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GGSRDN

PHYSICAL & INORGANIC CHEMISTRY

DPP

FOR CLASS 12th

Set Your Target and Keep Try in Until You Reach It.

SOLUTIONS

PHYSICAL / INORGANIC CHEMISTRY

DPP No. # 1

1. $M = \dfrac{0.2 \times 3}{\left(\dfrac{250}{1000}\right)} = 2.4\ M.$

2. Vapour pressure is depend upon temperature
So at equilibrium, partial pressure of $H_2O(g)$ is equal to aqueous tension at that temperature.

3. The vapour pressure of a mixture of two immiscible liquids is the sum of their vapour pressures in the pure states, independent of their relative amounts. Hence, B.Pt. of the mixture will be less than that of either of the liquids, remaining constant throughout.

4. Mole fraction of more volatile substance is greater in vapour phase.

5.* Temperature ↑ , vapour pressure ↑.

6.* (A) $i = 1 + (n - 1)\alpha$
$i = 1 + (4 - 1)$ ´ $0.8 = 3.4$
(B) For $BaCl_2$, $i = 1 + (3 - 1) \times 0.9 = 2.8$
(C) For Na_3PO_4, $i = 1 + (4 - 1) \times 0.9 = 3.7$
(D) For $K_4[Fe(CN)_6]$, $i = 1 + (5 - 1) \times 0.7 = 3.8$

7. $P = X_A P_A^0 + X_B P_B^0 = (P_A^0 - P_B^0)X_A + P_B^0$
So $P_B^0 = 265$
$P_A^0 - P_B^0 = -130$ $\qquad P_A^0 = 135$
$P_A^0 + P_B^0 = 300.$
$(P_A^0 + P_B^0) / 100 = 3.$

8. If terpinene is designated by A, and water by B, it follows that at 95°C, the boiling point of the mixture, p_B^0 is 634 mm, and hence p_A^0 is equal to $P - p_B^0$, i.e,
$744 - 634 = 110$ mm.

now using equation (3), $\dfrac{55}{45} = \dfrac{110 \times M_A}{634 \times 18} \Rightarrow M_A = 127$

9. Only immiscible liquids are efficiently steam distilled ethanol dissolves in water.

10. $P_{t^\circ C} = P^0_{water\ ,t^\circ C} + P^0_{subs.\ ,t^\circ C}$
$P_{t = 98.5C} = 720.15 + 7.8 = 727.95$ mm of Hg
$P_{t = 99^\circ C} = 733.24 + 7.97 = 741.21$ mm of Hg

temp. at which $P_t = 740$ mm of Hg $= 98.5 + \dfrac{(740 - 727.95)}{(741.21 - 727.95)} \times 0.5 = 98.95^\circ C.$

DPP No. # 2

1. For gas,
$\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$
$\dfrac{760 \times 91.9}{273} = \dfrac{P_2 \times 100}{288} \quad \Rightarrow \quad P_2 = 736.8$ mm of Hg
$P_{total} = P_{2,\ gas} + V.P. \quad \Rightarrow \quad V.P. = 750 - 736.8 = 13.2$ mm of Hg

2. $P = X_A P_A^0 + X_B P_B^0 = (P_A^0 - P_B^0)X_A + P_B^0$
So $P_B^0 = 254$
$P_A^0 - P_B^0 = -119$ $\qquad P_A^0 = 135$

3. For immiscible solution $= P_T = P_A^0 + P_B^0$
$= 400 + 200 = 600.$

4. For ideal solution, $\Delta V_{mix} = 0$, $\Delta H_{mix} = 0$, $\Delta S_{mix} = +\text{ ve}$, $\Delta G_{mix} = -\text{ ve}$,

5. $x_A P_A^\circ + x_B P_B^\circ = 700$ ...(i)
$x_A'' P_A^\circ + x_B'' P_B^\circ = 0.30 P_A^\circ + 0.70 P_B^\circ = 600$ ...(ii)
if moles of A & B initially are x & y then

$$x = 0.75 \times \frac{2}{3}(x+y) + 0.30 \times \frac{1}{3}(x+y)$$

& $x_A = \dfrac{x}{x+y}$ or $x_B = \dfrac{y}{x+y}$

Solving gives

$x_A = 0.6,$ $x_B = 0.4$, $P_A^\circ = \dfrac{2500}{3}$ torr & $P_B^\circ = 500$ torr.

6. 1 mole glucose is present in 1000 ml solution
180 gm glucose is present in 1000 × 1.18 gm solution
180 gm glucose is present in 1180 – 180 gm solvent

$$\text{molality} = \frac{1}{1000} \times 1000 = 1$$

$$\%\ w/v = \frac{180}{1000} \times 100 = 18$$

$$\%\ w/w = \frac{180}{1180} \times 100 = 15.25$$

7. Only single solution have all these
means 100 ml solution have 5.85 gm NaCl = 0.1 mole
and 5.55 gm $CaCl_2$ = 0.05 mole
and 6 gm NaOH = 0.15 mole

$[Cl^-] = \dfrac{(0.1+0.05\times 2)\times 1000}{100} = 2\text{ M}$ ⇒ $[Na^+] = \dfrac{(0.1+0.15)\times 1000}{100} = 2.5\text{ M}$

$[Ca^{2+}] = \dfrac{0.05}{100} \times 1000 = 0.5\text{ M}$ ⇒ $[OH^-] = 1.5\text{ M}$

8. For vessel X
$400 \times 1.5 = P_X \times 4 \Rightarrow P_X = 150$ mm Hg
For vessel Y,
$208 \times 2.5 = 4 \times P_Y = 130$ mm of Hg
Total pressure $P_T = 150 + 130 + 160$
= 440 mm of Hg.

9. Millimoles of $Na_2SO_4 = 20 \times 0.5 = 10$
Millimoles of $H_2SO_4 = 50 \times 0.2 = 10$
Millimoles of $Al_2(SO_4)_3 = 30 \times 0.4 = 12$
⇒ Millimoles of $Na^+ = 20$
Millimoles of $H^+ = 20$
Millimoles of $Al^{3+} = 24$
Millimoles of $SO_4^{2-} = 10 + 10 + 36 = 56$
Total volume = 20 + 50 + 30 = 100 ml

$$[Na^+] = \frac{20}{100} = 0.2\text{ M}$$

$$[H^+] = \frac{20}{100} = 0.2\text{ M}$$

$$[Al^{3+}] = \frac{24}{100} = 0.24\text{ M}$$

$$[SO_4^{2-}] = \frac{56}{100} = 0.56\text{ M}$$

10. (a) $[Cl^-] = \dfrac{50 \times 3 + 150 \times 1 \times 3}{200} = \dfrac{600}{200} = 3\text{ M}$ & $[H^+] = \dfrac{50 \times 3}{200} = 0.75\text{ M}$

(b) Molality = $\dfrac{0.1}{0.9 \times 18} \times 1000 = 6.17\text{ m}$

(c) Molality = $\dfrac{\frac{10}{60}}{90} \times 1000 = 1.85\text{ m}$

(d) Molarity of HCl = $\dfrac{\frac{10.95}{36.5}}{100} \times 1000 = 3\text{ M} \Rightarrow [H^+] = [Cl^-] = 3M$

DPP No. # 3

1. $i = 1 + (n-1)\,\alpha$

(A) For KCl, $i = 1 + 0.5 = 1.5$

(B) For K_2SO_4, $i = 1 + 2 \times 0.4 = 1.8$

(C) For $SnCl_4$, $i = 1 + 4 \times 0.2 = 1.8$

(D) For $FeCl_3$, $i = 1 + 3 \times 0.3 = 1.9$

2. Osmotic pressure will be same for equimolar solutions if Van't Hoff factor is same.

$K_4[Fe(CN)_6] \rightarrow i = 1 + (n-1)\,\alpha = 1 + 4 = 5$

$Al_2(SO_4)_3 \rightarrow i = 1 + (n-1)\,\alpha = 1 + 4 = 5$

3. The loss in weight should be proportional to vapour pressure above that solution :

So, $P_{S_A} \propto 2gm \Rightarrow P_{S_B} \propto 1.5gm \Rightarrow P_{S_C} \propto 2.5gm$

So, maximum vapour pressure is above C solution hence, it is having minimum lowering and hence minimum mole fraction (hence minimum number of moles of solute) So max. molar mass of substance.

