SOLUTIONS

1. This is because the rate of reaction at any time depends upon the concentration of the reactants at that time and concentration keeps on decreasing with time.
2. The fraction of total molecules of an electrolyte which dissociate into constituent ions in the solution is the degree of dissociation of an electrolyte.
3. Zero order, because in zero order reactions, $t_{1/2} \propto a$.
4. Higher the critical temperature of gas, greater is the ease of liquefaction, *i.e.*, greater are the van der Waals' forces of attraction and hence greater is the adsorption.
5. pH of the solution in which hydrogen electrode is dipped (and which is attached to another NHE) is given by the relation, $\text{pH} = \frac{E_{\text{cell}}}{0.0591}$
6. Adsorption isobar for physical adsorption shows that the extent of adsorption decreases with increase in temperature. The adsorption isobar of chemical adsorption shows that the extent of adsorption first increases and then decreases with increase in temperature. The initial unexpected increase in the extent of adsorption with temperature is due to the fact that the heat supplied acts as activation energy required for chemical adsorption which is much more than that of physical adsorption.
7. Let initial concentration be $[R]_0$.

   For a first order reaction, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

   At time t, $[R] = \frac{[R]_0}{4}, k = 2.4 \times 10^{-3}\ \text{s}^{-1}$

   Thus, $2.4 \times 10^{-3} = \frac{2.303}{t} \log \frac{[R]_0}{[R]_0/4}$

   $$t = \frac{2.303}{2.4 \times 10^{-3}} \log 4 = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021 = 5.77 \times 10^2\ \text{s}$$
8. Demulsification is the separation of an emulsion into its constituent liquids. The different techniques applied for demulsification are centrifugation, freezing, boiling, electrostatic precipitation etc.

   OR

   The catalytic reaction that depends upon the size of the reactant and product molecules and the shape of catalyst (*i.e.*, its porous structure), is known as shape-selective catalysis *e.g.*, ZSM-5, that converts alcohol directly into gasoline by dehydrating them to give a mixture of hydrocarbons.

9. Cell constant = conductivity × resistance
= 1.29 S/m × 100 Ω = 129 m^{-1} = 1.29 cm^{-1}
Conductivity of 0.02 mol L^{-1} KCl solution

$$= \text{cell constant/resistance} = \frac{129\ m^{-1}}{520\ \Omega} = 0.248\ S\ m^{-1}$$

Concentration = 0.02 mol L^{-1}
= 1000 × 0.02 mol m^{-3} = 20 mol m^{-3}

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c} = \frac{248\times10^{-3}\ S\ m^{-1}}{20\ mol\ m^{-3}}$$

$$= 124 \times 10^{-4}\ S\ m^2\ mol^{-1}$$

10. $Ni_{(s)} + 2Ag^+_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05 - \frac{0.0591}{2}\log\frac{0.16}{(0.002)^2}$$

$$= 1.05 - 0.1359 = 0.9141\ V$$

11. (i) Being larger in size, sol particles absorb the light and become self luminous and then scatter the light in all possible directions, thus they exhibit Tyndall effect.

(ii) Blue colour of the sky is due to scattering of light by colloidal dust particles present in air. As blue colour of the white sunlight has minimum wavelength, it shows in more intense scattering and sky looks blue.

12. $$k = \frac{2.303}{t}\log\frac{a}{a-x} \Rightarrow 2.2\times10^{-5} = \frac{2.303}{30\times60}\log\frac{a}{a-x}$$

$$\frac{a}{(a-x)} = \text{antilog } 0.01719 = 1.0404$$

$$0.0404a = 1.0404x \Rightarrow \frac{x}{a} = \frac{0.0404}{1.0404} = 0.0388 = 3.88\%$$

13. (i) $Cd|Cd^{2+}||Ag^+|Ag$
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = (0.80) - (-0.40) = 1.20\ V$

(ii) $Pt, I^-_{(aq)}|I_{2(s)}||\ Cl_{2(g)}|Cl^-_{(aq)}, Pt$
$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = (1.36) - (0.54) = 0.82\ V$

14. (i) The combination of the two layers (fixed and diffused) of opposite charges around the colloidal particles is called Helmholtz electrical double layer.

(ii) Dialysis is used for purification of colloidal solutions. It is carried out by putting impure colloidal solution in a parchment paper bag and then dipping it in distilled water. After some time all the crystalloids in solution diffuse through the membrane into the water leaving behind the pure colloidal solution. An important application of dialysis is during the purification of blood in the artificial kidney machine.

