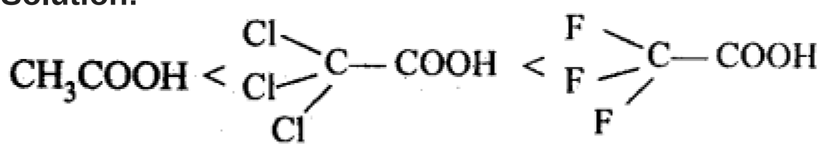
SOLUTION

2.31 The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

Solution:



Fluorine being more electronegative than chlorine has the highest electron withdrawing inductive effect. Thus, triflouroacetic acid is the strongest trichloroacetic acid is second most and acetic acid is the weakest acid due to absence of any electron withdrawing group. Thus, F_3CCOOH ionizes to the largest extent while CH_3COOH ionizes to minimum extent in water. Greater the extent of ionization greater is the depression in freezing point. Hence, the order of depression in freezing point will be $CH_3COOH < Cl_3CCOOH < F_3CCOOH$.

2.32 Calculate the depression in the freezing point of water when 10g of $CH_3CH_2CHClCOOH$ is added to 250g of water. Ka = $1.4 \times 1o^{-3}$ Kg = 1.86 K kg mol^{-1}.

Solution:

Molar mass of $CH_3CH_2CHClCOOH$

$= 122{\cdot}5 \text{ g mol}^{-1}$

No. of moles of $CH_3CH_2CHClCOOH$ present

$$= \frac{10}{122{\cdot}5} = 8.16 \times 10^{-2} \text{ mole.}$$

$$\text{Molality} = \frac{8{\cdot}16 \times 10^{-2}}{250} \times 1000 = 0{\cdot}3264 \text{ m}$$

Let a be the degree of dissociation of $CH_3CH_2CHClCOOH$, then and C be the initial concentration of $CH_3CH_2CHClCOOH$

	$CH_3CH_2CHClCOOH \rightleftharpoons$	$CH_3CH_2CHClCOO^-$	$+ H^+$
Initially	C	0	0
At Equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$\therefore K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2$$

{α being very very small)

$$\therefore \quad K_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1{\cdot}4 \times 10^{-3}}{0{\cdot}3264}} = 0{\cdot}065 .$$

Calculation of van't Hoff factor:

Initially the concentration

$CH_3CH_2CHClCOOH$ will be 1 mole.

	$CH_3CH_2CHClCOOH \rightleftharpoons$	$CH_3CH_2CHClCOO^-$	$+ H^+$
Initially	1	0	0
At Equilibrium	$(1-\alpha)$	α	α

$$\therefore \quad i = \frac{1+\alpha}{1} = 1 + \alpha = 1 + 0{\cdot}065 = 1{\cdot}065$$

$$\therefore \quad \Delta T_f = i K_f m$$

$$= 1{\cdot}065 \times 1{\cdot}86 \times 0{\cdot}3264 = 0{\cdot}65° \text{K}$$

2.33 19.5g of CH_2FCOOH is dissolved in 500g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van's Hoff factor and dissociation constant of fluoroacetic acid.

Solution:

Using the relation,

$$\underset{\text{(observed)}}{M_2} = \frac{1000\ K_f\ W_2}{W_1\ \Delta T_f}$$

$$= \frac{1000 \times 1{\cdot}86 \times 19{\cdot}5}{500 \times 1} = 72{\cdot}54\ \text{g mol}^{-1}$$

$$M_2\ (\text{Calculated}) = 12 + 2 + 19 + 12 + 2 \times 16 + 1$$
$$= 78\ \text{g mol}^{-1}$$

$$\therefore\ i = \frac{M_2\ (\text{calculated})}{M_2\ (\text{observed})} = \frac{78}{72{\cdot}54} = 1{\cdot}0753.$$

Calculation of dissociation constant :

Let α be the degree of dissociation and C be the initial concentration of CH_2FCOOH

	CH_2FCOOH	$\rightleftharpoons$	CH_2FCOO^-	$+ H^+$
Initially	C		0	0
At equilibrium	$C(1-\alpha)$		$C\alpha$	$C\alpha$

$$i = \frac{C\ (1+\alpha)}{C} = 1 + \alpha$$

$$\alpha = i - 1 = 1{\cdot}0753 - 1 = 0{\cdot}0753$$

$$K_a = \frac{C\alpha\ C\alpha}{C\ (1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.5 \times (0.0753)^2}{(1 - 0.0753)} = 3.07 \times 18^{-3}$$

2.34 Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25g of glucose is dissolved in 450g of water.

Solution:

$P^\circ = 17{\cdot}535$ mm

Molar mass of glucose = 180 g mol^{-1}

Molar mass of water = 18 g mol^{-1}

According to Raoult's's Law,

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1}$$

$$1 - \frac{P_s}{P^\circ} = \frac{25/180}{450/18} = \frac{25 \times 18}{180 \times 450}$$

$$1 - \frac{P_s}{P^\circ} = \frac{450}{81000}; \; 1 - \frac{450}{81000} = \frac{P_s}{P^\circ}$$

$$1 - 0.0055 = \frac{P_s}{17{\cdot}535}$$

$$0.9945 = \frac{P_s}{17{\cdot}535}$$

$$\therefore \quad P_s = 0.9945 \times 17.535 = 17{\cdot}44 \text{ mm Hg.}$$

2.35 Henry's law constant for the molality of methane in benzene at 298 K is 4.27 x 10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

Solution:

Using relation, $P = K_H x$

$$\therefore \; x = \frac{P}{K_H} = \frac{760 \text{ mm Hg}}{4{\cdot}27 \times 10^5 \text{ mm Hg}} = 1{\cdot}78 \times 10^{-3}$$

i.e., mole fraction of methane in benzene

$= 1{\cdot}78 \times 10^{-3}$.