - x & & 2x \end{array}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{2.94 - x}{v}\right)\left(\frac{8.1 - x}{v}\right)} = \frac{4x^2}{(2.94 - x)(8.1 - x)}$$

But $2x = 5.6$ (amount of HI Present at equilibrium); $x = 2.8$

Substituting the value of x in above K_c expression gives, $K_c = 42.26$

So the equilibrium constant is 42.26

Question 102

Write the most common form of equilibrium constant expression for the following reactions:

(i) $N_2H_4\,(g) + O_2(g) \rightleftharpoons N_2\,(g) + 2H_2O(g)$
(ii) $3Fe\,(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
(iii) $2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$
(iv) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$
(v) $Cr(s) + 3Ag^+(aq) \rightleftharpoons Cr^{3+}(aq) + 3Ag(s)$

Solution

(i) $K_p = \frac{(P_{N_2})(P_{H_2O})^2}{(P_{N_2H_4})(P_{O_2})}$

(ii) $K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4}$ or $K_p = \left(\frac{P_{H_2}}{P_{H_2O}}\right)^4$

(i) $K_p = \frac{(P_{N_2})(P_{H_2})^3}{(P_{NH_3})^2}$

(ii) $K_p = \frac{(P_{CO})}{(P_{CO_2})(P_{H_2})}$

(iii) $K_c = \frac{[Cr^{3+}]}{[Ag^+]^3}$

Question 103

Pure phosphorous pentachloride gas is introduced into an evacuated vessel and comes to equilibrium at $250°C$, the reaction being $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

The total pressure is $202kPa$ and the mole fraction of the chlorine gas is 0.407.

(iv) What are the partial pressure of phosphorous trichloride and phosphorous pentachloride gases?

(v) Calculate K_p for the reaction at $250°C$.

Solution

(a)$X_{PCl_3} = X_{Cl_2} = 0.407$ (Both PCl_3 and Cl_2 are produced from the decomposition of the phosphorous pentachloride introduced in the vessel and their mole ratio is 1:1).

$$X_{PCl_3} + X_{Cl_2} + X_{PCl_5} = 1$$

Thus; $X_{PCl_5} = 1 - (X_{Cl_2} + X_{PCl_3}) = 1 - (0.407 + 0.407) = 0.186$

Using; $P' = XP_T$

(i) Partial pressure of $PCl_3, P_{PCl_3} = 0.407 \times 202kPa = 82.214kPa$

Partial pressure of $PCl_5, P_{PCl_5} = 0.186 \times 202kPa = 37.572kPa$

(ii) $P_{PCl_3} = P_{Cl_2} = 82.214kPa$ (They have the same mole fraction)

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{82.214kPa \times 82.214kPa}{37.572kPa} = 179.9kPa$$

Question 104

0. 5 moles of hydrogen gas and 0.5 moles of iodine gas react in a 10L evacuated vessel at 440°C, hydrogen iodide is formed. The equilibrium constant, K_C for the reaction at 440°C is 50.

(i) Calculate the value of K_p

(ii) Calculate number of moles of I_2 remain unreacted at equilibrium

Solution

$K_P = K_c(RT)^{n-m}$

When $n = m = 2$

$K_p = K_c(RT)^0 = K_c$

Hence the value of K_P is 50

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
At equilibrium	$0.5-x$		$0.5-x$		$2x$

$$K_c = \frac{[HI]^2}{[H_2\ ][I_2]} = \frac{4x^2}{(0.5-x)^2} = 50$$

Solving above equation gives;

$x = 0.39$moles and $0.5 - x = 0.5 - 0.39 = 0.11$moles

Thus the amount of I_2 remain unreacted is 0.11moles.

Question 105

Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(K_c = \frac{K_f}{K_b}\right)$.

> It is known that the magnitude of both rate constants are affected by catalyst. However the catalyst is said to have no effect on the equilibrium constant; explain why.

Solution

Catalyst lowers the activation energy of both forward reaction and backward reaction by the same magnitude. This makes K_f and K_b to increase by the same proportion and hence the K_c value remains unchanged.

Question 106

1 mole of H_2, 2moles of I_2 and 3moles of HI are injected in 1L vessel. What will be the concentration of H_2, I_2 and HI at equilibrium at 490 °C? (The equilibrium constant for the reaction at 490°C is 45.9M).

Solution

Initially: $[H_2\ ] = 1M, [I_2] = 2M$ and $[HI] = 3M$

$$Q_c = \frac{[HI]^2}{[I_2][H_2]} = \frac{(3M)^2}{(1M) \times (2M)} = 4.5M$$

But $K_c = 45.9M$; so $Q_c < K_c$ and hence the reaction proceed forward to establish the equilibrium

	H_2 +	I_2 ⇌	$2HI$
Initially	1	2	3
At equilibrium	$1 - x$	$2 - x$	$3 + 2x$

$$K_c = \frac{[HI]^2}{[H_2\ ][I_2]} = \frac{(3 + 2x)^2}{(1 - x)(2 - x)} = 45.9$$

Solving above equation gives $x = 0.684$

Hence at equilibrium:

$[H_2\ ] = 1 - x = 0.316M$

$[I_2] = 2 - X = 1.316M$

$[HI] = 3 + 2x = 4.368M$

Question 107

Consider the following reaction equations representing Haber process and contact process:

Haber process: $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92kJ/mol$

Contact process: $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3(g)\ \Delta H = -196kJ/mol$

(i) Which reaction whose equilibrium position is more affected by temperature? Give reason(s) for your answer.

(ii) Which reaction whose equilibrium position is more affected by pressure? Give reason(s) for your answer.

Solution

(i) Reaction for contact process

Reason

The reaction is accompanied with greater heat change.

(ii) Reaction for Haber process

Question 108

For the reaction: $A + B \rightleftharpoons 2C$; 2 moles of A and 3 moles of B reacts. If the equilibrium constant for the reaction, $K_c = 4$ at 900℃ .What will be the equilibrium amount of C?

Solution

Reason

Reaction is accompanied with greater change of number of gas molecules.

$$\begin{array}{lcccc} & A & + & B & \rightleftharpoons & 2C \\ \text{At equilibrium} & 2 - x & & 3 - x & & 2x \end{array}$$

$$K_c = \frac{[C]^2}{[A][B]} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{3-x}{v}\right)\left(\frac{2-x}{v}\right)} = \frac{4x^2}{x^2 - 5x + 6}$$

But $K_c = 4$

Then $4 = \frac{4x^2}{x^2-5x+6}$

Solving above equation gives $x = 1.2$ and $2x = 2 \times 1.2 = 2.4$moles

Hence number of moles of C at equilibrium is 2.4 moles

Question 109

At 700K, CO_2 and H_2 react to form CO and H_2O. For this process, K_c value is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated;

(a) Calculate the amount of each at equilibrium

(b) After equilibrium is reached another 0.34moles of CO_2 and 0.34 moles of H_2 are added to the reaction mixture. Find out the composition of the mixture of the new equilibrium state.

Solution

	CO_2	+	H_2	$\rightleftharpoons$	CO	+	H_2O
At equilibrium	$0.45 - x$		$0.45 - x$		x		x

$$K_c = \frac{[CO][H_2O]}{[CO_2][H_2]} = \frac{x^2}{(0.45 - x)} = 0.11$$

Solving above equation gives $x = 0.11$

Hence at equilibrium:

Numbers of moles CO_2

$= \text{Number of moles of } H_2 = 0.45 - x = 0.34\text{moles}$

Number of moles of CO

$= \text{Number of moles of } H_2O = x = 0.11\text{moles}$

(ii) Addition of CO_2 and H_2 will shift the position of equilibrium to the right so as to re – establish the equilibrium:

	CO_2	+	H_2	$\rightleftharpoons$	CO	+	H_2O
Just after the addition	0.68		0.68		0.11		0.11
At new equilibrium	$0.68 - x$		$0.68 - x$		$0.11 + x$		$0.11 + x$

Then $0.11 = \frac{(0.11+x)^2}{(0.68-x)^2}$ or $x = 0.0869$

From which x = 0.0869

Hence at new equilibrium:

Number of moles of CO_2

$= \text{Number of moles of } \quad H_2 = 0.68 - x = 0.5931\text{moles}$

Number of moles of CO

$= \text{Number of } H_2O = 0.11 + x = 0.1969\text{moles}$

Question 110

High pressure increases product yield of both Haber process and contact process. However unlike Haber process, contact process is carried out at just almost atmospheric pressure. Explain.

Solution

The reaction for contact process has smaller change of number of gas molecules implying that high pressure has less effect (compared to Haber process) while the higher heat change in the contact process ensures that the contact process respond more to temperature change.

Question 111

At 250°C, K_p for the reaction: $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ is 8×10^{-4} . Nitrogen and oxygen gas are mixed in a volume ration of 4:1 respectively; calculate the percentage of nitric oxide by volume in the gas produced by allowing air to reach equilibrium at 250°C.

Solution

$$N_2 \quad + \quad O_2 \quad \rightleftharpoons \quad 2NO$$

At equilibrium $\quad 4 - x \qquad 1 - x \qquad 2x$

n_T at equilibrium $\quad (4 - x) + (1 - x) + (2x) = 5\text{moles}$

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(X_{NO}P_T)^2}{(X_{N_2}P_T)(X_{O_2}P_T)} = \frac{(X_{NO})^2}{(X_{N_2})(X_{O_2})}$$

But $X_{NO} = \frac{2x}{5}, \; X_{N_2} = \frac{4-x}{5}, \; X_{O_2} = \frac{1-x}{5}$

Then $0.0008 = \frac{4x^2}{(4-x)(1-x)} = \frac{4x^2}{4-5x+x^2}$

Solving above equation gives $x = 0.028$

$$\% \text{ NO} = \left(\frac{2x}{5}\right) \times 100\% = \frac{2 \times 0.028}{5} \times 100\% = 1.12\%$$

Hence the percentage of nitric oxide is 1.12%

Question 112

5g of PCl_5 were completely vapourised at 250°C in a vessel of 1.9L capacity. The equilibrium mixture exerted a pressure of 1atm. Calculate:

(i) The degree of dissociation

(ii) K_c and K_p for the reaction

Solution

Equation to show dissociation of PCl_5:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g); \quad N = 2$$

Using $M_r = \frac{mRT}{PV}$

Thus observed molar mass of $PCl_5 = \frac{5 \times 0.082 \times 523}{1 \times 1.9} = 112.86 \text{g/mol}$

Expected molar mass of $PCl_5 = 31 + (5 \times 35.5) = 208 \text{g/mol}$

$$i = \frac{\text{Expected molar mass}}{\text{observed molar mass}} = \frac{208.5}{112.86} = 1.85$$

$$\alpha = \frac{i - 1}{N - 1} = \frac{1.85 - 1}{2 - 1} = 0.85 \quad \text{or} \quad 85\%$$

Degree of dissociation of PCl_5 is 85%

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$
At equilibrium	$1 - \alpha$	α	α

$$n_T = (1 - \alpha) + (\alpha) + (\alpha) = (1 + \alpha)\text{moles}$$

Where α is numerically equal to the degree of dissociation of PCl_5

$$K_p = \frac{(PCl_3)(Cl_2)}{(PCl_5)} = \frac{\left(X_{PCl_3}\right)\left(X_{Cl_2}\right)P_T}{\left(X_{PCl_5}\right)}$$

But $X_{PCl_3} = X_{Cl_2} = \frac{\alpha}{1+\alpha}$ and $X_{PCl_5} = \frac{1-\alpha}{1+\alpha}$

Then $K_p = \frac{\alpha^2 P_T}{(1-\alpha^2)}$ but $\alpha = 0.85$ and $P_T = 1atm$

So $K_p = \frac{0.85^2 \times 1}{(1-0.85^2)} = 2.6atm$

Hence K_P for the reaction is 2.6atm

Using;
$K_P = K_c(RT)^{n-m}$; where $n = 2, m = 1$

$K_P = K_c(RT)^{2-1} = K_C(RT)$

Or $K_c = \frac{K_p}{RT} = \frac{2.6}{0.082 \times 523} = 0.06mol/dm^3$

Hence K_c for the reaction is $0.06mol/dm^3$

Question 113

Write down two advantages of employing high pressure in the Haber process.