4. Boiling point of solution = boiling point + $\Delta T_b = 100 + \Delta T_b$

Freezing point of solution = freezing point – $\Delta T_f = 0 - \Delta T_f$

Difference in temperature (given) = $100 + \Delta T_b - (-\Delta T_f)$

$103.57 = 100 + \Delta T_b + \Delta T_f = 100 + \text{molality} \times K_b + \text{molality} \times K_f$

$= 100 + \text{molality}\,(0.52 + 1.86)$

Molality = $\dfrac{103.57 - 100}{2.38} = \dfrac{3.57}{2.38} = 1.5\text{ m}$

and molality = $\dfrac{\text{moles} \times 1000}{W_{gm\ (solvent)}}$; $1.5 = \dfrac{\text{moles} \times 1000}{500}$

Moles of solute = $\dfrac{1.5 \times 500}{1000} = 0.75$ moles

Ans. 750 mmoles

5. $\Delta T_f = iK_f\,m$

$0.74 = i \times 1.36 \times 0.4 \Rightarrow i = 0.9945 \approx 1 \Rightarrow i = 1 + \alpha \approx 1 \Rightarrow \alpha \approx 0$

6. Suppose V_1 litres of the solution contains n moles of the solute at 12°C which was diluted to V_2 litres at 27°C.

Thus we have

$$\frac{500}{760} = \frac{n}{V_1} \times 0.082 \times 285 \qquad \text{...(i)}$$

and $$\frac{100}{760} = \frac{n}{V_2} \times 0.082 \times 300$$

Dividing (1) by (2), we get $\dfrac{V_2}{V_1} = 5.3.$

8.* The substance which will produce maximum particles pergram will be most efficient.

Particles produced by 1 g of LiCl = $\frac{1}{42.5} \times 2 = 0.047$

Particles produced by 1 g of NaCl = $\frac{1}{58.5} \times 2 = 0.034$

Particles produced by 1 g of glucose = $\frac{1}{180} \times 2 = 0.011$

Particles produced by 1 g of $CaCl_2$ = $\frac{1}{111} \times 3 = 0.027$

Answer is LiCl.

9. $\Delta T_f = K_f m$

$$0.19 = 4.9 \times \frac{\frac{1}{M}}{\frac{86}{1000}}.$$

$$0.19 = 4.9 \times \frac{1000}{M \times 86}. \quad \Rightarrow \quad M = \frac{4.9 \times 1000}{86 \times 0.19} = 300. \quad \Rightarrow \quad \text{Atomicity} = \frac{300}{75} = 4.$$

10. Hexane & Heptane solution do not form azeotrope, but have different boiling points, so can be separate by fractional distillation. Acetione & chloroform form maximum boiling azeotrope ethanol & water form minimum boiling azeotrope. Azeotropes cannot be separated completely by fractional distillatio chlorobenzene & bromobenzene do not form azeotrope but have different boiling points. so can be separate by fractional distillation.

DPP No. # 4

1. (b) $\pi \propto$ No. of particles/ions.
$BaCl_2 = 3$, NaCl = 2 glucose = 1
So. order of $\pi = BaCl_2 > NaCl >$ glucose

2. $Na_2SO_4 \rightleftarrows 2Na^+ + SO_4^{2-}$
a (1 – α) 2aα aα

$i = \frac{a(1+2\alpha)}{a} = 1 + 2\alpha$

Where α is degree of dissociation of Na_2SO_4
Solution of Na_2SO_4 & glucose are isotonic

So $\pi_{Na_2SO_4} = \pi_{glucose}$

$\Rightarrow$ $i \times 0.004 \times R \times T = 0.010 \times R \times T$

$\Rightarrow$ $(1 + 2\alpha) = \frac{10}{4}$

$1 + 2\alpha = 2.5$

$\alpha = 0.75$

$\Rightarrow$ % dissociation = 75 %

3. Experimental molarity = 3 × 0.05 = 0.15; So osmotic pressure = 1.5P.

4. $\Delta T_f = K_f m$
$10^{-2} = 0.1 \times m \Rightarrow m = 0.1$ m

$$\text{molality} = \frac{2.56 \times 1000}{M \times 100} = 0.1 \Rightarrow M = 256 \quad \Rightarrow \quad \text{atomicity} = \frac{256}{32} = 8.$$

5. On addition of non volatile solute, freezing point decreases.
Entropy of solution is more than entropy of pure solvent.

6. $\Delta T_f = 0.0358°\,C$
$\Delta T_f = i \times K_f \times m$
$0.0358 = i \times 1.86 \times 0.01$
$i = 1.9247$
For NH_4Cl. $i = (1 + \alpha)$
$\Rightarrow 1 + \alpha = 1.9247$
$\alpha = 0.9247$

$$\& \qquad i = \frac{M_T}{M_{ob}}$$

$$\Rightarrow M_{ob} = \frac{53.5}{1.9247} = 27.796 \text{ g/mole}$$

7. 0.2 percent solution means 0.2 g of cellulose acetate dissolved in 100 ml of solution.
Osmotic pressure = 2.58 cm of acetone

$$P = 2.58 \times \frac{0.80}{13.6} \text{ cm of Hg} = 0.152 \text{ cm of Hg}$$

$$P = \frac{0.152}{76} \text{ atm} = 2\times 10^{-3} \text{ atm } (1\text{atm} = 76 \text{ cm of Hg})$$

suppose M is the molecular weight of cellulose acetate.

$$n = \frac{0.2}{M}, \; V = 100 \text{ ml} = 0.1 \text{ litre} \; ; \; R = 0.082$$

and T = 300 K

$$\text{Now } P = \frac{n}{V} RT$$

$$2 \times 10^{-3} = \frac{0.2/M}{0.1} \times 0.082 \times 300$$

M = 24,600

8. Cryoscopic constant $K_f = \Delta T_f$ of solution having unit molality of normal solutes

$$\text{Molality of glucose solution in (c)} = \frac{9 \times 1000}{(59-9) \times 180} = 1$$

9. Since the solution has greater entropy (disorder) than the pure liquid, so former has lesser tendency to freeze i.e., the temperature has to be lowered to freeze the solution.

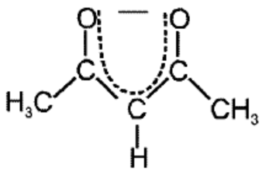
10. $2Na^+ (aq) + 2I^- (aq) + HgI_2(s) \longrightarrow 2Na^+ (aq) + HgI_4^{2-} (aq)$
The number of mole particle decreases from 4 ($2Na^+ + 2I^-$) to 3 ($2Na^+ + HgI_4^{2-}$). Hence, the colligative property will decrease and, the vapour pressure will increase to a constant value until NaI is completely consumed.

11. $K_f = \frac{RT_f^{02}M}{1000\Delta H_{fus}}$ would be larger for larger value of $T°_f$ and smaller value of enthalpy of fusion of the solid solvent.

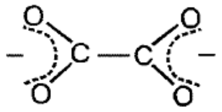
12. The vapour pressure of a mixture of two immiscible liquids is the sum of their vapour pressures in the pure states, independent of their relative amounts. Hence, B.Pt. of the mixture will be less than that of either of the liquids, remaining constant throughout.

