CHEMISTRY

PHYSICAL / INORGANIC CHEMISTRY

1. After mixing

$[NaCl] = 0.02$ M ; $K[Ag(CN)_2] = 0.05$ M.

$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$ $\quad 4 \times 10^{-19}$

$0.05-x \quad x \quad 2x$

x is going to be very small in comparison to 0.05 as K_{inst} is very small.

So, $\quad 4 \times 10^{-19} = \dfrac{x \times (2x)^2}{0.05 - x} = \dfrac{4x^3}{0.05}$

$\Rightarrow \quad x^3 = 5 \times 10^{-21} \quad \Rightarrow \quad x \simeq 1.7 \times 10^{-7}$

Q_{sp} of AgCl $= 1.7 \times 10^{-7} \times 0.02 = 3.4 \times 10^{-9} > 2.8 \times 10^{-10}$

Hence, AgCl will be precipitated.

Further, $[Ag(CN)_2]^-$ dissociates on dilution and $[K^+]$ is halved on dilution.

2. O^{2-} ion = 4 [ccp lattice]

$A^{x+} = 8\,[TV]\dfrac{1}{4} = 2.$; $B^{y+} = 4[OV]\dfrac{1}{2} = 2.$

$\Rightarrow$ By charge balancing.

$2x + 2y - 8 = 0$ $\quad$ So, $\quad x + y = 4.$

3. (A) $t\ 100\% = \dfrac{a}{k}$

$$\frac{(t_{100\%})I}{(t_{100\%})II} = \frac{a_I}{a_{II}} \times \frac{k_{II}}{k_I} = \frac{1}{0.5} \times \frac{1/\sqrt{3}}{\sqrt{3}} = \frac{2}{3}$$

(B) $a - x = -k_A t + a$ $\quad$ or $\quad (1 - x) = -\sqrt{3}\,t + 1$ or $x = +\sqrt{3}\,t$

simiarly $0.5 - y = -\dfrac{1}{\sqrt{3}}t + 0.5$ or $y = \dfrac{t}{\sqrt{3}}$

when $\quad [A] = [C]$

$1 - x = 0.5 - y$

or $\quad 1 - \sqrt{3}\,t = 0.5 - \dfrac{t}{\sqrt{3}}$

$$0.5 = t\left(\sqrt{3} - \frac{1}{\sqrt{3}}\right) ; \quad t = \frac{\sqrt{3}}{4}\,\text{min.}$$

(D) $$\frac{(t_{50\%})I}{(t_{50\%})II} = \frac{a_I}{a_{II}} \cdot \frac{k_{II}}{k_I} = \frac{\frac{1}{\sqrt{3}}}{\sqrt{3}} = \frac{1}{3}$$

4. $\pi = iCRT$

$\frac{\pi}{RT} = iC$

$C_{17}H_{35}g\,COONa \rightarrow CH_3COO^- + Na^+$

1 0 0

$1-\alpha$ α α

$i = \frac{1+\alpha}{1} = 2$

$\pi_1 = 0.02$

$\pi_2 = 0.04$

$(\pi_3)_{Theo.} = 0.06$ and $(\pi_3)_{exp.} = 0.058$

$(\pi_3)_{exp.} < (\pi_3)_{Theo.}$ So. association.

So here at this point micelle formation has taken place and colloid has been formed. We can say at 0.04 M concentrate mixture will be heterogeneous.

6. (a)

$$\underset{}{Ca(NH)} + 2H_2O \longrightarrow \underset{(B)}{Ca(OH)_2} + NH_3\,(g)$$

$$\underset{(B)}{2NH_3} + 3CaOCl_3 \longrightarrow \underset{(C)}{N_2(g)} + 3CaCl_2 + 3H_2O$$

$$N_2(g) + 3Mg \longrightarrow \underset{(D)}{Mg_3N_2}$$

$$\underset{(D)}{Mg_3N_2} + 6H_2O \longrightarrow \underset{(B)}{3Mg(OH)_2} + 2NH_3$$

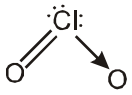
7. (B) PCl_5 (A) $+ H_2O \longrightarrow POCl_3$ (B) $+ 2HCl$

$POCl_3$ (B) $+ 3H_2O \longrightarrow H_3PO_4$ (C) $+ 3HCl$

8._ Due to less reactivity of Be.