15. Given : $I = 1.5$ A, $W = 1.45$ g Ag, $t = ?$, $E = 108$, $n = 1$
Using Faraday's 1st law of electrolysis, $W = ZIt$

$$\text{or, } W = \frac{E}{nF}It \Rightarrow 1.45\ g = \frac{108}{1\times96500}\times1.5t$$

$$\text{or, } t = \frac{1.45\times96500}{1.5\times108} = 863.73\ \text{seconds}$$

Now, for Cu, W_1 = 1.45 g Ag, E_1 = 108, W_2 = ?,

$$E_2 = \frac{63.5}{2} = 31.75$$

From Faraday's 2nd law of electrolysis,

$$\text{Using formula, } \frac{W_1}{W_2} = \frac{E_1}{E_2}$$

$$\frac{1.45}{W_2} = \frac{108}{31.75} \quad \therefore\ W_2 = 0.426\ \text{g of Cu}$$

Similarly, for Zn, W_1 = 1.45 g Ag, E_1 = 108,

$$W_2 = ?,\ E_2 = \frac{65.3}{2} = 32.65$$

$$\frac{1.45}{W_2} = \frac{108}{32.65} \quad \therefore\ W_2 = 0.438\ \text{g of Zn}$$

OR

Diameter of column = 1 cm
Thus, the radius, r = 1/2 cm = 0.5 cm
Area = πr^2 = 3.14 × $(0.5)^2$ = 0.785 cm^2

$$\text{We know that, resistivity, } \rho = \frac{R\times A}{l}$$

As, l = 50 cm and $R = 5.55 \times 10^3\ \Omega$

$$\text{Thus, } \rho = \frac{5.55\times10^3\times0.785}{50} = 87.135\ \Omega\ cm$$

$$\text{Conductivity, } \kappa = \frac{1}{\rho} = \frac{1}{87.135} = 11.48\times10^{-3}\ S\ cm^{-1}$$

$$\text{Molar conductivity} = \frac{1000\times\kappa}{M}$$

$$= \frac{11.48\times10^{-3}\ S\ cm^{-1}\times1000}{0.05\ mol\ L^{-1}} = 229.6\ S\ cm^2\ mol^{-1}$$

16. (i) $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{0.07}{0.02} = \left(\frac{E_a}{2.303\times8.314\ JK^{-1}\ mol^{-1}}\right)\left[\frac{700-500}{700\times500}\right]$$

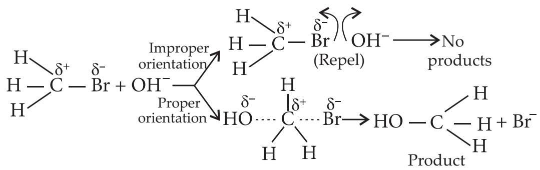
$E_a = 1.823 \times 10^4$ J
Since, $k = Ae^{-E_a/RT}$

$$0.02 = Ae^{-1.823\times10^4/8.314\times500} \Rightarrow A = \frac{0.02}{0.012} = 1.66$$

(ii) A reaction that takes place in one step is called an elementary reaction. For example, dissociation reaction of HI to form H_2 and I_2 is an elementary reaction.

17. During a reaction, the reacting molecules collide with each other. But all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy called threshold energy and proper orientation can lead to breaking of bonds of reactants and formation of new bonds to form products are called effective collisions. The improper orientation makes them simply bounce back without the formation of products *e.g.*, formation of methanol from bromomethane.

$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$



18. (i) The standard electrode potential, $E°$ for silver is 0.80 V and that of gold is 1.5 V, hence silver can replace gold from its solution. The replaced gold is deposited on silver object due to which golden tinge is obtained. On the other hand $E°$ for Cu is 0.34 V which is lower than that of silver, thus silver cannot replace copper from its solution.

(ii) Consider the following reduction reaction,

$$M^+ + e^- \longrightarrow M \quad ; \quad E = E° + \frac{RT}{nF}\ln[M^+]$$

It is clear from the above equation that the electrode potential of a given half cell will increase with the increase in concentration of ions and temperature.

19. (i) (a) Colloidal particles of test tube (*A*) are positively charged whereas colloidal particles of test tube (*B*) are negatively charged.