DPP No. # 5

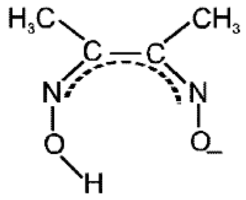
7. (A) Acetyl acetonato ($CH_3COCHCOCH_3^-$)



(B) Oxalato ($C_2O_4^{2-}$)

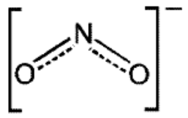


(C) Dimethylglyoximato ($HONCC(CH_3)C(CH_3)NO^-$)



(D) Nitrito (NO_2^-)

It may link to central metal ion either through nitrogen or oxygen ; so it is ambidentate ligand.



DPP No. # 6

1. By defination.

2. Azide ion (N_3^-) does not act as bidenate ligand because it is linear and it is not possible to donate both the electrons simultaneously to same metal ion/atom.

DPP No. # 7

1. $Co\,(NH_3)_5\,NO_2\,Cl_2$

1 mole of this complex gives 3 moles of ions in aq. solution.

1 mole of this complex gives 2 mole of AgCl ⇒ $2Cl^-$ outside the coordination sphere.

$\therefore \quad [Co(NH_3)_5\,NO_2]\,Cl_2$

$Co\,(NH_3)_5\,NO_2\,Cl_2$

2. $[Cr\,Cl_2\,(H_2O)_4]\,Cl.2H_2O$ will liberate $\frac{1}{3}$ of the total chloride ions for precipitation.

3. Eq. conductance at infinite dilution depends on no. of ions produced in the sol.

$[Pt(NH_3)_6]\,Cl_4 > [Pt(NH_3)_3\,Cl]Cl_3 > [Pt(NH_3)_4\,Cl_2]\,Cl_2 > [Pt\,(NH_3)_3\,Cl_3]\,Cl \longrightarrow$ no. of ions produced in the solution.

4. (B) E.A.N. = 26 – 2 + 12 = 36

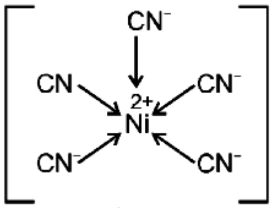
5. In $[CuCl_2]^-$ EAN = 28 + 4 = 32

6. According rule of bridging ligand(s) naming

7. Bridging ligands are NH_2^- and OH^-

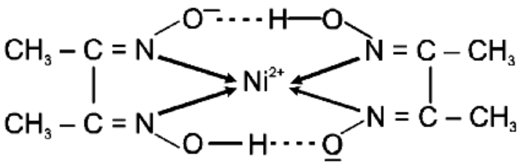
DPP No. # 8

1. According to the question, $k_3[Ni(CN)_5]$ is diamagnetic and square pyramidal with non-zero dipole moment.



dsp^3 & $\mu \neq 0$
square pyramidal

2. The complex is



square planar (dsp^2)

3. **(A)** On the basis of number of electrons the correct order is P > Q > R > S.

Complex		**No. of unpaired electrons.**
(P)	$[FeF_6]^{3-}$	5
(Q)	$[CoF_6]^{3-}$	4
(R)	$[V(H_2O)_6]^{3+}$	2
(S)	$[Ti(H_2O)_6]^{3+}$	1.

4. **(C)** In the first complex, ligand is O_2^{2-} which is oxidised into O_2^{1-} hence, O – O bond length decreases.

5. SeF_4 and XeO_2F_2 are both sp^3d hybridized, trigonal bipyramidal and see-saw shaped with 1 lone pair of electrons each.
SF_4 has 1 lone pair, XeF_2 has 3 lone pairs. $XeOF_4$ is square pyramidal with 1 lone pair, TeF_4 is see-saw shaped with 1 lone pair, $SeCl_4$ has see-saw shape with 1 lone pair, XeF_4 has planar shape with 2 lone pairs.

6. **(a)** Increase Order of ligands Strength $I^- < H_2O < NH_3 < CN^-$

(b) SFL $d^6 = t_{2g}^{2,2,2} eg^{0,0}$ – diamagnetic
WFL $d^6 = t_{2g}^{2,1,1} eg^{1,1}$ – Paramagnetic.

7. **(a)** Since this is a d^1 system.

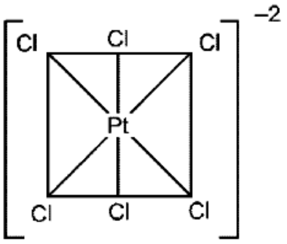
(b) In $[Fe(CN)_6]^{4-}$; Fe(II) is t_{2g}^6 , e_g^0 due to strong ligands.

8. CFSE depends on the strength of ligands which follows order
$CN^- > NH_3 > H_2O > F^-$.
On the basis of nature of ligands the correct order is Q > R > S > P.

9. $2[Ag(CN)_2]^- + Zn \longrightarrow 2Ag + [Zn(CN)_4]^{2-}$.
$Zn^{2+} \longrightarrow 3d^{10}$, Shape of $[Zn(CN)_4]^{2-}$ is tetrahedral.

10. $2KCl + PtCl_4 \longrightarrow K_2[PtCl_6]$

11.



d^2sp^3

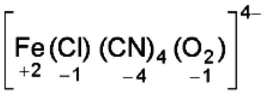
12. Meq. of complex = Meq. of base

$$\frac{0.319}{268.5} \times 1000 \times \text{V.F.} = 0.125 \times 28.5 \times 1$$

V.F. $\approx$ 3

DPP No. # 9

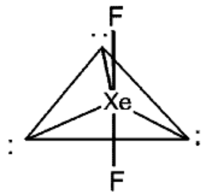
1. The given complex is actually.



$$\left[\underset{+2}{\text{Fe}}\,\underset{-1}{(\text{Cl})}\,\underset{-4}{(\text{CN})_4}\,\underset{-1}{(\text{O}_2)}\right]^{4-}$$

hence Fe(II) is $t_{2g}^{\,6}$, $e_g^{\,0}$ due to effect of strong ligands but it is paramagnetic due to O_2^{-1} ligand.

2.



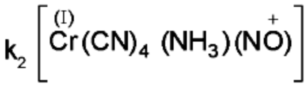
3. **(a)** The options can give CFSE = – 0.6 Δ_0 with weak field ligands ⇒ d^4 and d^9.
(b) Ammonia is a stronger field ligand than water.
So, CFSE of $[Ni(NH_3)_6]^{2+}$ is greater than $[Ni(H_2O)_6]^{2+}$

4. In A, NO^+ has no unpaired e^-s. So, complex is diamagnetic but in B, NO is odd e^- molecule, having one odd e^-. So, B is paramagnetic.

5. Diamagnetic complexes shows decrease in weight when placed in magnetic balance.
$Ni(CO)_4 \rightarrow$ Tetrahedral & diamagnetic
$K[AgF_4] \rightarrow$ Square planar & diamagnetic
$Na_2[Zn(CN)_4] \rightarrow$ Tetrahedral & diamagnetic

6. It is not showing geometrical isomerism ⇒ Tetrahedral & paramagnetic.

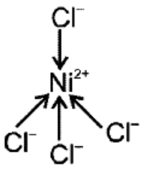
7. The complex is actually



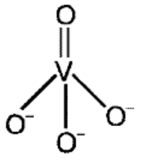
$$k_2\left[\overset{(I)}{\text{Cr}}(\text{CN})_4\,(\text{NH}_3)(\overset{+}{\text{NO}})\right]$$ in which Cr(I) is d^2sp^3 hybridised with one unpaired electron.