Solution

1. It increases the percentage yield of ammonia.
2. It increases the rate of producing ammonia (ammonia is produced in shorter time)

Question 114

At 25°C and 1atm pressure, the partial pressures in the equilibrium pressures of N_2O_4 and NO_2 gases are 0.7atm and 0.3atm respectively. Calculate the partial pressure of these gases when they are in the equilibrium at 25°C and at a total pressure of 10atm.

Solution

(a) Equation for dissociation of N_2O_4 into NO_2: $N_2O_4 \rightleftharpoons 2NO_2(g)$

$$K_p = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O_2}} = \frac{(0.3\text{atm})^2}{(0.7\text{atm})} = 0.1286\text{atm}$$

If $P_T = 10\text{atm}$

By Dalton's law of partial pressure

$$P_{NO_2} + P_{N_2O_4} = 10\text{atm}$$

Then $0.1286 =$

Then $0.1286 = \frac{\left(P_{NO_2}\right)^2}{1-P_{NO_2}} =$

$$\left(P_{NO_2}\right)^2 + 0.1286P_{NO_2} - 1.286 = 0$$

This is the quadratic equation in P_{NO_2}; thus solving the equation gives $P_{NO_2} = 1.07\text{atm}$.

$$P_{N_2O_4} = 10 - P_{NO_2} = 8.93\text{atm}$$

Hence:

The partial pressure of NO_2 is 1.07atm

The partial pressure of N_2O_4 is 8.93atm

Alternative solution

$$K_p = \frac{\left(X_{NO_2}P_T\right)^2}{\left(X_{N_2O_4}P_T\right)} = \frac{\left(X_{NO_2}\right)^2 P_T}{\left(X_{N_2O_4}\right)}$$

Where $P_T = 10\text{atm}$

$$\begin{array}{lcccc} & N_2O_4(g) & \rightleftharpoons & 2NO_2(g) \\ \text{At equilibrium} & 1-\alpha & & 2\alpha \end{array}$$

$$X_{NO_2} = \frac{2\alpha}{1+\alpha} \quad \text{and} \quad X_{N_2O_4} = \frac{1-\alpha}{1+\alpha}$$

Then $K_p = \frac{4\alpha^2 P_T}{1-\alpha^2} = \frac{4\times10\alpha^2}{1-\alpha^2} = 0.1286$

Solving above equation gives $\alpha = 0.0568$

$$P_{N_2O_2} = \left(\frac{1-\alpha}{1+\alpha}\right)P_T = \left(\frac{1-0.0568}{1+0.0568}\right)10\text{atm}$$

$$P_{NO_2} = \left(\frac{2\alpha}{1+\alpha}\right)P_T = \left(\frac{2\times 0.0568}{1+0.0568}\right)10\text{atm} = 1.07\text{atm}$$

Hence

The partial pressure of NO_2 is 1.07atm

The partial pressure of N_2O_2 is 8.93atm

Question 115

Which physical factor(s) affect the magnitude of equilibrium constant?

Solution

Temperature only.

Question 116

How the factor(s) mentioned in **Question 115** above, affect the magnitude of equilibrium constant?

Solution

Increase in temperature increases the magnitude of equilibrium constant for endothermic reaction while it decreases the magnitude of equilibrium constant for exothermic reaction and vice-versa.

Question 117

An equilibrium mixture at 300K contains N_2O_4 and NO_2 gases at 0.28atm and 1.1atm respectively; if the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.

Solution

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At equilibrium 0.28atm 1.1atm

$$K_P = \frac{\left(P_{NO_2}\right)^2}{P_{N_2O_4}} = \frac{(1.1atm)^2}{(0.28atm)} = 4.32atm$$

Total pressure, P_1 at equilibrium

$= P_{N_2O_4} + P_{NO_2}$ (By Dalton's law of partial pressure)

If the volume is doubled from V_1 to V_2 such that $V_2 = 2V_1$

By Boyle's law; $P_1V_1 = P_2V_2$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{P_1V_1}{2V_1} = \frac{P_1}{2}$$

For N_2O_4; $P_2 = \frac{0.28atm}{2} = 0.14atm$

For NO_2; $P_2 = \frac{1.1atm}{2} = 0.55atm$

The decrease in pressure will shift equilibrium position to the NO_2 side.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At new equilibrium $0.14 - x$ $0.55 + 2x$

Then;

$$4.32 = \frac{(0.55 + 2x)^2}{0.14 - x}$$

From which;

$4x^2 + 6.52x - 0.3023 = 0;\ x = 0.045$

Hence at new equilibrium:

Partial pressure of N_2O_4

$$= 0.14 - 0.045 = (0.14 - 0.045)atm = 0.095atm$$

Partial pressure of NO_2

$$= 0.55 + 2x = (0.55 + 2 \times 0.045)\text{atm} = 0.64\text{atm}$$

Question 118

In a mixture of nitrogen gas and hydrogen gas at molar ratio of 1:3, the molar percent of NH_3 at equilibrium was found to be 1.2 at 500℃ and 10atm

(a) Calculate K_p

(b) Find the pressure at which the equilibrium mixture at this temperature contain 10.4 molar percent?

Solution

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

	N_2	H_2	NH_3
Initially	1	3	0
At equilibrium	$1 - x$	$3 - 3x$	$2x$

$n_T = (1 - x) + (3 - 3x) + 2x = 4 - 2x$

But $\left(\frac{2x}{4-2x}\right) \times 100 = 1.2$ (molar percent of NH_3 is 1.2)

From which $x = 0.024\text{moles}$

At equilibrium:

Number of moles of $N_2 = 1 - x = 0.97\text{moles}$

Number of moles of moles of $H_2 = 3 - 3x = 2.928\text{moles}$

Number of moles of $NH_3 = 2x = 0.048\text{moles}$

Total number of moles, $n_T = 4 - 2x = 3.952\text{moles}$

$$P_{NH_3} = X_{NH_3}P_T = \frac{0.048 \times 10\text{atm}}{3.952} = 0.12\text{atm}$$

$$P_{H_2} = X_{H_2}P_T = \frac{2.928 \times 10\text{atm}}{3.952} = 7.4\text{atm}$$

$$P_{N_2} = X_{N_2}P_T = \frac{0.976 \times 10\text{atm}}{3.952} = 2.47\text{atm}$$

$$K_P = \frac{\left(P_{NH_3}\right)^2}{\left(P_{N_2}\right)\left(P_{H_2}\right)^3} = \frac{0.12^2}{2.47 \times 7.4^3} = 1.44 \times 10^{-5}\text{atm}^{-2}$$

Hence K_p for the reaction is $1.44 \times 10^{-5}\text{atm}^{-2}$

Molar percent of NH_3 is 10.4

Then $\left(\frac{2x}{4-2x}\right) \times 100 = 10.4$

From which $x = 0.188$

Then at new equilibrium:

Number of moles of $N_2 = 1 - x = 0.812$moles

Number of moles of $H_2 = 3 - 3x = 2.436$ moles

Number of moles of $NH_3 = 2x = 0.376$moles

Total number of moles, $n_T = 4 - 2x = 3.624$ moles

$$P_{NH_3} = X_{NH_3}P_T = \frac{0.376P_T}{3.624} = 0.1P_T$$

$$P_{H_2} = X_{H_2}P_T = \frac{2.436\,P_T}{3.624} = 0.672P_T$$

$$P_{N_2} = X_{N_2}P_T = \frac{0.812P_T}{3.624} = 0.224P_T$$

$$K_P = \frac{(0.1P_T)^2}{(0.224P_T)(0.672P_T)^3} = \frac{0.147}{(P_T)^2} = 1.44 \times 10^{-5}; \quad P_T = 101\text{atm}$$

Thus the required pressure for molar percent of NH_3 to be 10.4 is 101atm.

Question 119

At 450°C, K_c for the equilibrium: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.8. How many moles of NH_3 must be placed in 1litre container in order to yield an equilibrium concentration of hydrogen gas of 6 moles per litre?

Solution

Let required number of moles of NH_3 be a

Then:

	$N_2(g)$	$+$	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initially	0		0		0
At equilibrium	x		3x		$a - 2x$

But at equilibrium $[H_2] = 6M$

Thus $3x = 6$ or $x = 2$

Hence concentration of each at equilibrium is as follows:

$[NH_3] = a - 2x = (a - 4)M$, $[N_2] = x = 2M$ and $[H_2] = 6M$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(a-4)^2}{(2) \times (6)^3}$$

Or $a - 4 = \sqrt{(1.8) \times (2) \times (6)^3} = 27.9$ or $a = 31.9$ moles

Hence 31.9 moles of ammonia must be places in 1 litre container

Question 120

What will be percentage of dissociation when 1 mole of H_2S gas is introduced in a vessel of 1.1L at 1000K? The value of K_c for the reaction is 10^{-6}.

Solution

	$2H_2S(g)$	$\rightleftharpoons$	$2H_2(g)$	$+$	$S_2(g)$
Initially	1		0		0
At equilibrium	$1 - 2x$		2x		x

$$K_c = \frac{[H_2]^2[S_2]}{(H_2S)^2} = \frac{\left(\frac{2x}{V}\right)^2\left(\frac{x}{V}\right)}{\left(\frac{1-2x}{V}\right)^2} = \frac{4x^3}{V(4x^2 - 4x + 1)}$$

But $K_C = 10^{-6}$ and $V = 1.1L$

Then;

$$10^{-6} = \frac{4x^3}{1.1(4x^2 - 4x + 1)}$$

Solving above equation gives $x = 6.4 \times 10^{-3}$

Degree of dissociation, $\alpha = \frac{2x}{1} = 2 \times 6.4 \times 10^{-3} = 0.0128$ or 1.28%

Hence percentage of dissociation of H_2S is 1.28%

Question 121

A mixture of SO_3, SO_2 gas and O_2 gas is maintained in 10litre flask at 500°C for which K_c for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ is 100.

(a) If the moles of SO_2 and SO_3 are equal in the flask how many moles of O_2 are present?

(b) If the number of moles of SO_3 is twice the number of moles of SO_2, how many moles of O_2 present?