(b) In test tube (*A*), Fe^{3+} ions are adsorbed on the ppt. $Fe_2O_3 \cdot xH_2O$ [or $Fe_2O_3 \cdot xH_2O/Fe^{3+}$ is formed].
In test tube (*B*), OH^- ions are adsorbed on the ppt. $Fe_2O_3 \cdot xH_2O$ [or $Fe_2O_3 \cdot xH_2O/OH^-$ is formed]

(ii) The adsorption of gases on the surface of metals is called occlusion.

20. (i) **Alcosol :** The sol in which alcohol is used as a dispersion medium is called alcosol *e.g.*, sol of cellulose nitrate in ethyl alcohol.

(ii) **Aerosol :** The sol in which dispersion medium is gas and dispersed phase is either solid or liquid, the colloidal system is called aerosol *e.g.*, fog, insecticide sprays, etc.

(iii) **Hydrosol :** The sol in which dispersion medium is water is called hydrosol *e.g.*, starch sol.

21. (i) The negative sign in rate of reaction indicates that the concentration of the reactant is decreasing with time while the positive sign indicates that the concentration of the product is increasing with time.

(ii) (a) This method can be used for those reactions which have more than one reactant.

(b) Order with respect to each reactant can be calculated.

22. (i) Molar conductivity, $\Lambda_m^c = \frac{\kappa \times 1000}{\text{Molarity}}$

$= \frac{0.0248 \times 1000}{0.20} = 124 \text{ S cm}^2 \text{ mol}^{-1}$

(ii) For the reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

$\because$ 63.5 of Cu (1 mole) requires charge
$= 2F = 2 \times 96500$ C

$\therefore$ 3.2 g of Cu will require charge

$= \frac{2 \times 96500}{63.5} \times 3.2 \text{ C} = 9726 \text{ C}$

Amount of electricity passed (q) = It
$= 8 \times 2 \times 60 \times 60 = 57600$ C

$\therefore$ Current efficiency $= \frac{9726}{57600} \times 100 = 16.89\%$

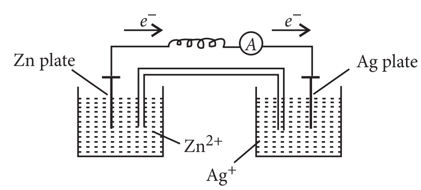
23. (i) The medicine is sold in anhydrous form to increase the shelf-life of medicine.

(ii) Shaking the content well will form a sol. Adsorption of medicine is easy in the form of colloidal sol formed.

(iii) Scientific knowledge and application of his knowledge in daily life incidents are the values shown by Suresh.

(iv) The process is peptisation in which freshly prepared precipitate converts into colloidal sol by shaking it with the dispersion medium in the presence of a small amount of electrolyte.

24. (i)



Electrons flow from Zn → Ag

(ii) Ag acts as cathode, because at Ag plate reduction of Ag^+ ions takes place as reduction potential of Ag^+ is greater than that of Zn^{2+} ion.

(iii) Cell will stop functioning since the movement of ions will be stopped.

(iv) As the reaction proceeds concentration of Zn^{2+} increases and concentration of Ag^+ decreases.

(v) The concentration of Zn^{2+} and Ag^+ will not change after the reaction ceases.

OR

The given reaction is

$2Hg + 2Fe^{3+} \rightleftharpoons Hg_2^{2+} + 2Fe^{2+}$

Initial concentration of $Fe^{3+} = 1.0 \times 10^{-3}$ M

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Equilibrium concentration of Fe^{3+} = 5% of 1.0×10^{-3} M

$$= \frac{5}{100} \times 10^{-3} = 5 \times 10^{-5} \text{ M}$$

Equilibrium concentration of Fe^{2+}
$= (1.0 \times 10^{-3}) - (5 \times 10^{-5})$ M $= 0.95 \times 10^{-3}$ M
Equilibrium concentration of Hg_2^{2+}

$$= \text{half of the } Fe^{2+} \text{ ion} = \frac{0.95 \times 10^{-3}}{2} \text{M}$$

We know that, $E_{cell} = E^\circ_{cell} - \frac{0.059}{n} \log \frac{[Hg_2^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$