8. (A) $H_3N \rightarrow Ag^+ \leftarrow NH_3$ (linear & sp hybridisation)

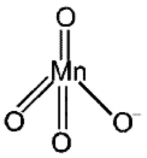
(B)



sp^3 Tetrahedral

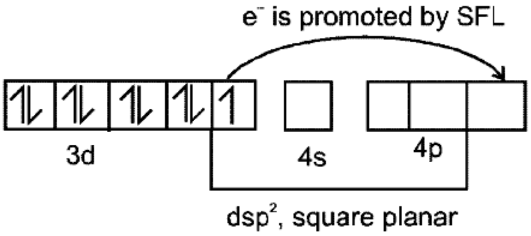


sp^3 Tetrahedral

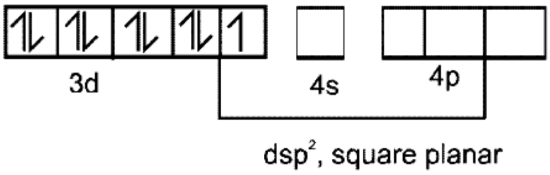


sp^3 Tetrahedral

(C) $[Cu(NH_3)_4]^{2+} \rightarrow$ $Cu^{2+} \rightarrow 3d^9$, $4s^0$



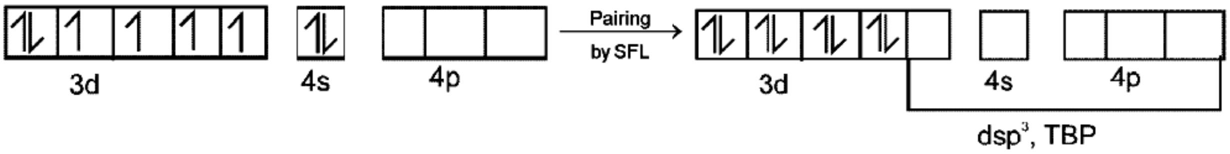
$[Ni(CN)_4]^{2-}$ → $Ni^{2+} \rightarrow 3d^8, 4s^0$



$[Pt(NH_3)_4]^{2+}$

4d & 5d metals always forms square planar with 4 ligands.

(D) $Fe(CO)_5$; $Fe \rightarrow 3d^6, 4s^2$

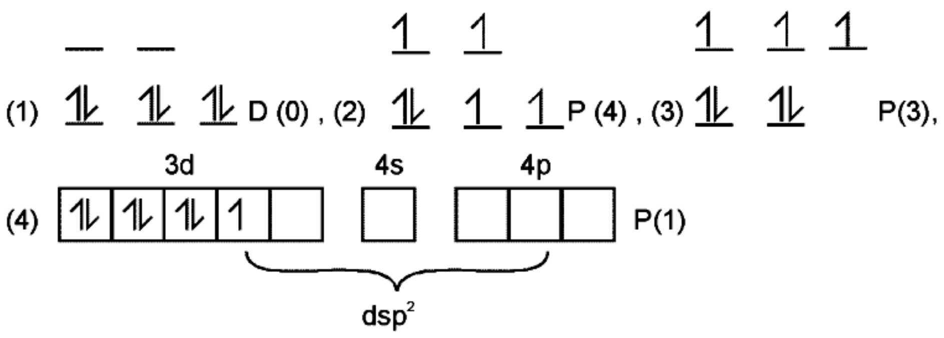


9. Stronger field ligand will split more so, more energy is required to transition of electrons from t_{2g} to e_g so, smaller wavelength light is required.

10. CFSE of V^{2+} = – 3917 – (– 3691).
= – 226 kJ/mol.
CFSE of Fe^{2+} = observed L.E. – L.E. (in absence of CFSE).
= – 3923 – (– 3856) = – 67 kJ/mol.

11. Ti^{+3} is $3d^1$ system, $\Delta_0 = 6.63 \times 10^{-34} \times 3 \times 10^8 \times 20300 \times 10^2$ J/ion
$= 6.63 \times 10^{-34} \times 3 \times 10^8 \times 20300 \times 10^2 \times 10^{-3} \times 6.02 \times 10^{23}$ kJ/mol = 243 kJ/mol.
Now, CFSE $= 0.4 \times \Delta_0 = 0.4 \times 243 = 97.2$ kJ/mol.

12.



13. (A) $[Cr(H_2O)_6]Cl_3\ (aq) \rightleftharpoons [Cr(H_2O)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$
$[Cr(H_2O)_5Cl]\ Cl_2.H_2O\ (aq) \rightleftharpoons [Cr(H_2O)_5Cl]^{2+}\ (aq) + 2Cl^-\ (aq)$

(B) $[Co(NH_3)_5Br]SO_4\ (aq) \rightleftharpoons [Co(NH_3)_5Br]^{2+}\ (aq) + SO_4^{2-}\ (aq)$
$[Co(NH_3)_5SO_4]Br\ (aq) \rightleftharpoons [Co(NH_3)_5SO_4]^{+}\ (aq) + Br^-\ (aq)$

(C) $[Co(NH_3)_5Cl]Cl_2\ (aq) \rightleftharpoons [Co(NH_3)_5Cl]^{2+}\ (aq) + 2Cl^-\ (aq)$
$[Co(NH_3)_6]Cl_3\ (aq) \rightleftharpoons [Co(NH_3)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$

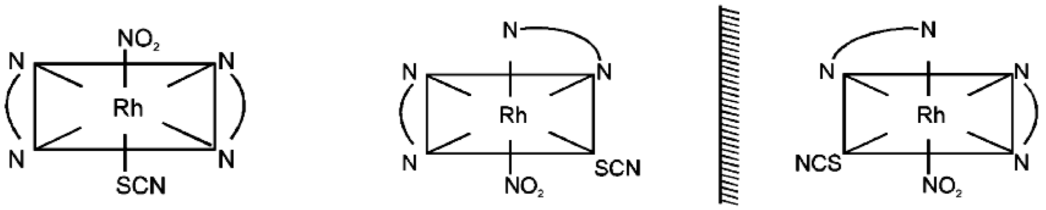
(D) $[Cu(H_2O)_4]SO_4.H_2O\ (aq) \rightleftharpoons [Cu(H_2O)_4]^{2+} (aq) + SO_4^{2-} (aq)$
$[Cu(H_2O)_6](NO_3)_2\ (aq) \rightleftharpoons [Cu(H_2O)_6]^{2+} (aq) + 2NO_3^- (aq)$

DPP No. # 10

1. (A) is tetrahedral. So, No G.I.
(B) is square planar [Pt(II) complex]. So, No optical isomerism
(C) is Fe(I) complex, contains three unpaired e⁻s.

2. Pt(II) is $5d^8$, forms square planar complex which is diamagnetic. $[PtCl_2(NH_3)(OH_2)]$ will show geometrical isomerism.

3.



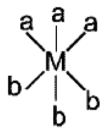
(1) NO_2 / SCN
(2) ONO / SCN
(3) NO_2 / NCS
(4) ONO NCS

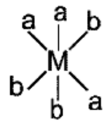
(5) NO_2 / SCN
(6) ONO / SCN
(7) NO_2 / NCS
(8) ONO / NCS

(9)
(10)
(11)
(12) } Mirror images of (5), (6), (7), (8)

* Only cis isomer is optically active.

4.



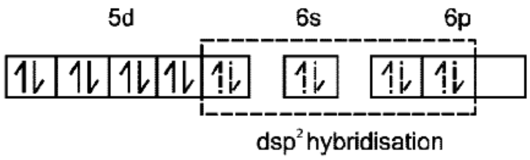


5. I and IV have POS.

6. (A) Both cation & anion are complex.
(B) SCN^- is ambidentate ligand. So, linkage isomerism.
(C) Anion are acting as ligand. So, it can show ionization isomerism.

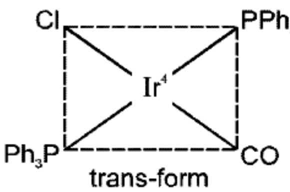
7. (A) $[IrCl(CO)(PPh_3)_2]$ carbonylchloridobis(triphenylphosphine)iridium(I).
(B) Coordination number of Ir is four. Ir is in (+1) oxidation state with $4d^8$ configuration. It is trans isomer, so its geometry should be square planar.

$[IrCl(CO)(PPh_3)_2]$

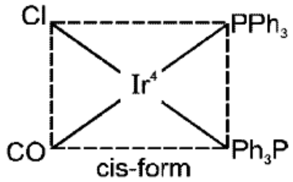


(C) All electrons are paired ; so magnetic moment is zero.