Solution

From the given reaction equation: $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

If number of moles $SO_2 =$ number of moles of SO_3;

Then $[SO_2] = [SO_3]$

$$K_c = \frac{1}{[O_2]}$$

$[O_2] = \frac{1}{K_c} = \frac{1}{100} = 0.01M$; then using $n = V[\quad]$

Number of moles in 10L flask $= 10 \times 0.01$ moles $= 0.1$moles

Hence 0.1moles of O_2 present in the flask

(b) If number of moles of $SO_3 = 2 \times$ number of moles of SO_2

Then $2[SO_2] = [SO_3]$

So $K_c = \frac{(2[SO_2])^2}{[SO_2]^2[O_2]} = \frac{4}{[O_2]}$

$$[O_2] = \frac{4}{K_c} = \frac{4}{100} = 0.04$$

Thus number of moles of O_2 in 10L flask

$= 10 \times 0.04\text{moles} = 0.4\text{moles}$

Hence 0.4 moles of O_2 present in the flask

Question 122

Hydrogen chloride may be prepared by direct combination of hydrogen and chlorine as per the following reaction equation:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)\ \Delta H = -184kJ/mol$$

What will be the effect on the percentage yield of HCl when:

(i) The volume of reaction flask is halved.
(ii) Temperature for the reaction is lowered.
(iii) Concentration of both hydrogen and chlorine gas is doubled.

Solution

(i) No effect.
(ii) The percentage yield will increase.
(iii) No effect.

Question 123

At 250℃ and 1atm of sulphur trioxide gas is 50% dissociated, calculate K_p and K_c for the reaction at 250℃

Solution

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

At equilibrium $\quad 1 - 2x \qquad 2x \qquad x$

Where $\alpha = \frac{2x}{1} = 0.5,\ x = 0.25$

$$P_{O_2} = X_{O_2}P_T = \left(\frac{x}{1+x}\right)1\text{atm} = 0.2\text{atm}$$

$$P_{SO_2} = X_{SO_2}P_T = \left(\frac{2x}{1+x}\right)1\text{atm} = 0.4\text{atm}$$

$$P_{SO_3} = X_{SO_3}P_T = \left(\frac{1-2x}{1+x}\right)1\text{atm} = 0.4\text{atm}$$

$$K_P = \frac{\left(P_{SO_2}\right)^2\left(P_{O_2}\right)}{\left(P_{SO_3}\right)^2} = \frac{0.2 \times 0.4^2}{0.4^2} = 0.2\text{atm}$$

Hence K_p is 0.2atm

$K_c = K_p(RT)^{m-n}$ for $m = 2$ and $n = 3$

$K_c = K_p(RT)^{2-3} = K_P(RT)^{-1}$ or $K_C = \frac{K_P}{RT} = \frac{0.2}{0.082 \times 523} = 4.66 \times 10^{-3}\text{moldm}^{-3}$

Hence K_c is $4.66 \times 10^{-3}\text{moldm}^{-3}$

Question 124

(a) Ammonia is manufactured by the Haber process in which the following equilibrium is established.

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

(i) Why catalyst has no effect on position of this equilibrium?

(ii) At equilibrium, with a pressure of 35MPa and a temperature of 600K, the yield of ammonia is 65%.

A: State why industry uses a temperature higher than 600K.

B: State why industry uses a pressure lower than 35MPa

Solution

(i) It increases the rate of both forward and backward reaction by the same amount.

(ii) A: To increase the production rate of ammonia.

B: To reduce the production cost of ammonia.

Question 125

Calculate the numerical value of K_p for the decomposition of SO_2Cl_2, if its degree of dissociation under atmospheric pressure is 90%.

Solution

$$\begin{array}{cccc} SO_2Cl_2(g) & \rightleftharpoons & SO_2(g) + & Cl_2(g) \\ 1-\alpha & & \alpha & \alpha \end{array}$$

Where α is numerically equal to the degree of dissociation = 0.9

$$P_{SO_2} = X_{SO_2}P_T = \left(\frac{\alpha}{1+\alpha}\right)P_T = \left(\frac{0.9}{1+0.9}\right)1\text{atm} = 0.474\text{atm} = P_{Cl_2}$$

$$P_{SO_2Cl_2} = \left(\frac{1-\alpha}{1+\alpha}\right)P_T = \left(\frac{1-0.9}{1+0.9}\right) \times 1\text{atm} = 0.053\text{atm}$$

$$K_p = \frac{(P_{SO_2})(P_{Cl_2})}{(P_{SO_2Cl_2})} = \frac{0.474 \times 0.474}{0.053} = 4.239\text{ atm}$$

Hence numerical value of K_p is 4.239

Question 126

(a) *Catalyst has no effect on chemical equilibrium.* What is wrong about this argument? Explain clearly.

Solution

Catalyst affect chemical equilibrium by enabling the equilibrium to be reached earlier. It has no effect on the **position** of chemical equilibrium (not chemical equilibrium in general).

Question 127

CO_2 dissociates according to; $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$.If under atmospheric pressure, 40% of CO_2 was dissociated; calculate the dissociation constant i.e K_p

Solution

$$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$$

At equilibrium $\quad 1 - 2x \qquad 2x \qquad x$

But $\alpha = \frac{2x}{1} = 0.4$ or $x = 0.2$

Atmospheric pressure $= 1$ atm

$$P_{CO} = X_{CO}P_T = \left(\frac{2x}{1+x}\right) \times 1atm = 0.33atm$$

$$P_{O_2} = X_{O_2}P_T = \left(\frac{x}{1+x}\right) \times 1atm = 0.17atm$$

$$P_{CO_2} = X_{CO_2}P_T = \left(\frac{1-2x}{1+x}\right) \times 1atm = 0.5atm$$

$$K_p = \frac{(P_{CO})^2(P_{O_2})}{(P_{CO_2})^2} = \frac{(0.33)^2(0.17)}{(0.5)^2} = 7.4 \times 10^{-2}atm$$

Hence the dissociation constant (K_p) for the reaction is 7.4×10^{-2}atm

Question 128

Calculate the value of K_P at 700K for each of the reaction represented below;

(i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g)$
(ii) $2H_2S(g) + N_2(g) + 3H_2(g) \rightleftharpoons 2NH_4HS(g)$
Given that:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3; \quad K_P = 3.1 \times 10^{-4} \text{ at } 700K$$

$$NH_3(g) + H_2s(g) \rightleftharpoons NH_4HS(g); \quad K_P = 8.3 \times 10^{-3} \text{ at } 700K$$

Solution

Given that:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \; K_{P_1} = 3.1 \times 10^{-4} \ldots\ldots\ldots\ldots..(1)$$

$$NH_3(g) + H_2S(g) \rightleftharpoons NH_4HS(g); \; K_{P_2} = 8.3 \times 10^{-3} \ldots\ldots\ldots.(2)$$

(i) $NH_4HS(g) \rightleftharpoons NH_3(g) + H_2S(g);\ K_p = \frac{1}{K_{P_2}}$

So K_p for the (i) above $= \frac{1}{8.3\times10^{-3}atm^{-1}} = 1.2\times10^{2}atm$

(ii) Taking $2\times(2)$gives;

$2NH_3(g) + 2H_2S(g) \rightleftharpoons 2NH_4HS;\ K_{P_3} = \left(K_{P_2}\right)^2 = 6.889\times10^{-5}$ ... (3)

Then taking (1) + (3) gives

$$N_2(g) + 3H_2(g) + 2NH_3(g) + 2H_2s(g) \rightleftharpoons 2NH_4HS(g) + 2NH_3;$$

$$K_p = K_{P_1}\times K_{P_3}$$

Or $N_2(g) + 3H_2(g) + 2H_2s(g) \rightleftharpoons 2NH_4Hs(g);$

$$K_p = (3.1\times10^{-4}atm^{-2})(6.889\times10^{-5}\ atm^{-2})$$

$$= 2.13559\times10^{-8}atm^{-4}$$

Hence the K_p value for the reaction (ii) is $2.13559\times10^{-8}atm^{-4}$

Question 129

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

For the reaction above the rate constant at 380℃ for the forward reaction is $2.6\times10^{3}\ L^{2}\ \ mol^{-2}s^{-1}$ and this reaction is first order in O_2 and second order in NO. The rate constant for the reverse reaction at 380℃ is 4.1 $Lmol^{-1}s^{-1}$ and this reaction is second order in NO_2.

(a) Write the equilibrium expression for the reaction as indicated by the equation above and calculate the numerical value for the equilibrium constant at 380℃.

(b) What is the rate of the production of NO_2 at 380℃ if the concentration of NO is 0.006mol/L and the concentration of O_2 is 0.29mol/L?

(c) The system above is studied at another temperature. A 0.2 mole sample of NO_2 is placed in a 5L container and allowed to come to equilibrium. When equilibrium is reached,15% of the original NO_2 has decomposed to NO and O_2. Calculate the value for the equilibrium constant at the second temperature.

Solution

(a) $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$

At the equilibrium; rate of forward reaction=rate of backward reaction

That is $K_f[NO]^2\ [O_2] = K_b\ [NO_2]^2$

From which $\frac{K_f}{K_b} = \frac{[NO_2]^2}{[NO_2]^2[O_2]} = K_c$

Substituting $\frac{2.6\times10^3 L^2 mol^{-2} s^{-1}}{4.1\ L\ \ mol^{-1}\ s^{-1}} = K_c$

(b) Hence the value of equilibrium constant is $634.15L\ \ mol^{-1}$

(c) $\frac{1}{2}\frac{d[NO_2]}{dt} = R = K[NO]^2[O_2]$

$= 2.6 \times 10^3 \times (0.006)^2 \times 0.29$ or $0.027Ms^{-1}$

Then $\frac{d[NO_2]}{dt} = 2R = 2 \times 0.027Ms^{-1}$

Hence the rate of the production of NO_2 is $0.054Ms^{-1}$

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$0 \qquad\qquad 0 \qquad\qquad 0.2$

$2x \qquad\qquad x \qquad\qquad 0.2 - 2x$

But $\frac{2X}{0.2} = 0.15$ or $x = 0.015mol$

Then $[NO_2] = \frac{(0.2-2\times0.015)}{5L} mol = 0.034M$

$[O_2] = \frac{0.015mol}{5L} = 0.003M$

$[NO] = \frac{2\times0.015mol}{5L} = 0.006M$

Then using $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{(0.034M)^2}{(0.006M)^2\times0.003M} = 1.07 \times 10^4 M^{-1}$

Hence the value of the equilibrium constant is $1.07 \times 10^4 M^{-1}$

Question 130

Define the following terms:

(i) Law of mass action

(ii) Catalyst

(a) Most metal ions combine with other ions in solution for example in aqueous ammonia; silver (I) ions are in equilibrium with different complex ions.

$$[Ag(H_2O)_2]^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + 2H_2O(l)$$

A room temperature,K_c for this reaction is 1×10^7.Which of the two silver complex ions is the more stable? Give a reason for your choice.

Solution

i) Is the principle which explains effect of different factors on the position of chemical equilibrium.

(ii) Is the chemical reaction which can proceed in both forward and backward direction.

(iii) Is the law which express the relationship between concentration of reactants and that of products when the chemical system of reversible reaction is allowed to attain the equilibrium.

(iv) Is the substance that alters the rate of chemical reaction but itself remain unchanged at the end of chemical reaction.