9. ClO_2 is powerful oxidising agent, also strong chlorinating agent. Its bleaching power is almost 30 times stronger than Cl_2. In alkaline solution undergoes disproportionation

$$2ClO_2 + 2NaOH \longrightarrow NaClO + NaClO_3 + H_2O$$



unpaired electron that`s why paramagnetic

10.* $NaHSO_4 \longrightarrow Na^+ + HSO_4^-$

0.08 0 0

(0.08) (0.08)

Suppose the degree of dissociation of HSO_4^- is α

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

At eq. $C(1-\alpha)$ $C\alpha$ $C\alpha$

$\Rightarrow$ $[H^+] = 0.08\,\alpha$

$[SO_4^{-2}] = 0.08\,\alpha$

$[HSO_4^-] = 0.08\,(1-\alpha)$

Total ions present $= 0.08 + 0.08\,(1-\alpha) + 0.08\,\alpha + 0.08\,\alpha$

$= 0.16 + 0.08\,\alpha$

$i = \frac{0.16 + 0.08\alpha}{0.08} = (2+\alpha)$

$\Delta T_f = K_f \times m \times i$

$0.372 = (2+\alpha) \times 1.86 \times 0.08$

$\Rightarrow$ $\alpha = 0.5$

$\Rightarrow K_{dissociation} = \frac{C\alpha^2}{1-\alpha} = \frac{0.08 \times \left(\frac{1}{2}\right)^2}{1/2} = 0.04$ RLVP $= x_{solute} = \frac{0.2}{0.2 + \frac{1000}{18}} = \frac{9}{2509}$

11.* (A) $\Delta T_b = iK_b \times m$
$= 0.52 \times 1 = 0.52$
$T_b = 100.52^oC$ So it will dissociate
hence $\Delta T_b = i\, K_b\, m = 1.04$
$T_b = 101.04K$
(B) $\Delta T_f = iK_f \times m = 1 \times 1.86 \times 1 = 1.86$; $T_f = -1.86^oC$ and X will not get dimerise

(C) $7.44 = \frac{1}{2} \times 1.86 \times \frac{1}{W_A} \times 1000$; $W_A = 125$ gm So weight of ice seprate $= 1000 - 125 = 875$

% of ice seprate= $\frac{875}{1000} \times 100 = 87.5\%$

(D) $2.08 = 2 \times 0.52 \times \frac{1}{W_A} \times 100$

$W_A = 500$ gm ; So 500 gm i.e. 50% of H_2O will evaporation

14. $\underset{(M)}{CuCO_3.Cu(OH)_2} + HCl \longrightarrow \underset{(blue)\ (P)}{CuCl_2(aq)} + \underset{(X)}{CO_2} \uparrow$

$Cu + HCl \longrightarrow$ No dissolution

$CaO + H_2O \longrightarrow Ca(OH)_2 \xrightarrow{+CO_2} CaCO_3 \downarrow (Z)$
(Y)

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$CuCl_2 + \underset{(gas\ Q)}{H_2S} \longrightarrow \underset{(R)}{CuS} \downarrow (black)$

$CuCl_2 + \underset{(gas\ S)}{NH_3} \longrightarrow [Cu(NH_3)_4]Cl_2$ (deep blue)

15. $Q = H_2S$, $S = NH_3$
Let distance travelled by $H_2S = x$

$\Rightarrow \frac{x}{100-x} = \frac{\sqrt{17}}{\sqrt{34}} \Rightarrow \frac{x}{100-x} = \frac{1}{\sqrt{2}} \Rightarrow \sqrt{2}\,x = 100 - x \Rightarrow (\sqrt{2}+1)\,x = 100$