(D)



trans-form



cis-form

The complex has plane of symmetry, so it does not show optical isomerism.

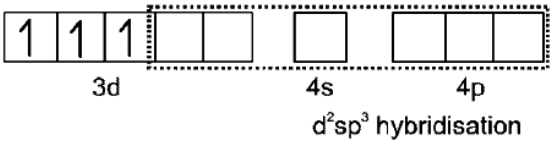
8.
$[Fe(H_2O)_6]^{3+} + en \rightarrow [Fe(H_2O)_4en]^{3+}$ $K_{eq} = K_1$
$[Fe(H_2O)_4\,en]^{3+} + en \rightarrow [Fe(H_2O)_2\,(en)_2]^{3+}$ $K_{eq} = K_2$
$[Fe(H_2O)_2\,(en)_2]^{3+} + en \rightarrow [Fe\,(en)_3]^{3+}$ $K_{eq} = K_3$
$[Fe(H_2O)_6]^{3+} + 3en \rightarrow [Fe\,(en)_3]^{3+}$ $K_f = K_1 \times K_2 \times K_3$
$\log K_f = \log K_1 + \log K_2 + \log K_3$
$= 4.44 + .41 + 2.15 = 10$ $\Rightarrow K_f = 10^{10}$

9. $[Co(NH_3)_5(NO_2)]Cl_2$ & $[Co(NH_3)_5(ONO)]Cl_2$ have different color

10. In this, donor atom can be 'N' or 'O' i.e. NO_2^-, ONO^-

11. NO_2^-, ONO^- are ambidentate ligands.

12. (A) $[Cr(NH_3)_6]^{3+}$
$Cr^{3+} \longrightarrow 3d^3, 4s^0$

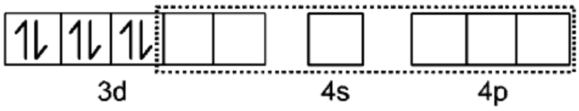


CFSE = – 3 × (– 0.4 Δ_0) = – 1.2 Δ_0

(B) $[Co(en)_3]^{3+}$

$Co^{3+} \longrightarrow 3d^6, 4s^0$

en is a SFL. so, pairing will take place.



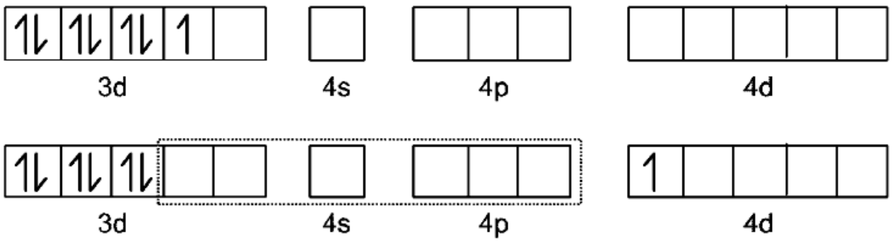
d^2sp^3 diamagnetic

CFSE = $6 \times (-0.4\ \Delta_0) + 2p = -1.2\ \Delta_0 + 2p$

(C) $[Co(NO_2)_6]^{4-}$

$Co^{2+} \longrightarrow 3d^7, 4s^0$

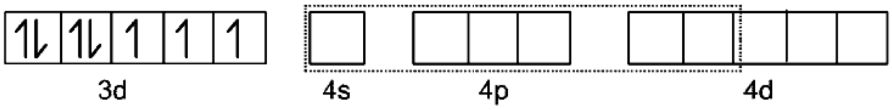
NO_2^- is a SFL, so, pairing will take place and 1 electron is promoted to higher d-orbitals



d^2sp^3 Paramagnetic

(D) $[Co(H_2O)_6]^{2+}$

$Co^{2+} \longrightarrow 3d^7, 4s^0$



sp^3d^2 Paramagnetic

13. In Tetrahedral All bond angle are 109°.28' So It is symmetrical

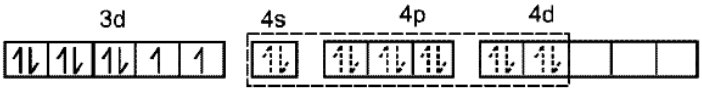
14. $[NiF_6]^{4-} \longrightarrow$ F^- is a weak ligand, so high spin complex with two unpaired electron.
$[NiF_6]^{2-} \longrightarrow$ Low spin complex even with weak field ligands. On d^6 arrangment with +4 oxidation state will have higher CFSE leading to pairing of electrons and complex will be diamagnetic.

DPP No. # 11

1. (A) $[Pt(NH_3)_2Cl(NO_2)]$ and $[Pt(NH_3)_2Cl(ONO)]$ are linkage isomers.
(B) $[Pt(NH_3)_2Cl\ (NH_2CH_3)]Br$ and $[Pt(NH_3)_2Br\ (NH_2CH_3)]Cl$ are ionisation isomers.
(C) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_6]Cl_3$ are hydrate isomers.
(D) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are coordination isomers.
Correct IUPAC name is hexaamminechromium(III) hexacyanidocobaltate(III).

2. (a) $_{28}Ni$ is in +2 oxidation state with electron configuration $[Ar]^{18}\ 3d^8\ 4s^0$, so

$[Ni\ (NH_3)_6]^{2+}$

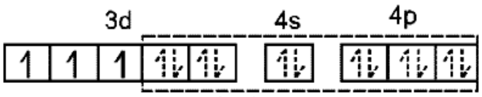


sp^3d^2 hybridisation

Number of unpaired electrons = 2

(b) $_{24}Cr$ is in +3 oxidation state with electron configuration $[Ar]^{18}\ 3d^3\ 4s^0$; so

$[Cr\ (NH_3)_6]^{3+}$

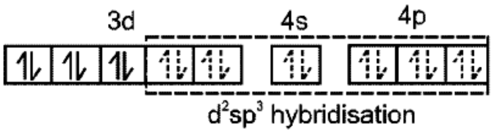


d^2sp^3 hybridisation

Number of unpaired electrons remains three, whether ligand is strong field or weak field ligand when electron configuration is $3d^3$.

(c) $_{27}$Co is in +3 oxidation state with electron configuration $[Ar]^{18}\ 3d^6\ 4s^0$, so

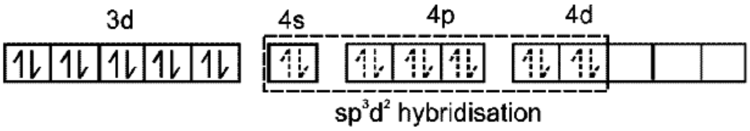
$[Co\ (NH_3)_6]^{3+}$



All electrons are paired, so complex ion is diamagnetic.

(d) $_{30}$Zn is in +2 oxidation state with electron configuration $[Ar]^{18}\ 3d^{10}\ 4s^0$, so

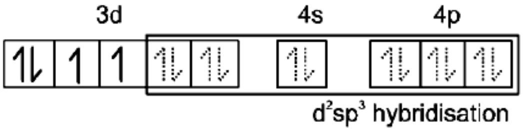
$[Zn\ (NH_3)_6]^{2+}$



All electrons are paired, so complex ion is diamagnetic.

3. $_{24}$Cr is in +2 oxidation state with $[Ar]^{18}3d^4$ configuration. It is inner orbital complex, so ;

$[\overset{II}{Cr}\ (NH_3)_4(NO_2)_2]$ -



Number of d-electrons is four and number of unpaired electrons is two.

It shows geometrical and linkage isomers.

$NO_2 – NO_2$	cis-trans.
$NO_2 – ONO$	cis-trans.
$ONO – ONO$	cis-trans.

Total number of isomers = 6.