Question 131

Dinitrogen tetraoxide in its liquid state was used as one of fuels on the Lunar lander expeditions for the NASA space vessels. In the gas phase it decomposes to gaseous nitrogen dioxide as shown in the following equation:

$$N_2O_4(g) \rightleftharpoons 2NO_2\ (g)$$

N_2O_4 was allowed to reach at equilibrium at $400°C$ where the value of $K_p = 0.133$atm. At equilibrium, the pressure of N_2O_4 was found to be 2.71atm.

(i) Write the equilibrium expression in terms of concentration.

(ii) Write the equilibrium expression in terms of partial pressures.

(iii) Calculate the equilibrium pressure of NO_2.

Solution

(a) ((b) $[Ag(NH_3)_2]^+$ is more stable.

Reason: Large value of K_c implies that the position of equilibrium lies to the $[Ag(NH_3)_2]^+$ side (right hand side)

(a) (i) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$ (ii) $K_p = \frac{(NO_2)^2}{(N_2O_4)}$

(iii) $K_p = \frac{\left(P_{NO_2}\right)^2}{\left(P_{N_2O_4}\right)} = \frac{\left(P_{NO_2}\right)^2}{2.71\text{atm}} = 0.133\text{atm}$

$\left(P_{NO_2}\right)^2 = 0.36043\text{atm}^2$; $P_{NO_2} = \sqrt{0.36043\text{atm}^2} = 0.6\text{atm}$

Equilibrium pressure of NO_2 is 0.6atm

Question 132

Define the following:

(i) Reaction quotient
(ii) Equilibrium constant

Solution

(i) Is the ratio of product of concentration of products to that of reactants raised to powers equal to their stoichiometric coefficients obtained in the course of the chemical reaction.
(ii) Is the temperature dependent fixed ratio which is obtained as the quotient of the product of equilibrium concentration of products to that of reactants raised to powers equal to their stoichiometric coefficient.

Question 133

When 20.85g of PCl_5 was heated in a sealed tube of $4dm^3$ volume, the pressure in the vessel was found to be 1.5 atm. At this pressure it was found that PCl_5 dissociated to 80%. Calculate the partial pressure of each gas.

Solution

(a)

(b) $$\mathrm{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$$

Pressure at $t = 0$ $\quad P_0 \quad 0 \quad 0$

Pressure at equilibrium $\quad P_0 - P \quad P \quad P$

(Since pressure is directly proportional to the number of moles, pressure ratio is equal to the mole ratio and therefore pressure can be treated as moles in the equation).

Also from, pressure-mole relationship:

Degree of dissociation, $\alpha = \frac{P}{P_0}$

And $\alpha = 20\% = 0.2$ (PCl_5 dissociated to 80%)

Thus $0.2 = \frac{P}{P_0}$ or $P = 0.2P_0$

Total pressure at equilibrium;

$P_0 - P + P + P = 1.5$

Or $P_0 + P = P_0 + 0.2P_0 = 1.2P_0 = 1.5$

From which $P_0 = 1.25$ atm

And $P = 0.2P_0 = 0.2 \times 1.25$ atm $= 0.25$ atm

Hence:

Partial pressure of $PCl_5 = P_0 - P = (1.25 - 0.25)$atm $= 1$ atm

Partial pressure of $PCl_3 = P = 0.25$ atm

Partial pressure of $Cl_2 = P = 0.25$ atm

Question 134

(a) Consider the production of HI by direct combination between I_2 and H_2 as per question;

$$\mathrm{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

Can you alter the yield of HI at equation by adding hydrogen gas or decreasing the volume of the container? Explain.

Solution

By adding hydrogen gas.

Explanation:

Decreasing volume of the container has no effect on the position of chemical equilibrium. This is because the decrease in volume will increase the total pressure of the system and since the reaction is not accompanied with change in number of gas molecules, the change in pressure has no effect on the position of equilibrium and thus no effect on the yield of HI too. However according to Le-Chatelier's principle, the increase in concentration of hydrogen gas shift the position of equilibrium to HI side and therefore increasing the yield of HI.

Question 135

Nitrogen and oxygen combine endothermically at elevated temperature according to the equation:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2\ (g)$$

If the equilibrium constant for the reaction is 4.3×10^{-3} at $3000℃$ and 1atm, calculate the composition of each in the equilibrium if 2 moles of each nitrogen and oxygen were heated.

Solution

(a) For gases, the most common method of representing equilibrium constant is K_P. So the given value of Equilibrium constant is K_P value.

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

At $t = 0$	2	2	0
At equilibrium	$2 - x$	$2 - 2x$	$2x$

$K_p = 4.3 \times 10^{-3}$

$$K_p = \frac{\left(P_{NO_2}\right)^2}{\left(P_{N_2}\right)\left(P_{O_2}\right)^2} = \frac{\left(X_{NO_2}P_T\right)^2}{\left(X_{N_2}P_T\right)\left(X_{O_2}P_T\right)^2} = \frac{\left(X_{NO_2}\right)^2}{\left(X_{N_2}\right)\left(X_{O_2}\right)^2 P_T}$$

Using $X = \frac{n}{n_T}$

Where $n_T = 2 - x + 2 - 2x + 2x = 4 - x$

Then;

$$K_p = \frac{\left(\frac{2x}{4-x}\right)^2}{\left(\frac{2-x}{4-x}\right)\left(\frac{2-2x}{4-x}\right)^2 \times 1} = 4.3 \times 10^{-3}$$

$$\frac{4x^2(4-x)}{(2-x)(2-2x)^2} = 4.3 \times 10^{-3}$$

$$\frac{16x^2 - 4x^3}{8 - 20x + 16x^2 - 4x^3} = 4.3 \times 10^{-3}$$

From which;

$3.982x^3 - 15.9312x^2 - 0.086x + 0.0344 = 0$

Solving the above equation, gives the practical value of x which is 0.044.

Hence the composition of each is as follows:

Number of moles of $N_2 = 2 - x = 1.956$ mol.

Number of moles of $O_2 = 2 - 2x = 1.912$ mol.

Number of moles of $NO_2 = 2x = 0.088$ mol.

Question 136

i) Briefly explain the dynamic nature of equilibrium reaction.

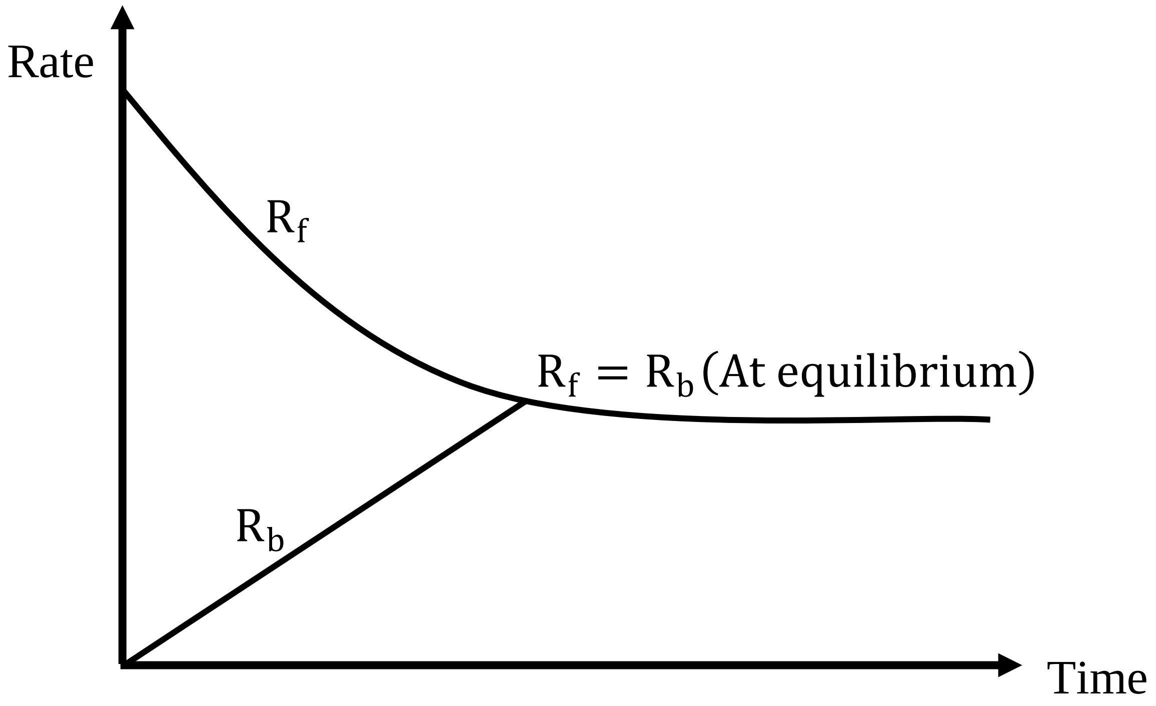
ii) Use hydrogen (H_2) and iodine (I_2) gases which produce hydrogen iodide (HI) gas to illustrate the point mentioned in (a)(i)

Solution

(i) Chemical equilibrium involves balance of the rate of the two reactions which are **proceeding at the same time** in **opposite directions.** So it involves the **constant interchange of particles in motion,** moving in opposite direction of forward and reverse reaction and hence the equilibrium is said to be dynamic.

(ii) Consider the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Initially the rate of forming HI (forward reaction) is maximum while that of dissociation of HI to form H_2 and I_2 (backward reaction) is zero because at the beginning, only H_2 and I_2 are present. As the reaction proceed concentration of H_2 and I_2 start to decrease and thus lowering the rate of forward reaction while HI is formed leading to backward reaction. Thus as the reaction proceed, the rate of forming HI is continuously decreasing while that of dissociation of HI is continuously increasing until they become equal where it said that the equilibrium has been attained as illustrated in the following graph:



Where:

R_f is the rate of formation of HI (forward reaction rate)

R_b is the rate of dissociation of HI (backward reaction)

Question 137

At temperature near $8000°C$, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called water gas. At $880°C$, the equilibrium constant for this reaction is $K_P = 14.1$. What are the equilibrium partial pressures of H_2O, CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.1000 mol of H_2O in a 1L vessel?

Solution

(a) From ideal gas equation; $P = \frac{nRT}{V}$

Then initial pressure exerted by H_2O $\left(P_{H_2O}\right)$ will be:

$$P_{H_2O} = \frac{0.1 \times 0.082 \times (880 + 273)}{1} \text{atm} = 9.4546 \text{ atm}$$

Since pressure exerted by gas varies directly proportional to the number of moles of the gas;

$$\text{Pressure ratio} = \text{Mole ratio}$$

Thus pressure can be treated as number of moles as follows:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

Pressure at $t = 0$ $\quad 9.4546 \quad 0 \quad 0$

Pressure at equilibrium $\quad 9.4546 - x \quad x \quad x$

$$K_p = \frac{P_{CO}P_{H_2}}{P_{H_2O}} = \frac{x^2}{9.4546 - x} = 14.1$$

$$x^2 + 14.1x - 133.30986 = 0$$

Solving above equation gives the practical value of x which is 6.4782

Hence:

$P_{H_2O} = 9.4546 - x = 2.9764$ atm

$P_{CO} = x = 6.4782$ atm

$P_{H_2} = x = 6.4782$ atm

Question 138

Concentrated sulphuric acid reacts with sodium chloride as follows: $H_2SO_4 + Cl^- \rightleftharpoons HCl + HSO_4^-$

(i) What would be observable result of this reaction?
(ii) Explain why this reaction goes almost completely to the right despite the hydrochloric and sulphuric acids are strong.