$\Rightarrow x = \frac{100}{(\sqrt{2}+1)} = 41.4$ cm

Comp # 17 to18

17. $n_A = 10$ mole $n_B = 20$ mole and $n_C = 5$ mole.
$P_A^o = 100$ torr, $P_B^o = 90$ torr

6A	$\rightarrow$	A_6 (s)
10		0
$10 - x$		$\frac{x}{6}$

$x = Kt = 10^{-1} \times 60 = 6$

after 1 hrs $\Rightarrow$ A = 4, B = 20, ; Solute = C + $\frac{x}{6} = 5 + 1 = 6$; $P^o = P_A^\circ x_A + P_B^\circ x_B$

$P^o = 100 \times \frac{4}{24} + \frac{20}{24} \times 90 = 16.66 + 75$

$P^o = 91.66$ torr $\frac{P^o - P^s}{P^s} = \frac{n}{N} \Rightarrow \frac{91.66 - P^s}{P^s} = \frac{6}{24} = \frac{1}{4} \Rightarrow 73.33 \text{ torr} = \frac{220}{3}$

18. After 100 min. A will be zero

6A	$\rightarrow$	A_6
10		0
0		$\frac{10}{6}$

A = 0 , B = 20 Solute = 5 + $\frac{10}{6}$ = 6.66

After 100 min.

$$\frac{p^o - P^s}{P^s} = \frac{n}{N} \Rightarrow \frac{90 - P^s}{P^s} = \frac{6.66}{20}$$

P_s = 67.5 torr

20. (P) $E^o_{Fe3+,\ Fe}$ $\quad Fe^{3+} \xrightarrow[n=1]{+0.77V} Fe^{2+} \xrightarrow[n=2]{-0.44V} Fe$; $Fe^{3+} \rightarrow Fe$: xV, n = 3

$\Rightarrow$ $1 \times 0.77 + 2 \times (-0.44) = 3 \times x$

$\Rightarrow$ $x = -\frac{0.11}{3}$ V $\simeq$ – 0.04 V.

(Q) $4H_2O \rightleftharpoons 4H^+ + 4OH^-$

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ $\quad$ – 1.23 V

+ $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ $\quad$ + 0.4 V

$4H_2O \rightleftharpoons 4H^+ + 4OH^-$ $\quad$ – 0.83 V

(R) $E^o_{(Cu2+ + Cu \rightarrow 2Cu+)}$ $\quad Cu^{2+} \xrightarrow[n=1]{xV} Cu^{+} \xrightarrow[n=1]{-0.52V} Cu$; $Cu^{2+} \rightarrow Cu$: + 0.34V, n = 2

$x \times 1 + 0.52 \times 1 = 0.34 \times 2$

x = 0.16 V.

$\Rightarrow$ $Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad$ 0.16 V

+ $Cu \longrightarrow Cu^+ + e^-$ $\quad$ – 0.52 V

$Cu^{2+} + Cu \longrightarrow 2Cu^+$ $\quad$ – 0.36 V

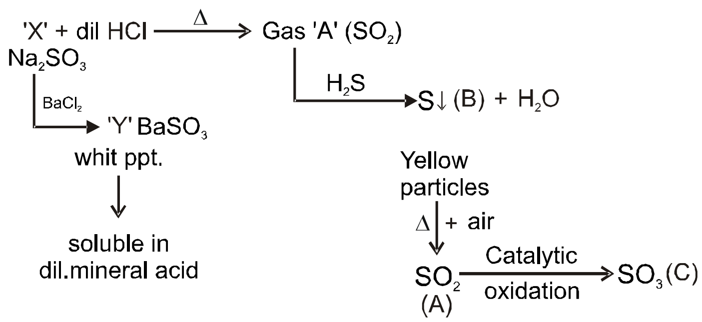
(S) $E^o_{(Cr3+,\ Cr2+)}$ $\quad Cr^{3+} \xrightarrow[n=1]{x} Cr^{2+} \xrightarrow[n=2]{-0.91V} Cr$; $Cr^{3+} \rightarrow Cr$: – 0.74V, n = 3

$x \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$

$x - 1.82 = -2.22$

$\Rightarrow$ x = – 0.4 V

22.