4. (A) $[\overset{II}{Co}\ (NH_3)_5(NO_2)]Cl$ and $[\overset{II}{Co}\ (NH_3)_5(ONO)]Cl$ - linkage isomerism

$[\overset{II}{Co}\ (NH_3)_5(NO_2)]Cl$ and $[\overset{II}{Co}\ (NH_3)_5Cl]NO_2$ - ionization isomerism

(B) $[\overset{III}{Co}\ (NH_3)_5(H_2O)](NO_2)_3$ and $[\overset{III}{Co}\ (NH_3)_5(NO_2)](NO_2)_2.H_2O$ - hydrate isomerism

$[\overset{III}{Co}\ (NH_3)_5(NO_2)](NO_2)_2.H_2O$ and $[\overset{III}{Co}\ (NH_3)_5(ONO](NO_2)_2.H_2O$

(C) $[\overset{II}{Pt}\ (NH_3)_4]^{2+}\ [\overset{II}{Pt}\ (SCN)_4]^{2-}$ and $[\overset{II}{Pt}\ (NH_3)_3(SCN)]^+\ [\overset{II}{Pt}\ (NH_3)(SCN)_3]^-$ - coordination isomerism

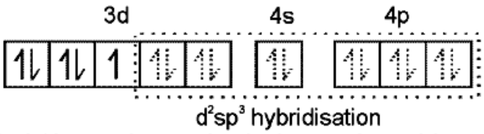
$[\overset{II}{Pt}\ (NH_3)_4]^{2+}\ [\overset{II}{Pt}\ (SCN)_4]^{2-}$ and $[\overset{II}{Pt}\ (NH_3)_4]^{2+}\ [\overset{II}{Pt}\ (NCS)_4]^{2-}$ - linkage isomerism

(D) $[Cr(NH_3)_4(NO_2)_2](NO_3)_2$ and $[Cr(NH_3)_4(NO_3)_2](NO_2)_2$ - ionization isomerism

$[Cr(NH_3)_4\ (NO_2)_2]\ (NO_3)_2$ and $[Cr(NH_3)_4\ (ONO)_2]\ (NO_3)_2$ - linkage isomerism

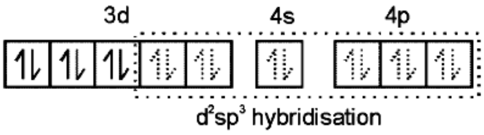
5. (i) $_{25}$Mn is in + II oxidation state. The electronic configuration of Mn^{2+} is $[Ar]^{18}\ 3d^5\ 4s^0$. The CN^- is strong field ligand, so

$[Mn(CN)_6]^{4-}$



It is inner orbital / low spin octahedral complex with one unpaired electron.

Similarly for $[Fe(CN)_6]^{4-}$

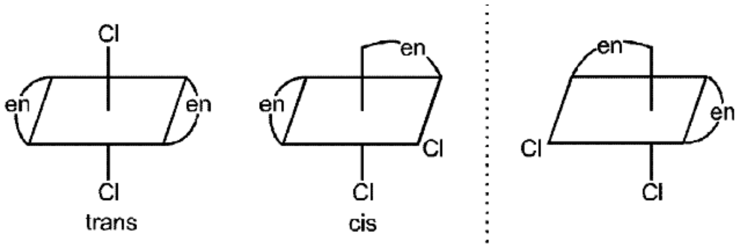


It is inner orbital / low spin octahedral complex with no unpaired electron.

(ii) As the negative charge on the metal increases from the manganese complex to vanadium complex, it is delocalised on to the ligands by the π back bonding. This strengthen the metal-carbon bond and weaken the C–O bond (as bond order of CO decreases).

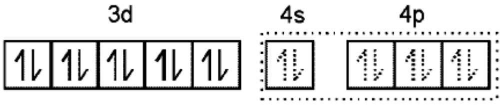
(iii) $[RhCl(PPh_3)_3]$ is Wilkinson's catalyst. Because of $4d^8$ configuration its higher CFSE favours square planar low spin complex (i.e. dsp^2). It is used as homogeneous catalyst for the hydrogenation of alkenes.

(iv) False statement : trans $[Co(en)_2Cl_2]^+$ has a centre and several planes of symmetry but the cis-form has neither, and (+) and (–) forms of cis $[Co(en)_2Cl_2]^+\ Cl^-$ have been separated.



(v) In $Ni(CO)_4$, the Ni is in zero oxidation state. The CO is strong field ligand, so

$[Ni(CO)_4]$



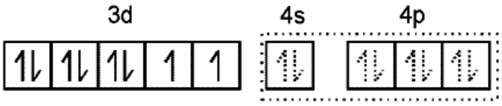
sp^3 hybridisation

It is outer orbital complex with $\mu_s = 0$. EAN = 28 + 8 = 36

In $[NiCl_2(PPh_3)_2]$ the Ni is in + II oxidation state.

Ligand triphenyl phosphine inspite of strong field ligand favours tetrahedral geometry on account of its bulkier nature. So

$[NiCl_2(PPh_3)_2]$



sp^3 hybridisation

It is also outer orbital complex with $\mu_s = \sqrt{8}$ B.M. ~ 2.73.

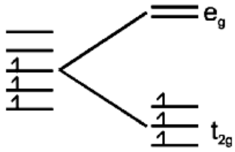
EAN = 26 + 8 = 34.

6. **S_1 :** Correct statement.

S_2 : As electron density on metal ion increases, the back donation into antibonding π orbitals of CO weakens the C–O bond and thus there is increase in inter atomic distance. Hence, C–O bond length is biggest in $[V(CO)_5]^{3-}$.

S_3 : Correct statement.

S_4 : Electron distribution of $3d^3$ configuration of Cr^{3+}



So, t_{2g} orbitals contain 3 electrons.

7. $Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}$ $\qquad K_f = \frac{1}{K_d}$.

10^{-3} $\qquad 2$

≈ 0 $\qquad 2-4\times10^{-3}\approx2$ $\qquad 10^{-3}$.

$[Cd^{2+}]_0 = 10^{-3}$ M $\qquad [NH_3]_0 = 2$ M.

$$K_f = \frac{[Cd(NH_3)_4]^{2+}}{[Cd^{2+}][NH_3]^4} = \frac{10^{-3}}{[Cd^{2+}][2]^{+}} = \frac{10^7}{2}.$$

$$\Rightarrow \quad [Cd^{2+}] = \frac{1}{8} \times 10^{-10} = \mathbf{1.25 \times 10^{-11}\ M.}$$

8. $NO_2–NO_2 \longrightarrow 2$ (cis/trans)

$NO_2–ONO \longrightarrow 2$ (cis/trans)

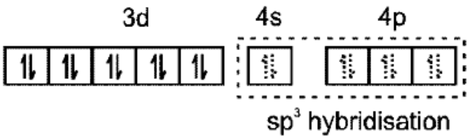
$ONO–ONO \longrightarrow 2$ (cis/trans)

$NO_2–NO_3 \longrightarrow 2$ (cis/trans)

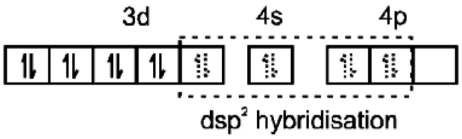
$ONO–NO_3 \longrightarrow 2$ (cis/trans)

Total = 10 isomers.