Solution

(i) White fumes (of hydrogen chloride gas).

(ii) HCl being gaseous is removed from the equilibrium system and thus the position of equilibrium shifts to the right.

Question 139

Explain conditions applied to increase the yield of ammonia in the Haber process indicating numerical values of pressure, temperature applied and also the kind of catalyst to be used.

Solution

In the Haber process, ammonia is produced as per equation:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ \Delta H = \text{negative}$$

The following conditions are applied to increase the yield of ammonia:

1. Very high pressure in the range of 200atm to 500atm

This shifts the position of equilibrium to the ammonia side (right hand side) as the production of ammonia per above equation is accompanied with significant reduction of volume.

2. Relative low temperature of 450°C.

The reaction is exothermic. So applying low temperature shifts the position of equilibrium to the ammonia side. However below 400°C no ammonia is produced.

3. Catalyst based on finely divided reduced iron promoted by alumina.

The low temperature favours production of ammonia but at very slow rate. So it is necessary to introduce catalyst which gives sufficient reaction rate inspite of relatively low temperature.

Question 140

Given with the equilibrium for the following reactions:

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g) \quad K_c = 10^2$$

$$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g) \quad K_c = 10^3$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \quad K_c = 10^4$$

Calculate the equilibrium constant for the following reaction

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

Solution

Given that:

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)\ K_c = 10^2$……. (i)

From which:

$K_c = \frac{[NO]}{[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}} = K_1 = 10^2$

$2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g) K_C = 10^3$…….. (ii)

From which:

$$K_c = \frac{[N_2O_4]}{[NO]^2[O_2]} = K_2 = 10^3$$

$N_2O_4(g) \rightleftharpoons 2NO_2(g) K_C = 10^4$ ………. (iii)

From which: $K_C = \frac{[NO_2]^2}{[N_2O_4]} = K_3 = 10^4$

Taking $2(i) + (ii) + (iii)$ gives

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ which is the same as given equation whose K_C is unknown.

Thus the K_C of the given equation will be given by the following relationship:

Required $K_C = (k_1)^2k_2k_3 = (10^2)^2 \times 10^3 \times 10^4 = 10^{11}$

Hence the equilibrium constant is 10^{11}

Question 141

State the equilibrium law and provide the corresponding equation.

Solution

The equilibrium law states that: When a chemical system is allowed to reach the equilibrium at a particular temperature, there is a fixed ratio of product of concentration of products to that of reactants raised to powers equals to stoichiometric coefficients regardless to the original concentration of the reagents present in the system.

For the hypothetical reaction: $\mathrm{aA\ +\ bB \rightleftharpoons cC\ +dD}$

Then according to equilibrium law; $\frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}} = \mathrm{Constant}\ (\mathrm{K_c})$

Question 142

The following dynamic equilibrium was established at temperature T in a closed container.

$$\mathrm{P(g) + 2Q(g) \rightleftharpoons 2R(g);\ \Delta H^{\theta} = -50\,kJ/mol}$$

The value of $\mathrm{K_c}$ for the reaction was $68.0\mathrm{mol^{-1}dm^3}$ when the equilibrium mixture contained 3.82mol of P and 5.24mol of R.

(i) Write an expression of $\mathrm{K_c}$ for this reaction.
(ii) The volume of container was $10\mathrm{dm^3}$. Calculate the concentration in $\mathrm{moldm^{-3}}$, of Q in the equilibrium mixture.
(iii) State the effect, if any, on the equilibrium amount of P, and on the value of $\mathrm{K_c}$ of increasing the temperature.
(iv) State the effect, if any, on the equilibrium amount of P, and on the value of $\mathrm{K_c}$ of using a container of larger volume.
(v) Deduce the value of the equilibrium constant, at temperature T, for the reaction;

$$\mathrm{2R(g) \rightleftharpoons P(g) + 2Q(g)}$$

Solution

(i) $\mathrm{K_c} = \frac{[\mathrm{R}]^2}{[\mathrm{P}][\mathrm{Q}]^2}$

(ii) $[\mathrm{P}] = \frac{3.82\mathrm{mol}}{10\mathrm{dm^3}} = 0.382\mathrm{moldm^{-3}};\ [\mathrm{R}] = \frac{5.24\mathrm{mol}}{10\mathrm{dm^3}} = 0.524\mathrm{moldm^{-3}}$

$$\mathrm{K_c} = 68.0\mathrm{mol^{-1}dm^3} = \frac{(0.524\mathrm{moldm^{-3}})^2}{0.382\mathrm{moldm^{-3}} \times [\mathrm{Q}]^2}$$

From which; $[\mathrm{Q}] = 0.103\mathrm{moldm^{-3}}$

(iii) The equilibrium amount of P will increase while the K_c value will decrease.

(iv) The equilibrium amount of P will increase.

(v) $K_c = \frac{[P][Q]^2}{[R]^2} = \frac{1}{\frac{[R]^2}{[P][Q]^2}} = \frac{1}{68.0\text{mol}^{-1}\text{dm}^3} = 0.0147\text{moldm}^{-3}$

Question 143

(a) The following equilibrium is established between colourless dinitrogen tetraoxide gas (N_2O_4) and dark brown nitrogen dioxide gas (NO_2).

$$N_2O_4(g) \rightleftharpoons 2NO_2(g);\ \ \Delta H = +58\text{kJ/mol}$$

(i) Give two main features of reaction at equilibrium.

(ii) Use Le Chatelier's principle to explain why the mixture of gases becomes darker in colour when the mixture is heated at constant pressure.

(iii) Use Le Chatelier's principle to explain why the amount of NO_2 decreases when the pressure is increased at constant temperature.

Solution

(a)

(i) **First feature:** Rate of forward reaction is equal to the rate of backward reaction.

Second feature: Concentration of reagents present in the system remain unchanged.

(ii) Heating will force the system to resist the change by absorbing the heat and therefore favouring forward reaction which is endothermic and hence more NO_2 which appears in brown colouration will be formed.

(iii) Increasing the pressure will force the system to resist the change by shifting the equilibrium position to the side with fewer gas molecules (N_2O_4 side) and hence the amount of NO_2 decreases.

Question 144

24.4g of ethanoic acid and 24.3g of ethanol were mixed in stoppered bottle and left for several days to reach equilibrium at room temperature. At the end of that time, the mixture was poured into pure water and made up to a total volume of 250cm^3. A 25.0cm^3 sample of this needed 26.5cm^3 of 0.400MNaOH to neutralise the remaining ethanoic acid. Calculate a value of K_c for the reaction:

$$\text{CH}_3\text{COOH(l)} + \text{CH}_3\text{CH}_2\text{OH(l)} \longrightarrow \text{CH}_3\text{COOCH}_2\text{CH}_3\text{(l)} + \text{H}_2\text{O(l)};$$

Solution

Using $n = \frac{m}{M_r}$;

Initial number of moles of $\text{CH}_3\text{COOH} = \frac{24.4\text{g}}{60\text{gmol}^{-1}} = 0.4\text{mol}$

Initial number of moles of $\text{CH}_3\text{CH}_2\text{OH} = \frac{24.3\text{g}}{46\text{gmol}^{-1}} = 0.53\text{mol}$

CH_3COOH reacts with NaOH according to the following equation; $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

From which mole ratio of NaOH to CH_3COOH is 1:1

Thus $n_{\text{NaOH}} = n_{\text{CH}_3\text{COOH}} = \frac{26.5}{1000} \times 0.4\text{mol} = 0.0106\text{mol}$

Whence number of moles of CH_3COOH in 25cm^3 of the solution is 0.0106mol.

Then number of moles of CH_3COOH in 250cm^3 of the solution

$$= \frac{0.0106 \times 250}{25}\text{mol} = 0.106\text{mol}$$

Hence number of moles of CH_3COOH at equilibrium was 0.106mol

	$\text{CH}_3\text{COOH(l)}$ +	$\text{CH}_3\text{CH}_2\text{OH(l)}$ ⇌	$\text{CH}_3\text{COOCH}_2\text{CH}_3\text{(l)}$ +	$\text{H}_2\text{O(l)}$
Initially	0.4	0.53	0	0
At equilibrium	$0.4 - x$	$0.53 - x$	x	x

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH\ ][CH_3CH_2OH]}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.4 - x}{V}\right)\left(\frac{0.53 - x}{V}\right)} = \frac{x^2}{(0.4 - x)(0.53 - x)}$$

But $0.4 - x = 0.106;\ x = 0.294$

Substituting;

$$K_c = \frac{0.294^2}{(0.4 - 0.294)(0.53 - 0.294)} = 3.46$$

Hence the equilibrium constant is 3.46

Question 145

By referring to Le-Chatelier's principle and behaviour of particles; explain clearly two advantages of using high pressure in Haber process.

Solution

In terms of Le-Chatelier's principle: To decrease the applied high pressure the equilibrium position will shift to the side with fewer gas particles (ammonia side) by producing more ammonia and hence high pressure has an advantage of increasing the ammonia yield in the Haber process.

In terms of behaviour of particles: High pressure makes gases to be more compressed into smaller volume and therefore more concentrated leading to greater collision frequency and hence higher reaction rate. So high pressure has another advantage of increasing the rate of ammonia production in the Haber process.

Question 146

A mixture was prepared using 1.00mol of propanoic acid, 2.00mol of ethanol and 5.00mol of water. At a given temperature, the mixture was left to reach equilibrium according to the following equation:

$CH_3CH_2COOH(l) + CH_3CH_2OH(l) \longrightarrow CH_3CH_2COOCH_2CH_3(l) + H_2O(l); \Delta H = -22kJ/mol$

The equilibrium mixture contained 0.54mol of the ester, ethyl propanoate.

(i) Write an expression for the equilibrium constant, K_c, for this equilibrium.
(ii) Calculate the number of moles of water in the equilibrium mixture.
(iii) Calculate a value for K_c for this equilibrium at this temperature. Why this K_c value has no units.
(iv) For this equilibrium, predict the effect of an increase in temperature on each of the following:
    A: The amount of ester at equilibrium.
    B: The time taken to reach equilibrium.
    C: The value of K_c

Solution

(i) $K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]}$

(ii) At equilibrium:

$n_{Acid} = 1 - x; \quad n_{Ethanol} = 2 - x$

$n_{Ester} = x; \quad n_{Water} = 5 + x$

But $n_{Ester} = x = 0.54mol$;

Thus $n_{Water} = 5 + x = (5 + 0.54) = 5.54mol$

The number of moles of water is 5.54mol

(iii)

$$K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]} = \frac{\left(\frac{x}{V}\right)\left(\frac{5+x}{V}\right)}{\left(\frac{1-x}{V}\right)\left(\frac{2-x}{V}\right)} = \frac{x^2 + 5x}{x^2 - 3x + 2}$$

Substituting;

$$\mathrm{K_c} = \frac{0.54^2 + 5(0.54)}{0.54^2 - 3(0.54) + 2} = 4.45$$

The value for $\mathrm{K_c}$ is 4.45

The $\mathrm{K_c}$ value has no units because there is an equal number of molecules in either side (reactants side and products side) of the reaction equation.

