SOLVED PROBLEM 2. Some nitrogen and hydrogen gases are pumped into an empty five-litre glass bulb at 500°C. When equilibrium is established, 3.00 moles of N_2, 2.10 moles of H_2 and 0.298 mole of NH_3 are found to be present. Find the value of K_c for the reaction

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

at 500°C.

SOLUTION

The equilibrium concentrations are obtained by dividing the number of moles of each reactant and product by the volume, 5.00 litres. Thus,

$$[N_2] = 3.00\ \text{mole}/5.00\ \text{L} = 0.600\ \text{M}$$
$$[H_2] = 2.10\ \text{mole}/5.00\ \text{L} = 0.420\ \text{M}$$
$$[NH_3] = 0.298\ \text{mole}/5.00\ \text{L} = 0.0596\ \text{M}$$

Substituting these concentrations (not number of moles) in the equilibrium constant expression, we get the value of K_c.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.0596)^2}{(0.600)(0.420)^3} = 0.080$$

Thus, for the reaction of H_2 and N_2 to form NH_3 at 500°C, we can write

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \mathbf{0.080}$$

SOLVED PROBLEM 2. The value of K_p at 25°C for the reaction

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

is 1.9×10^3 atm^{-1}. Calculate the value of K_c at the same temperature.

SOLUTION

We can write the general expression as

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

Here,

$$T = 25 + 273 = 298 \text{ K}$$

$$R = 0.0821$$

$$\Delta n = 2 - (2 + 1) = -1$$

$$K_p = 1.9 \times 10^3$$

Substituting these values in the general expression

$$K_c = \frac{1.9 \times 10^3}{(0.0821 \times 298)^{-1}}$$

$$= \mathbf{4.6 \times 10^4}$$

goes on increasing.

SOLVED PROBLEM. The following data was obtained on hydrolysis of methyl acetate at 25°C in .5N hydrochloric acid. Establish that it is a first order reaction.

t (secs)	0	4500	7140	∞
ml alkali used	24.36	29.32	31.72	47.15

SOLUTION

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid duced by hydrolysis.

The volume of alkali used for total change from t_0 to t_∞ gives the initial concentration of ester. ıs,

$$a = 47.15 - 24.36 = 22.79 \text{ ml}$$

$$(a-x) \text{ after } 4500 \text{ sec} = 47.15 - 29.32 = 17.83 \text{ ml}$$

$$(a-x) \text{ after } 7140 \text{ sec} = 47.15 - 31.72 = 15.43 \text{ ml}$$

Substituting values in the rate equation above, we have

$$k = \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455$$

$$k = \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546$$

Since the values of k in the two experiments are fairly constant, the reaction is of the first order.

SOLVED PROBLEM 2. In an electrolysis of copper sulphate between copper electrodes the total mass of copper deposited at the cathode was 0.153 g and the masses of copper per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 g respectively. Calculate the transport number of the Cu^{2+} and SO_4^{2-} ions.

SOLUTION

$$\text{Wt. of copper in the anode liquid before electrolysis} = 0.79\text{ g}$$

$$\text{Wt. of copper in the anode liquid after electrolysis} = 0.91\text{ g}$$

$$\text{Increase in weight} = 0.91 - 0.79 = 0.12\text{ g}$$

$$\text{Increase in weight of copper cathode in the coulometer} = 0.153\text{ g}$$

This means that if no copper had migrated from the anode, increase in weight would have been 0.153 g.

$$\text{But actual increase} = 0.12$$

$$\text{Fall in concentration due to migration of } Cu^{2+} \text{ ions} = 0.153 - 0.12 = 0.033$$

$$\therefore \quad \text{Transport number of } Cu^{2+} \text{ ion} = \frac{0.033}{0.153} = 0.216$$

$$\text{and Transport number of } SO_4^{2-} \text{ ion} = (1 - 0.216) = \mathbf{0.784}$$

SOLVED PROBLEM. Calculate the vapour pressure lowering caused by the addition of 100 g of sucrose (mol mass = 342) to 1000 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

SOLUTION

Using Raoult's Law Equation

$$\frac{p - p_s}{p} = \frac{\Delta p}{p} = \frac{n}{n + N} \quad ...(1)$$

where

Δp = lowering of vapour pressure

p = vapour pressure of water = 23.8 mm Hg

n = moles of sucrose $= \frac{100}{342} = 0.292$ mole

N = moles of water $= \frac{1000}{18} = 55.5$ moles

Substituting values in equation (1)

$$\frac{\Delta p}{23.8} = \frac{0.292}{0.292 + 55.5}$$

$$\Delta p = 23.8 \times \frac{0.292}{55.792} = \mathbf{0.125\ mm}$$

Thus the lowering of vapour pressure = **0.125 mm Hg**