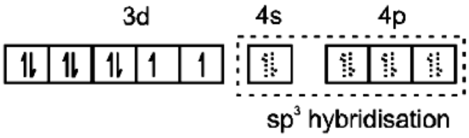
9. $[Ni(CO)_4]$,



$[Ni(CN)_4]^{2-}$,

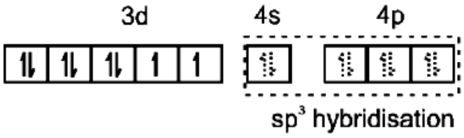


$[NiCl_2(PPH_3)_2]$,



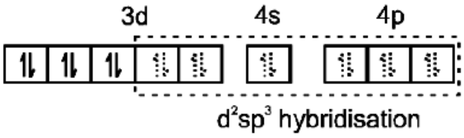
$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[NiCl_4]^{2-}$,

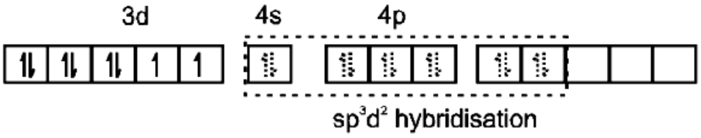


$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[NiF_6]^{2-}$,

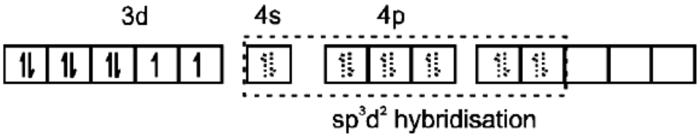


$[NiF_6]^{4-}$,



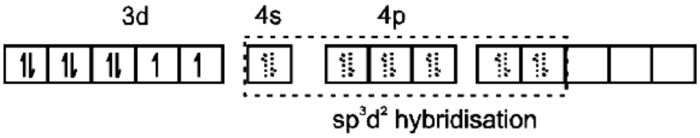
$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[Ni(NH_3)_6]^{2+}$,



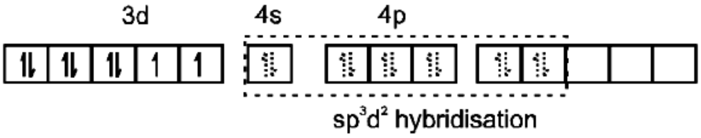
$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[Ni(en)_3]^{2+}$,



$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[Ni(H_2O)_6]^{2+}$,



$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

Note : With coordination number six and oxidation state +2, two (n–1) d-orbitals are not available for d^2sp^3 hybridisation.
Hence, nd orbitals participitate in hybridisation.

10. (A) (NO_2) (NO_2) → cis + trans
(B) (ONO) (NO_2) → 3
(C) (ONO) (ONO) → cis + trans

DPP No. # 12

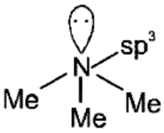
1. According to IUPAC nomenclature.

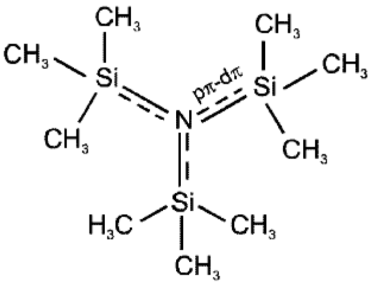
2. For all three EAN = 36

3. In $K_4[VO_4]$ vanadium is d^1 and paramagnetic.

4. **S_1 :** I^- ion is a stronger reducing agent than Cl^- ion. It reduces Cu^{2+} to Cu^+ ion.
S_2 : Both diamagnetic but $[Ni(CO)_4]$ is tetrahedral and $[RhCl(Ph_3P)_3]$ is square planar.

S_3 :





not isostructural

5. $\lambda_{ab} = \frac{1}{38500} = 259 \times 10^{-7}$ cm = 259 nm (U.V. region).

and $t_{2g}^{2,1,1}\ eg^{0,0}$

C.F.S.E = $-1.6\Delta_0 + P = 1.6 \times 38500 + 28000 = -33600\ cm^{-1}$

6. (A) Cr^{3+}–$3d^3$ configuration $(t_{2g}^{1,1,1}.e_g^{0,0})$; $Mn^{3+} - 3d^4$ configuration $(t_{2g}^{2,1,1}.e_g^{0,0})$; V – $3d^5$ configuration $(t_{2g}^{2,2,1}.e_g^{0,0})$

(B) $\Delta_o \propto$ strength of ligand for same oxidation state of central metal.

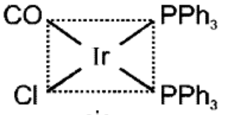
(C) In carbonylate anion, the metal has a greater electron density to be dispersed, with the result that M–C, π bonding is enhanced in strength. Hence the correct order is $[Ni(CO)_4] < [Co(CO)_4]^- < [Fe(CO)_4]^{2-}$ for strength of M–C, π bond.

(D) Chelate effect.

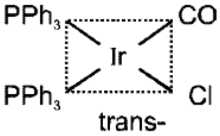
7. $[MnCl_4]^{2-}$, $[Ni(H_2O)_6]Cl_2$, $[Co(NH_3)_2(H_2O)_4]Cl_2$, $K_3[Cr(CN)_6]$.

8. The O.N. of Fe in $[\overset{x}{Fe}(\overset{0}{H_2O})\overset{+1}{NO}]^{2+}\ SO_4^{2-}$ is x + 0 + 1 = +2 or x = +1

9. In complex, Ir with +1 oxidation state has $5d^8$ configuration. Hence, the complex would be square planar and diamagnetic. It will have two geometrical isomers as given below.



cis-



trans-

10. $[Mn(CN)_6]^{4-}$ - $3d^5$, d^2sp^3; +2 oxidation sate

$[Ni(NH_3)_6]^{2+}$ - $3d^8$, sp^3d^2; +2 oxidation sate

$[Co(ox)_3]^{3-}$ - $3d^6$, d^2sp^3; +3 oxidation sate

$[Cu(NO_2)_6]^{4-}$ - $3d^9$, sp^3d^2; +2 oxidation sate

$[AgF_4]^-$ - $4d^8$, dsp^2; +3 oxidation sate

$[Ni(CN)_4]^{2-}$ - $3d^8$, dsp^2; +2 oxidation sate

$[PdCl_4]^{2-}$ - $4d^8$, dsp^2; +2 oxidation sate

$[Pd(CN)_4]^{2-}$ - $4d^8$, dsp^2; +2 oxidation sate

$[Co(SCN)_4]^{2-}$ - $3d^7$, sp^3; +2 oxidation sate

DPP No. # 13

2. **(a)** At 45°C

$K_w = 4 \times 10^{-14} = [H^+][OH^-]$. ⇒ $[H^+] = 2 \times 10^{-7}$. ⇒ pH = 7 – log2 = 6.7.

(b) For H_2O $K_w \propto T$.

∴ $[H^+] \propto T$.

∴ $pH \propto \frac{1}{T}$.

4. **(a)** $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$.

in self ionisation of NH_3.

$[NH_4^+] = [NH_2^-]$.

$K_{(Amm)} = [NH_4^+][NH_2^-] = 1 \times 10^{-30}$.

(b) $K = [HCOOH_2^+][HCOO^-] = 10^{-6}$.

$[HCOO^-] = 10^{-3}$ mol/L.

1 liter solution of HCOOH has = 1150 g mass.

moles of (HCOOH) in 1 litre solution = $\frac{1150}{46}$ = 25 mol.

out of 25 mol HCOOH 10^{-3} mol are ionised into $HCOO^-$ ions.

$\therefore$ % dissociation = $\frac{10^{-3}}{25} \times 100 = 0.004\%$.

5.

(i). (i) $HNO_2\,(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

Since, HNO_2 ionises to give H^+ hence, it is a Arrhenius acid.

(ii) $HNO_2(l) + H_2O(aq) \rightleftharpoons H_3O^+\,(aq) + NO_2^-(aq)$

acid 1 base 2 acid 2 base 1

HNO_2 donates a proton hence, it is an acid and changes to NO_2^- (conjugate base). $H_2O(l)$ accepts the proton hence, it is a base and change to H_3O^+ (conjugate acid). Thus HNO_2 is a Bronsted Lowry acid.

(ii) (a) $H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

acid 1 base 2 acid 2 base 1 (conjugatete)

(iii) (A) to the left (B) to the right

Reaction proceed to words the side favoring formation of weak acid and weak base.

(vi) (a) Acid strength $H_2SO_4 > H_2CO_3$.

Basic strength $HCO_3^- > HSO_4^-$.

(b) Acid strength $HCl > HF$.

Basic strength $F^- > Cl^-$.