(iv) A: The amount will decrease.
B: The time will decrease.
C: The value will decrease.

Question 147

When 3-methylbutanoic acid reacts with ethanol in the presence of an acid catalyst, an **equilibrium** is established. The organic product is a pleasant-smelling ester.

$$\mathrm{(CH_3)_2CHCH_2COOH + CH_3CH_2OH \rightleftharpoons \underbrace{(CH_3)_2CHCH_2COOCH_2CH_3}_{\textbf{Ester}} + H_2O}$$

The carboxylic acid is very expensive and ethanol is inexpensive. In the manufacture of this ester, the mole ratio of carboxylic acid to ethanol used is 1 to 10 rather than theoretical ratio of 1 to 1.

(i) By referring to the reaction between the 3-methylbutanoic acid and ethanol above; explain clearly the meaning of the term **equilibrium**.
(ii) Explain why 1 to 10 mole ratio is used and not the theoretical one. (You should **not** refer to cost).
(iii) Explain the effect of catalyst in the equilibrium.

Solution

(a)

(i) *Is the condition which occurs in the reversible reaction when the rate of forward reaction is equal to the rate of reverse reaction.* In this case the equilibrium occurs when the rate of consumption of 3-menthlybutanoic acid and ethanol is equal to the rate of producing ester and water at which concentration of all reagents (acid ,ethanol ,ester and water) remain unchanged.

(ii) In order to increase the yield of ester. This is because, according to Le-Chatelier's principle; using high concentration of ethanol shifts equilibrium position to ester side (side with lower concentration) and therefore forming more ester.

(iii) Catalyst enable the equilibrium to be reached in shorter time. However it has no effect in equilibrium position because it increases the rate of both forward and reverse reaction by equal amount.

Question 147

The equilibrium constant for the reaction;

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at 986℃ is 0.63. A mixture of 1.0 mole of water vapour and 3.0 mole of CO is allowed to come to equilibrium. The equilibrium pressure is 2.0atm.

(i) Calculate the number of moles of H_2 present at equilibrium.

(ii) Calculate the partial pressure of gases at equilibrium mixture.

Solution

	$CO(g) +$	$H_2O(g) \rightleftharpoons$	$CO_2(g) +$	$H_2(g)$
Number of moles (At = 0)	3	1	0	0
Number of moles (at equilibrium)	3 – x	1 – x	x	x

$$K_p = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \frac{(X_{CO_2}P_T)(X_{H_2}P_T)}{(X_{CO}P_T)(X_{H_2O}P_T)}$$

$$K_p = \frac{(X_{CO_2})(X_{H_2})}{(X_{CO})(X_{H_2O})} = \frac{\left(\frac{n_{CO_2}}{n_T}\right)\left(\frac{n_{H_2}}{n_T}\right)}{\left(\frac{n_{CO}}{n_T}\right)\left(\frac{n_{H_2O}}{n_T}\right)} = \frac{n_{CO_2} \times n_{H_2}}{n_{CO} \times n_{H_2O}}$$

$$K_p = 0.65 = \frac{(x)(x)}{(3 - x)(1 - x)} = \frac{x^2}{x^2 - 4x + 3}$$

From which $0.37x^2 + 2.52x - 1.89x = 0$

Solving above equation gives practical value of x which is 0.68

(i) Hence the number of moles of H_2 is 0.68mol

(ii) $n_T = (3 - x) + (1 - x) + x + x = 4\text{mol}$

$$P_{CO} = X_{CO}P_T = \left(\frac{n_{CO}}{n_T}\right)P_T = \left(\frac{3 - x}{4}\right)P_T$$

Substituting;

$$P_{CO} = \left(\frac{3 - 0.68}{4}\right)2\text{atm} = 1.16\text{atm}$$

Similarly;

$$P_{H_2O} = \left(\frac{n_{H_2O}}{n_T}\right)P_T = \left(\frac{1-x}{4}\right)P_T = \frac{(1-0.68)}{4} \times 2\text{atm} = 0.16\text{atm}$$

$$P_{H_2} = P_{CO_2} = \left(\frac{x}{4}\right)P_T = \left(\frac{0.68}{4}\right) \times 2\text{atm} = 0.34\text{atm}$$

Hence:

Partial pressure of CO = 1.16atm

Partial pressure of H_2O = 0.16atm

Partial pressure of H_2 = 0.34atm

Partial pressure of CO_2 = 0.34atm

Question 148

Each of the following mixture was placed in a closed container and allowed to stand. Which is capable of attaining the equilibrium? $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.

In each case, provide an explanation for your answer.

(i) Pure $CaCO_3$

(ii) CaO and a CO_2 pressure greater than the value of K_p

(iii) Some $CaCO_3$ and a CO_2 pressure greater than the value of K_p

(iv) $CaCO_3$ and CaO

Solution

(i) Capable of attaining equilibrium

Explanation:

$CaCO_3$ Decomposes, forming CaO(s) and $CO_2(g)$ until the equilibrium pressure of CO_2 is attained (However there must be enough $CaCO_3$ to produce enough amount of CO_2 to exert equilibrium pressure).

(ii) Capable of attaining equilibrium

Explanation:

CO_2 continues to combine with CaO until the partial pressure of the CO_2 decrease to the equilibrium value.

(iii) Not capable of attaining equilibrium

Explanation:

There is no CaO present, so equilibrium cannot be attained because there is no way the CO_2 pressure can decrease to its equilibrium value (which would require some of the CO_2 to react with CaO).

(iv) Capable of attaining equilibrium

Explanation:

$CaCO_3$ decomposes until the equilibrium pressure of CO_2 is attained.

Question 149

Given the following information:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g); K_p = 54$ at 700K

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); K_p = 1.04 \times 10^{-4}$at 700K

Determine the value of K_p of the following reaction at 700K

$2NH_3(g) + 3I_2(g) \rightleftharpoons 6HI(g) + N_2(g)$

Solution

(b) Given that:

$H_2(g) + I_2(g) \rightleftharpoons 2HI_{(g)}; K_{P1} = 54$ ………………………... (i)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ K_{P2} = 1.04 \times 10^{-4}$ …….. (ii)

Taking 3 × (i) gives:

$3H_2(g) + 3I_2(g) \rightleftharpoons 6HI_{(g)};\ K_{P3} = (K_{P1})^3$……………. (iii)

Reversing (ii) gives;

$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g);\ K_{P4} = \frac{1}{K_{P2}}$ ……………..… (iv)

Taking (iii) + (iv) gives the required equation which is:

$2NH_3(g) + 3I_2(g) + \cancel{3H_2(g)} \rightleftharpoons 6HI_{(g)} + N_2(g) + \cancel{3H_2(g)}$

Or $2NH_3(g) + 3I_2(g) \rightleftharpoons 6HI(g) \quad + N_2(g); K_P = K_{P3} \times K_{P4}$

Thus the required $K_P = (K_{P1})^3 \times \frac{1}{K_{P2}}$

$$= 54^3 \times \frac{1}{1.04 \times 10^{-4}} = 1.51 \times 10^9$$

The value of K_P is 1.51×10^9

Question 150

(a) For the reaction $A_2 + 2B \rightleftharpoons 2AB$, the rate of the forward reaction is 18M/s and the rate of the reverse reaction is 12M/s. The reaction is not at equilibrium. Will the reaction proceed in the forward or reverse direction to attain equilibrium?

Solution

Forward direction

Explanation

Greater rate of forward reaction, means that there is much high concentration of reactants. So it must proceed in forward direction to decrease the concentration and the rate of forward reaction as well till the equilibrium.

Question 151

Consider the reaction:

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g) \quad \text{where } K_c = 1 \times 10^{-2}$$

In an experiment, 5mol of $HF(g)$, 0.5mol of $H_2(g)$, and 0.75mol of $F_2(g)$ are mixed in a 5L flask and allowed to react to equilibrium, calculate concentrations of all species at equilibrium.

Solution

Calculating the value of reaction quotient to know the reaction direction:

$$Q_c = \frac{[H_2][F_2]}{HF^2} = \frac{\left(\frac{0.5}{V}\right)\left(\frac{0.75}{V}\right)}{\left({}^{5}/_{V}\right)^2} = 0.015 = 1.5 \times 10^{-2}$$

But the given K_c value is 1×10^{-2}which is smeller than the reaction quotient (1.5×10^{-2})

Since $Q_c > K_c$, the reaction will proceed in reverse direction to establish the equilibrium.

	$2HF_{(g)} \rightleftharpoons$	$H_{2(g)} +$	$F_{2(g)}$
Initial (At t = 0)	5	0.5	0.75
At equilibrium	$5 + x$	$0.5 - x$	$0.75 - x$

$$K_c = \frac{[H_2][F_2]}{HF^2} = \frac{\left(\frac{0.5 - x}{V}\right)\left(\frac{0.75 - x}{V}\right)}{\left(\frac{5 + x}{V}\right)^2}$$

Then;

$$1 \times 10^{-2} = \frac{x^2 - 1.25x + 0.375}{x^2 + 10x + 25}$$

From which; $0.99x^2 - 1.35x + 0.125 = 0; x = 0.1$

Hence:

$$[HF] = \frac{5 + x}{V} = \frac{(5 + 0.1)\text{mol}}{5L} = 1.02M$$

$$[H_2] = \frac{0.5 - x}{V} = \frac{[0.5 - 0.1]\text{mol}}{5L} = 0.08\ M$$

$$[F_2] = \frac{0.75 - x}{V} = \frac{[0.75 - 0.1]\text{mol}}{5L} = 0.13M$$

Question 152

For the reaction:

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g), K_p = 794$ at 298K and $K_p = 54$ at 700K. Is the formation of HI favoured more at the higher or lower temperature? Give a reason for your answer

Solution.

When a 0.218mol of hydrogen iodide was heated in a flask of volume $V\text{dm}^3$, the following equilibrium was established at 700K.

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

Question 153

The equilibrium mixture was found to contain 0.023mol of hydrogen.

(i) Write an expression for K_c for the equilibrium
(ii) State why the volume of the flask need not be known when calculating a value of K_c
(iii) Calculate the value of K_c at 700K
(iv) Calculate the value of K_c for the equilibrium $H_2(g) + I_2 \rightleftharpoons 2HI(g)$

Solution

(i) $K_c = \frac{[H_2][I_2]}{[HI]}$

(ii) V cancels in the K_c expression (as the reaction is not accompanied by change in number of moles of reagents present in the system).

(iii)

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

Initially $\quad 0.218 \quad 0 \quad 0$

At equilibrium $\quad 0.218 - 2x \quad x \quad x$

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{0.218 - 2x}{V}\right)^2} = \frac{x^2}{(0.218 - 2x)^2}$$

But $x = 0.023$ (Amount of hydrogen at equilibrium)

$$K_c = \frac{(0.023)^2}{\left(0.218 - 2(0.023)\right)^2} = 0.0179$$

The value of K_c is 0.0179

(iv) $K_c = \frac{[HI]^2}{[H_2][F_2]} = \frac{1}{\frac{[H_2][F_2]}{[HI]^2}} = \frac{1}{0.0179} = 55.9$

The value of K_c is 55.9

Question 154

(a) Three reactions, and their equilibrium constants, are gives below.

I. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = 4.7 \times 10^{-31}$

II. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 1.8 \times 10^{-6}$

III. $N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 0.025$

Arrange above equations in order of their tendency to form products.

Solution

$$\xrightarrow{\text{I} < \text{II} < \text{III}}$$

Increase in tendency of forming products

Question 155

Consider the gas-phase hydration of hexafluoroacetone, $(CF_3)_2CO$;

$$(CF_3)_2CO(g) + H_2O(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CF_3)_2C(OH)_2(g)$$

At 76°C, the forward and reverse rate constant are $K_f = 0.13M^{-1}s^{-1}$ and $K_r = 6.02 \times 10^{-4}s^{-1}$.

What is the value of the equilibrium constant, K_c?

Solution

$$K_c = \frac{K_f}{K_r} = \frac{0.13^{-1}s^{-1}}{6.02 \times 10^{-4}s^{-1}} = 215.9M^{-1}$$

The value of equilibrium constant is $215.9M^{-1}$

Question 156

Consider the following heterogeneous equilibrium reaction: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

At 800°C, the pressure of CO_2 gas is 0.236 atm. Calculate: (i) K_p and (ii) K_c for the reaction at this temperature.

Solution

From the given reaction equation;

(i) $K_p = P_{CO_2} = 0.236atm$

(ii) $\Delta n = 1 - 0 = 1$

Then $K_P = K_c(RT)^{\Delta n} = K_c(RT)^1$

Substituting;$0.236atm = K_c \times 0.082atmLmol^{-1K^{-1}} \times 1073K$

From which K_c=$2.68 \times 10^{-3}moldm^{-3}$

Question 157

(a) A platinum catalyst is used in automobile catalytic converter to hasten the oxidation of carbon monoxide:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad \Delta H^{\theta} = -566kJ/mol$$

Suppose that you have a reaction vessel containing an equilibrium mixture of CO (g), O_2(g) and CO_2(g). Under the following conditions, will the amount of CO increase, decrease, or remain the same?

(i) A platinum is added is added
(ii) The temperature is increased
(iii) The pressure is increased by decreasing the volume
(iv) The pressure is increased by adding argon gas
(v) The pressure is increased by adding O_2 gas.

Solution

(i) Remain the same
(ii) Decrease
(iii) Increase
(iv) Remain the same
(v) Increase

Question 158

For the equilibrium: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$,

The equilibrium constant, K_p, has the value of 0.497 at 500K. A gas cylinder at 500K is charged with $PCl_5(g)$ at initial pressure of 1.66atm.What are equilibrium pressures of PCl_5, PCl_3 and Cl_2 at this temperature?

Solution

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+ Cl_2(g)$
Pressure at t = o	1.66	0	0
Pressure at equilibrium	$166 - x$	x	x

$$K_P = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})}$$

Substituting;

$$0.497 = \frac{(x)(x)}{1.66 - x} = \frac{x^2}{1.66 - x}$$

From which; $x^2 + 0.497x - 0.82502 = 0;\ x = 0.693$

Hence:

Partial pressure of $P_{PCl_3} = x = 0.693\text{atm}$

Partial pressure of $Cl_2 = x = 0.693\text{atm}$

Partial pressure of $P_{PCl_5} = 1.66 - x = 0.967\text{atm}$

Question 159

At temperature near $800°C$, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2.

$$C\ (s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called **water gas**.

(a) At $880°C$, the equilibrium constant for this reaction is $K_p = 14.1$.What are the equilibrium partial pressures of H_2O,CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100mol of H_2O in a 1L vessel?

(b) What is the minimum amount of carbon required to achieve equilibrium under these conditions?

Solution

(a) From ideal gas equation;

$$P = \frac{nRT}{V}$$

Then;

$$P_{\text{initial}} = \frac{n_{H_2O}RT}{V} = \frac{0.1 \times 0.082 \times 1153\text{atm}}{1} = 9.4546\text{atm}$$

	$C(s)\quad + H_2O(g)$	$\rightleftharpoons CO(g)$	$+ H_2(g)$
Initial pressure	9.4546	0	0
Equilibrium pressure	$9.4546 - x$	x	x

$$K_p = 14.1 = \frac{(P_{CO})(P_{H_2})}{(P_{H_2O})} = \frac{x^2}{9.4546 - x}$$

From which; $x^2 + 14.1x - 133.3 = 0; x = 6.5$

Hence:

Partial pressure of $CO = x = 6.5atm$

Partial pressure of $H_2 = x = 6.5atm$

Partial pressure of $H_2O = 9.4546 - x = 2.95atm$

(b) Amount of $H_2O(g)$ reacted is equiralent to the pressure of 6.5atm(decrease in pressure)

Using; $n = \frac{PV}{RT}$

$$n_{H_2O} \text{ reacted } = \frac{6.5 \times 1mol}{0.082 \times 1153} = 0.069mol$$

From the reaction equation, mole ratio of $C(s)$ to $H_2O(g)$ is 1:1

So number of moles of $C(s)$ required to react with 0.069mol was also 0.069mol.

Using $m = nM_r$;

Minimum amount of $C(s)$ required is $0.069mol \times 12gmol^{-1} = 0.83g$

Question 160

(a) Listed in the table are forward and reverse rate constant for the reaction: $NO(g) \rightleftharpoons N_2(g) + O_2(g)$

Temperature (K)	$K_f(M^{-1}s^{-1})$	$K_r(M^{-1}s^{-1})$
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in the terms of kinetics.

Solution

Exothermic

Explanation:

K_r increases more than K_f when temperature is increased. This means that E_a of reverse reaction is greater than E_a of forward reaction. The reaction is exothermic when $E_a(\text{reverse}) > E_a(\text{forward})$.

Question 161

The equilibrium mixture, $SO_2 + NO_2 \rightleftharpoons SO_3 + NO$ was found to contain 0.6mol SO_3, 0.4mol of NO, 0.8mol of SO_2 and 0.1mol of NO_2 in a 1L vessel. One mole of NO was then forced into the reaction vessel with volume and temperature being constant. Calculate the amounts of each gas in the new equilibrium mixture.

Solution

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

At equilibrium $\quad 0.8 \quad 0.1 \quad 0.6 \quad 0.4$

$$K_c = \frac{[SO_2][NO]}{[SO_2][NO_2]} = \frac{\left(\frac{0.6}{V}\right)\left(\frac{0.4}{V}\right)}{\left(\frac{0.8}{V}\right)\left(\frac{0.1}{V}\right)} = 3$$

Addition of 1 mole of NO to the equilibrium mixture will favour reverse reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

After addition of 1mol of NO $\quad 0.8 \quad 0.1 \quad 0.6 \quad 1.4$

At new equilibrium $\quad 0.8 + x \quad 0.1 + x \quad 0.6 - x \quad 1.4 - x$

Then;

$$K_c = 3 = \frac{\left(\frac{0.6 - x}{V}\right)\left(\frac{1.4 - x}{V}\right)}{\left(\frac{0.8 + x}{V}\right)\left(\frac{0.1 + x}{V}\right)}$$

From which; $2x^2 + 4.7x - 0.6 = 0;\ x = 0.12$

Hence at new equilibrium (by substituting $x = 0.12$):

Number of moles of $SO_2 = 0.8 + x = 0.92mol$

Number of moles of $NO_2 = 0.1 + x = 0.22mol$

Number of moles of $SO_3 = 0.6 - x = 0.48mol$

Number of moles of $NO = 1.4 - 4 = 1.28mol$

Question 162

When 1mol of PCl_5 is introduced into a 5L container at 500K, 78.5% of the PCl_5 dissociates to give an equilibrium mixture of PCl_5, PCl_3 and Cl_2.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g).$$

Calculate the value of K_p and K_c

Solution

(a)	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$
Initially	1	0	0
At equilibrium	$1 - \alpha$	α	α

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{\alpha}{V}\right)\left(\frac{\alpha}{V}\right)}{\left(\frac{1-\alpha}{V}\right)} = \frac{\alpha^2}{(1-\alpha)V}$$

But $\alpha = \frac{78.5}{100} = 0.785$ and $V = 5L$

$$K_c = \frac{0.785^2}{(1-0.785) \times 5} mol/L = 0.573mol/L$$

$K_p = K_c(RT)^{\triangle n}$ where $\triangle n = 2 - 1 = 1$

$K_p = 0.573molL^{-1} \times 0.082atmLmol^{-1}K^{-1} \times 500K = 23.5atm$

The value of K_p is 23.5atm

Question 163

If the initial concentrations in a particular mixture of reactants and products (in (a) above) are $[\mathrm{PCl_5}] = 0.5\mathrm{M}$,$[\mathrm{PCl_3}] = 0.15\mathrm{M}$ and $[\mathrm{Cl_2}] = 0.6\mathrm{M}$;

(i) In which direction does the reaction proceed to reach equilibrium?
(ii) What are the concentrations when the mixture reaches equilibrium?

Solution

$$\mathrm{Q_c} = \frac{[\mathrm{PCl_3}][\mathrm{Cl_2}]}{[\mathrm{PCl_5}]} = \frac{0.15\mathrm{M} \times 0.6\mathrm{M}}{0.5\mathrm{M}} = 0.18\mathrm{M}$$

So $\mathrm{Q_c}(0.18) < \mathrm{K_c}(0.573\mathrm{M})$ and hence **the reaction will proceed in forward direction to reach the equilibrium.**

$$\mathrm{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$$

At new equilibrium $\quad 0.5 - \mathrm{x} \quad 0.15 + \mathrm{x} \quad 0.6 + \mathrm{x}$

$$\mathrm{K_c} = 0.573 = \frac{(0.15 + \mathrm{x})(0.6 + \mathrm{x})}{(0.5 - \mathrm{x})}$$

From which: $\mathrm{x}^2 + 1.323\mathrm{x} - 0.1965 = 0; \mathrm{x} = 0.135$

Hence at the new equilibrium (by substituting x=0.135):

$[\mathrm{PCl_5}] = 0.5 - \mathrm{x} = 0.365\mathrm{M}$

$[\mathrm{PCl_3}] = 0.15 + \mathrm{x} = 0.285\mathrm{M}$

$[\mathrm{Cl_2}] = 0.6 + \mathrm{x} = 0.735\mathrm{M}$

Question 164

Suggest four ways in which concentration of hydrazine $\mathrm{N_2H_4}$ could be increased in an equilibrium described by the equation:

$$\mathrm{N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g); \quad \Delta H = +95kJ/mol}$$

Solution

(i) Increasing concentration of $\mathrm{N_2}$(adding $\mathrm{N_2}$)
(ii) Increasing concentration of $\mathrm{H_2}$(adding $\mathrm{H_2}$)
(iii) Increasing temperature
(iv) Increasing pressure

Question 165

PCl_5 dissociates according to the reaction;

$PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g); K_p = 1.78 \text{atm at } 523K$

Find the density of the equilibrium mixture at a total pressure of 1atm.