23. $a - 2r = 1.2$ Å and $\sqrt{3}\,a = 4r$; $a - 2 \times \frac{\sqrt{3}}{4} a = 1.2$ Å

$a\left(1-\frac{\sqrt{3}}{2}\right) = 1.2$ Å $a = 8$Å ; $d = \frac{2 \times 307.2}{6 \times 10^{23} \times \left(8 \times 10^{-8}\right)^3} = 2$ g/mL

24. (A) $(NO_2)\,(NO_2) \rightarrow$ cis + trans (B) $(ONO)\,(NO_2) \rightarrow 3$ (C) $(ONO)\,(ONO) \rightarrow$ cis + trans

25. Monoclinic sulphur, Diamond, O_3 (g), Br_2 (g), O (g), $I_2(\ell)$, Liquid sodium.

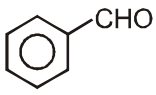
26. $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$
At equi. 4 atm 2 atm

$K = \frac{P_{NO_2}^2}{P_{N_2O_4}} = 1$; Let $p_{N2O4} = x$, $p_{NO2} = 60 - x$

$\Rightarrow \frac{(60-x)^2}{x} = 1$ $\Rightarrow$ $3600 + x^2 - 120\,x - x = 0$

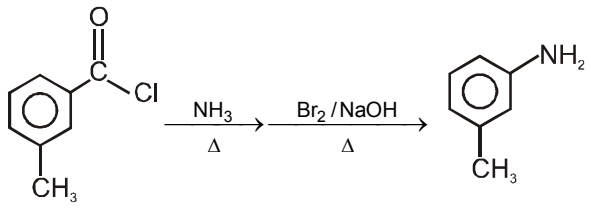
$\Rightarrow$ $x^2 - 121\,x + 3600 = 0$; $x = 52.73$; $x \simeq 53$ atm

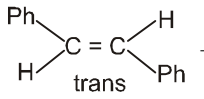
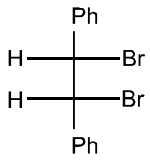
ORGANIC CHEMISTRY

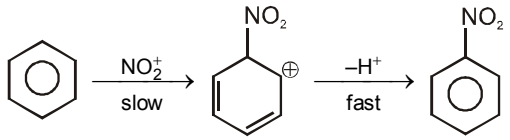
30. It is aldol formation reaction between  and .

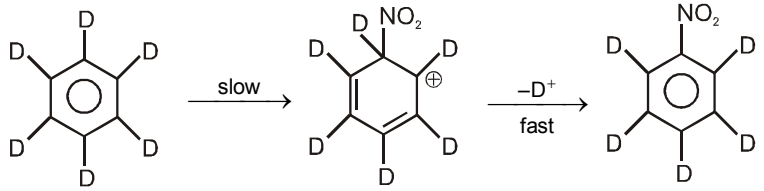
31.

k_1'	<	k_1	$\Leftarrow$	due to steric hinderence of nucleophile
k_2'	<	k_2	$\Leftarrow$	due to steric hinderence of nucleophile
k_1	>	k_2	$\Leftarrow$	due to steric hinderence of R – X
k_1'	>	k_2'	$\Leftarrow$	due to steric hinderence of R – X

32. 

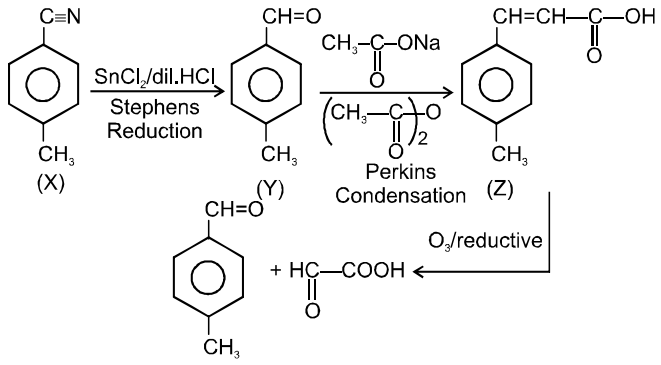
34. $Ph - C \equiv C - Ph \xrightarrow[Na(NH_3(\ell))]{X}$  $\xrightarrow[CCl_4]{Br_2}$ 

37. 