But $E_{cell} = 0$ (Because reaction is at equilibrium)

$$\therefore \quad 0 = E^\circ_{cell} - \frac{0.059}{2} \log \frac{\left[\frac{0.95 \times 10^{-3}}{2}\right][0.95 \times 10^{-3}]^2}{[5 \times 10^{-5}]^2}$$

or $E^\circ_{cell} = -0.0226$
But $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = E_{Fe^{3+}/Fe^{2+}} - E^\circ_{Hg^{2+}/Hg}$
$-0.0226 = 0.77 - E^\circ_{Hg^{2+}/Hg}$
or $E^\circ_{Hg^{2+}/Hg} = 0.7926$ V

25. (i) Let the rate law be $r_0 = [A]^m[B]^n$
$(r_0)_1 = 5.07 \times 10^{-5} = (0.20)^m(0.30)^n$ ...(i)
$(r_0)_2 = 5.07 \times 10^{-5} = (0.20)^m(0.10)^n$ ...(ii)
$(r_0)_3 = 7.16 \times 10^{-5} = (0.40)^m(0.05)^n$ ...(iii)
Dividing equation (i) by equation (ii),

$$\frac{(r_0)_1}{(r_0)_2} = \frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{(0.20)^m(0.30)^n}{(0.20)^m(0.10)^n}$$

$1 = 3^n$ or $3^0 = 3^n \Rightarrow n = 0$
Dividing equation (iii) by equation (ii),

$$\frac{(r_0)_3}{(r_0)_2} = \frac{7.16 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{(0.40)^m(0.05)^n}{(0.20)^m(0.10)^n}$$

$1.412 = 2^m$ or $2^{1/2} = 2^m \Rightarrow m = \frac{1}{2}$ or $m = 0.5$
Thus order of reaction w.r.t. A = 0.5, order of reaction *w.r.t.* $B = 0$

(ii) As $t_{75\%} = 2t_{50\%}$, this shows that $t_{1/2}$ is independent of initial concentration. Hence, it is a first order reaction.

OR

(i) Radioactive disintegration follows first order kinetics. Hence,

$$\text{Decay constant of } ^{90}\text{Sr}, (\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$$
$$= 2.466 \times 10^{-2} \text{ yr}^{-1}$$

To calculate the amount left after 10 years,
Given, $[R_0] = 1$ μg, $t = 10$ years,
$\lambda = 2.466 \times 10^{-2}$ yr^{-1}, $[R] = ?$

Using formula, $\lambda = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$

or $2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$
or, $\log [R] = -0.1071$
or, $[R]$ = Antilog $(-0.1071) = 0.7814$ μg
To calculate the amount left after 60 years,
$t = 60$ years, $[R_0] = 1$ μg, $[R] = ?$
or, $2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{[R]}$
or, $\log [R] = -0.6425$
or, $[R]$ = Antilog $(-0.6425) = 0.2278$ μg

(ii) Arrhenius equation, $k = Ae^{-E_a/RT}$
Given equation is $k = (4.5 \times 10^{11} \text{ s}^{-1})e^{-28000\text{K}/T}$
Comparing both the equations, we get

$$-\frac{E_a}{RT} = -\frac{28000}{T} \Rightarrow E_a = 232.79 \text{ kJ mol}^{-1}$$

26. (i) **Activity :** The ability of a catalyst to accelerate a chemical reaction, is known as its activity. High catalytic activity is shown by a good catalyst. For example, platinum catalyst accelerate the reaction of hydrogen and oxygen to form water to 10^{10} times.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Selectivity : The ability of a catalyst to catalyse a group reaction to yield a specific product is known as selectivity of catalyst. For example, acetylene and hydrogen give ethane with Pt while they give ethene with Lindlar's catalyst.

(ii) $Fe(OH)_3$ is positively charged sol, hence the anion having maximum charge will be more effective. Therefore, Na_3PO_4 (having PO_4^{3-} ion) will be most effective.

OR

(i) Micelles are substances that behave as normal, strong electrolytes at low concentration but at high concentrations behave as colloids due to the formation of aggregates. They are also called associated colloids, *e.g.*, soaps and detergents. They can form ions and may contain 100 or more molecules to form a micelle.

(ii) In froth floatation process, the sulphide ore is mixed with pine oil and water. Then air is passed through it. Pine oil is adsorbed on sulphide ore particles, which forms an emulsion and comes out in the form of froth while impurities are wetted by water.

(iii) The minimum quantity in milligrams, of protective colloid which is just sufficient to prevent coagulation of 10 mL of standard gold sol when 1 mL of 10% solution of NaCl is added to it, is known as gold number.

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