Solution

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+ Cl_2(g)$
Initially	1	0	0
At equilibrium	$1-\alpha$	α	α

$$K_p = \frac{(P_{PCl_3})(P_{Cl_2})}{(P_{PCl_5})} = \frac{(X_{PCl_3}P_T)(X_{Cl_2}P_T)}{(X_{PCl_5}P_T)}$$

$$K_p = \frac{\left(\frac{n_{PCl_3}}{n_T}\right)\left(\frac{n_{Cl_2}}{n_T}\right)P_T}{\left(\frac{n_{PCl_5}}{n_T}\right)} = \frac{(n_{PCl_3})(n_{Cl_2})P_T}{(n_{PCl_5})(n_T)}$$

$$K_p = 1.78 = \frac{\alpha \times \alpha}{(1-\alpha)(1+\alpha)} (n_T = 1 - \alpha + \alpha + \alpha = 1 + \alpha)$$

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

From which; $2.78\alpha^2 = 1.78; \alpha = 0.8$

Thus the degree of dissociation (α) is 0.8

Then using $\alpha = \frac{i-1}{N-1}$

Where: is the Van't Hoff's factor,

N is the number of molecules formed after dissociation of 1 molecule of $PCl_5 = 2$

Substituting $0.8 = \frac{i-1}{2-1}; i = 1.8$

But also;

$$\mathrm{i} = \frac{\text{Expected } \mathrm{M_r}}{\text{Observed } \mathrm{M_r}}$$

Where; expected $\mathrm{M_r}$ = Molar mass of $\mathrm{PCl_5}$ before dissociation

$$= \big(31 + (5 \times 35.5)\big)\mathrm{gmol^{-1}} = 208.5\mathrm{gmol^{-1}}$$

Then $1.8 = \frac{208.5\mathrm{gmol^{-1}}}{\text{Observed } \mathrm{M_r}}$; Observed $\mathrm{M_r} = 115.8\mathrm{gmol^{-1}}$

From ideal gas equation;

$$\rho = \frac{\mathrm{PM_r}}{\mathrm{RT}}$$

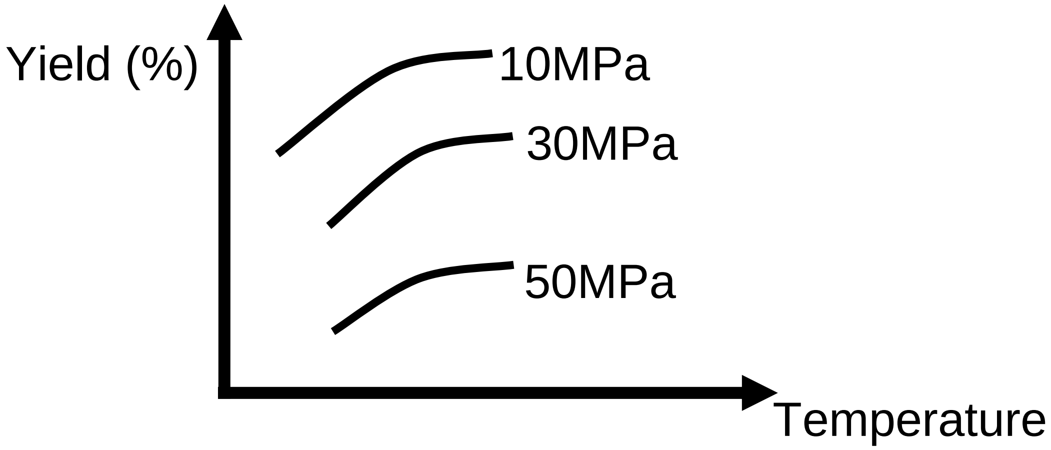
Thus density of the mixture (density of $\mathrm{PCl_5}$ after dissociation)

$$= \frac{1\mathrm{atm} \times 115.8\mathrm{gmol^{-1}}}{0.082\mathrm{atmLmol^{-1}K^{-1}} \times 523\mathrm{K}} = 2.7\mathrm{gL^{-1}}$$

Density of the equilibrium mixture is 2.7g/L

Question 166

(a) The diagram below shows the effect of temperature and pressure on the equilibrium yield of the product in a gaseous equilibrium.



(i) Use the diagram to deduce whether the forward reaction involves increase or decrease in the number of moles of gas. Explain your answer.

(ii) Use the diagram to deduce whether the forward reaction is exothermic or endothermic. Explain your answer.

Solution

(i) Increase

Explanation:

Low pressure gives higher yield.

(ii) Endothermic

Explanation:

Increase in temperature of given pressure increase the yield.

Question 167

Solid ammonium carbamate(NH_2COONH_4) dissociates as;

$$NH_2COONH_4 \rightleftharpoons 2NH_3(g) + CO_2(g)$$

In a closed vessel, solid ammonium carbamate is in equilibrium with dissociation products. At equilibrium, ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at equilibrium to that of original total pressure.

Solution

For gases, pressure ratio = mole ratio.

So, if initially was only solid ammonium carbamate in the vessel, at the first equilibrium; $P_{NH_3} = 2P_{CO_2}$

Thus if we let $P_{CO_2} = P$, then $P_{NH_3} = 2P$

And if P_{CO_2} at new equilibrium is P'

Then P_{NH_3} at new equilibrium will be P'' (Not $2P'$ because after the addition of ammonia the mole ratio is disturbed).

But P_{NH_3} at new equilibrium $=$ Total pressure in the first equilibrium

$$= \mathrm{P} + 2\mathrm{P} = 3\mathrm{P}$$

Thus $\mathrm{P}'' = 3\mathrm{P}$ or $\mathrm{P}'' = \frac{3}{2}\mathrm{P}$

$$\mathrm{NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)}$$

At the first equilibrium	$2\mathrm{P}$	P
At the final equilibrium	$3\mathrm{P}$	P'

$\mathrm{K_p} = \left(\mathrm{P_{NH_3}}\right)^2 \times \mathrm{P_{CO_2}} = (2\mathrm{P})^2 \times \mathrm{P} = (3\mathrm{P})^2 \times \mathrm{P}'$

From which $\mathrm{P}' = \frac{4}{9}\mathrm{P}$

Original total pressure $= 2\mathrm{P} + \mathrm{P} = 3\mathrm{P}$

Final total pressure $= 3\mathrm{P} + \mathrm{P}'$

$$\frac{\text{Final total pressure}}{\text{Original total pressure}} = \frac{3\mathrm{P} + \mathrm{P}'}{3\mathrm{P}} = \frac{3\mathrm{P} + \frac{4}{9}\mathrm{P}}{3\mathrm{P}} = \frac{31}{27}$$

Hence the ratio is $\frac{31}{27}$

Question 168

Consider the following reversible equilibrium:

$$\mathrm{2C_2H_6(g) + 7O_2(g) \rightleftharpoons 4CO_2(g) + 6H_2O(l)}$$

Derive the relationship between $\mathrm{K_c}$ and $\mathrm{K_p}$.

Solution

(a)

$$\mathrm{K_p} = \frac{\left(\mathrm{P_{CO_2}}\right)^4}{\left(\mathrm{P_{C_2H_6}}\right)^2\left(\mathrm{P_{O_2}}\right)^7}$$

But from ideal gas equation; P = [ ]RT

$$\text{Then } K_p = \frac{([CO_2]RT)^4}{([C_2H_6]RT)^2([O_2]RT)^7}$$

$$K_p = \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} \times (RT)^{4-(2+7)}$$

$$\text{But } \frac{[CO_2]^4}{[C_2H_6]^2[O_2]^7} = K_c$$

Hence $K_p = K_c(RT)^{-5}$

Question 169

At 90°C, the following equilibrium is established:

$$H_2(g) + S(s) \rightleftharpoons H_2S(g); \;\; K_p = 6.8 \times 10^{-2}$$

If 0.2mol of hydrogen and 1.0mol of sulphur are heated to 90°C, in a litre vessel; what will be partial pressure of H_2S at equilibrium?

Solution

Initial total pressure

$$= P_{H_2} = \frac{n_{H_2}RT}{V} = \frac{0.2 \times 0.082 \times 363}{1} \text{atm} = 5.9532\text{atm}$$

	$H_2(g) + S(s)$	$\rightleftharpoons H_2S(g)$
Initial pressure	5.9532	0
Equilibrium pressure	$5.9532 - x$	x

$$K_p = \frac{P_{H_2S}}{P_{H_2}} = \frac{x}{5.9532 - x} = 6.8 \times 10^{-2}$$

From which ; $1.068x = 0.4048; x = 0.379$

The partial pressure of H_2S is 0.379atm

Question 170

Equilibrium constant is the ratio of rate constant of forward reaction to that of backward reaction $\left(K_c = \frac{K_f}{K_b}\right)$. It is known that the magnitude of both rate constants increases with an increase in temperature. Explain why the K_c value changes as the result of the increase in temperature despite the fact that both K_f and K_b values are increased by the temperature rise.

Solution

This is because the increase in temperature does not increase values of K_f and K_b by the same amount due to the difference in activation energy of forward and backward reaction. If the activation energy of forward reaction is greater than that of backward reaction (for endothermic reactions), the increase in K_f value will be greater than that of K_b and therefore the K_c value will increase while the K_c value will decrease if the activation energy of forward reaction is smaller (for exothermic reactions).

Question 171

A 16g sample of sulphur trioxide was placed in an empty container where it decomposed at 800K according to the following chemical reaction:

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

At equilibrium, the total pressure and the density of the gaseous mixture were 3.6atm and 3.2gdm^{-3} respectively. Calculate K_p for this reaction.

Solution

$$\text{From ideal gas equation: } M_r = \frac{mRT}{VP} = \frac{\rho RT}{P}$$

$$\text{Then } M_{\text{mixture}} = \frac{3.2 \times 0.0821 \times 800}{3.6}\text{g/mol} = 58.3822\text{g/mol}$$

$$i = \frac{\text{Expected } M_r}{\text{Observed } M_r} = \frac{80\text{g/mol}}{58.3822\text{g/mol}} = 1.37$$

$$\text{But also } i = \frac{P_{\text{observed}}}{P_{\text{expected}}} = \frac{3.6}{P_{\text{expected}}} = 1.37$$

From which $P_{\text{expected}} = \frac{3.6}{1.37}\text{atm} = 2.63\text{atm}$

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

$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2; N = 1.5$

$$\alpha = \frac{i - 1}{N - 1} = \frac{1.37 - 1}{1.5 - 1} = 0.74$$

	$2SO_3(g)$	$\rightleftharpoons 2SO_2(g)$	$+\ O_2(g)$
Initial pressure	2.63	0	0
Equilibrium pressure	$2.63 - 2x$	$2x$	x

But $\alpha = \frac{2x}{2.63} = 0.74; x = 0.9731$

Equilibrium pressure for each:

$P_{SO_2} = 2.63 - 2x = 0.6838\text{atm}$

$P_{SO_2} = 2x = 1.9462\text{atm},$

$P_{O_2} = x = 0.9731\text{atm}$

$$K_p = \frac{\left(P_{SO_2}\right)^2 \times P_{O_2}}{\left(P_{SO_3}\right)^2} = \frac{(1.9462\text{atm})^2 \times 0.9731\text{atm}}{(0.6838\text{atm})^2} = 7.88\text{atm}$$

The K_p value is 7.88atm.