Both benzene ring have nearly same electron density so attack of E^+ occur at same rate.

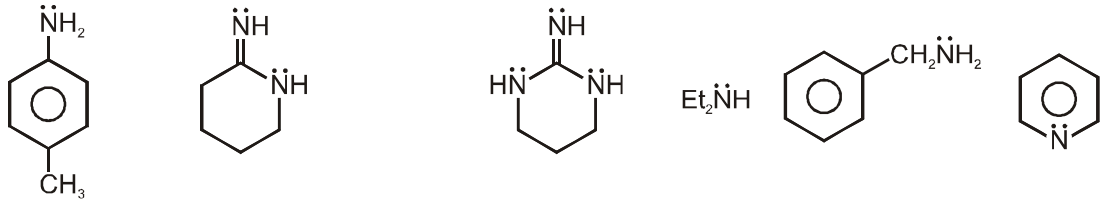
40.



41. $CH_3–CH_2–CH=CH–CH_3$ (cis + trans) $\xrightarrow{Br_2}$ $CH_3–CH_2–\overset{*}{C}H(Br)–\overset{*}{C}H(Br)–CH_3$ (dℓ + dℓ)

$CH_3–CH_2–CH_2–CH=CH_2 \xrightarrow{Br_2} CH_3–CH_2–CH_2–\overset{*}{C}H(Br)–CH_2(Br)$ (dℓ)

42.



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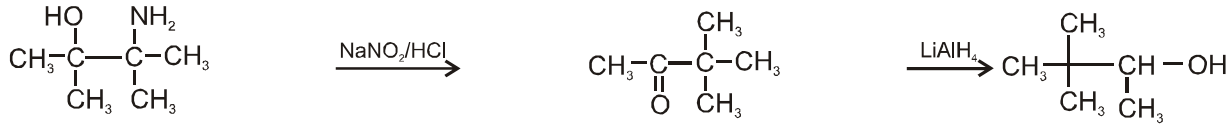
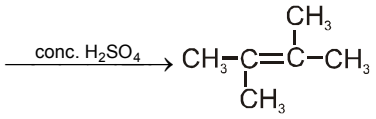
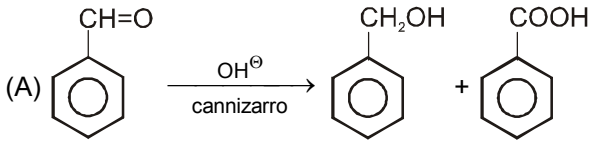
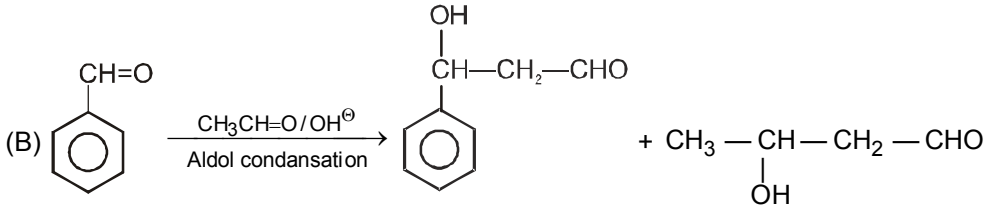


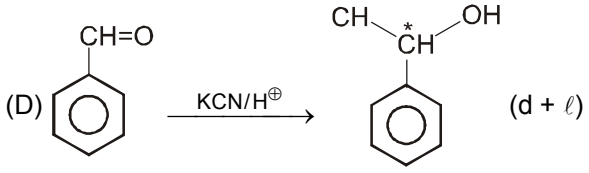


; Molecular formula = C_6H_{12} Molecular weight = 84

45.







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