(c) Acid strength $HF > NH_4^+$

Basic strength $NH_3 > F^-$.

(d) Acid strength $HSO_4^- > HCN$.

Basic strength $CN^- > SO_4^{2-}$.

c and d will move to the right.

8. Relative acidic strength of weak acids = $\sqrt{\frac{K_{a_1}}{K_{a_2}}} = \sqrt{\frac{2\times10^{-4}}{1.6\times10^{-5}}} = \sqrt{\frac{20}{1.6}} = \sqrt{12.5}$.

DPP No. # 14

11. $3A_2(g) + XY_2\,(g) \rightleftharpoons 2A_2Y(g) + A_2X\,(g)$.

$4 - 3x \qquad 1 - x \qquad 2x \qquad x \qquad \therefore \qquad [n_T = 5 - x]$

$\frac{4+1}{5-x} = \frac{1.25}{1.05} \Rightarrow x = 0.8 \Rightarrow n_T = 4.2.$

$$K_p = \frac{\left(\frac{2x}{n_T}P_{eq}\right)^2\left(\frac{x}{n_T}P_{eq}\right)}{\left(\frac{4-3x}{n_T}P_{eq}\right)^3\left(\frac{1-x}{n_T}P_{eq}\right)} = \frac{4x^3}{(4-3x)^3(1-x)} \times \frac{n_T}{P_{eq}} = 10.$$

DPP No. # 15

2. **(a)** Initially pH = 7

finally [NaOH] = 10^{-3} so pOH = 3

pH = 11

so Δ(pH) = 4

6. $pH + pOH = 14$

$pOH = 14 - 10.48 = 3.52$

$[OH^-] = 3 \times 10^{-4}$ mol/litre

NO. of OH^- moles in 250 ml = $\frac{3 \times 10^{-4}}{4} = 7.5 \times 10^{-5}$

No. of moles of $Ca(OH)_2$ dissolved = $\frac{1}{2} \times 7.5 \times 10^{-5} = 3.75 \times 10^{-5}$

DPP No. # 16

1. **(b)** $pH = \frac{1}{2}\{pK_a - \log C\}$

so, $\Delta(pH) = \frac{1}{2}[\log C_i - \log C_f] = \frac{1}{2}\{-1 + 2\} = 0.5$ [pH will increase].

3. Degree of dissocation of WA & WB will increase.

$[H^+]$ in WA and $[OH^-]$ in WB will decrease so pH of WA and pOH of WB will increase.

6. **(a)** Initially degree of dissociation $\alpha = \sqrt{\frac{K_a}{C}}$

Now degree of dissociation, $\alpha_1 = 2\alpha = \sqrt{\frac{4K_a}{C}} = \sqrt{\frac{K_a}{C_1}}$

so $C_1 = \frac{C}{4}$ ⇒ Hence we have

$$300 \times 0.2 = V_f \times \frac{0.2}{4} \quad \text{so } V_f = 1200 \text{ ml}$$

Hence water added = 1200 – 300 = 900 ml

(b) $pH = \frac{1}{2}\{pK_a - \log C\} = \frac{1}{2}\{5 - \log 2 - \log 1\} = \frac{4.7}{2} = 2.35.$

Now on dilution pH will increase degree of dissociation a will also increase so we might not be able to use the approximate formula hence

where $a = \sqrt{\frac{K_a}{C}} = \sqrt{K_a}$

$$K_a = \frac{C_1\alpha_1^2}{(1-\alpha_1)} = \frac{C\alpha^2}{(1-\alpha)} \qquad \text{...(1)}$$

Also we must have $pH_f = 2pH_i$

so $-\log[H^+]_f = -2\log[H^+]_i$

⇒ $-\log[C_1\alpha_1] = -2\log(C\alpha) = -\log\alpha^2$

so $C_1\alpha_1 = \alpha^2$ ...(2)

From (1) equation $K_a = \frac{C_1\alpha_1^2}{(1-\alpha_1)} = \frac{(C_1\alpha_1)\alpha_1}{(1-\alpha_1)} = \frac{\alpha^2 - \alpha_1}{(1-\alpha_1)} = \frac{K_a \cdot \alpha_1}{(1-\alpha_1)}$

Hence $\alpha_1 = \frac{1}{2}$

so we get $2 \times 10^{-5} = \frac{C_1 \times 1/4}{1/2} = \frac{C_1}{2}$

so $C_1 = 4 \times 10^{-5}$

Now $M_1V_1 = M_2V_2$ gives ⇒ $1 \times 1 = 4 \times 10^{-5}\,V_f$

so $V_f = 2.5 \times 10^4$ litre

7. Calculation of $[H^+]$ and [HSac] at start

$[HSac] = \frac{4 \times 10^{-4} \times 1000}{200} = 0.002$ M

The dissociation of HSac is as below

	HSac	H^+	+	Sac^-
At start	0.002	0.001		0
At equi.	0.002-x	0.001 + x		x

$$\therefore K_a = \frac{[H^+][Sac^-]}{[HSac]} = \frac{(0.01+x)x}{0.002-x} = 2\times10^{-12}$$

$x = 4 \times 10^{-12}$ M

$[Sac^-]_{equi.} = 4 \times 10^{-12}$ M.

8. $K_{a_1} >> K_{a_2}$

$[H^+] = [HS^-] = \sqrt{CK_{a_1}} = \sqrt{0.01\times9\times10^{-8}}$

$[H^+] = 3 \times 10^{-5}$.

pH = 4.52.

DPP No. # 17

1. **(b)** $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$.

$$8\times10^{-8} = \left(\frac{HPO_4^{2-}}{H_2PO_4^-}\right)\times 4\times10^{-8}. \quad \Rightarrow \quad \left(\frac{HPO_4^{2-}}{H_2PO_4^-}\right) = \frac{2}{1}.$$

3. $K_a = \dfrac{[H^+]^2[S^{2-}]}{(H_2S)} \Rightarrow 10^{-21} = \dfrac{4\times10^{-8}\times[S^{2-}]}{10^{-1}}$

so $[S^{2-}] = \dfrac{1}{4} \times 10^{-14} = 2.5\times10^{-15}$ M.

6. $C_1\alpha_1 = C_2\alpha_2$

$\sqrt{K_{a_1}C_1} = \sqrt{K_{a_2}C_2}$

$2\times10^{-5}\times C_1 = 2.4\times10^{-4}\times0.5 = \quad C_1 = 6$ M.

When two weak acids are mixed in such concentration that their $[H^+]$ ions are same the % dissociation of both the acids will not change.

9.

H_2S	$\rightleftharpoons$	H^+ +	HS^-	.....(i)
$0.1 - x$		0.25	x	
HS^-	$\rightleftharpoons$	H^+ +	S^-	.....(ii)
$x - y$		0.25	y	

$HCl \longrightarrow H^+ + Cl^-$ .....(iii)

0.25

(i) $10^{-7} = \dfrac{0.25\times[HS^-]}{0.1-x}$ $\quad [HS^-] = 4\times10^{-8}$.

(ii) $1.3\times10^{-13} = \dfrac{0.25\times[S^{2-}]}{4\times10^{-8}-y}$ $\quad [S^{2-}] = 2.08\times10^{-20}$.

DPP No. # 18

1. From the information, $\dfrac{[salt]}{[acid]} = 2$; so, pH = pKa + log $\dfrac{[salt]}{[acid]}$ = 5.05.

2. $7.4 = (7 - \log 4.2) + \log\dfrac{[B]}{[A]} \Rightarrow \log\dfrac{[B]}{[A]} = 1.03 \Rightarrow \dfrac{[B]}{[A]} = 10.7$

3.

	K_h	pH	%Hydrolysis
(i)	5×10^{-10}	8.7	0.01%
(ii)	5×10^{-10}	5.7	0.025%
(iii)	10.0	13.68	95%
(iv)	2.5×10^{-5}	11.60	0.625%
(v)	2.5×10^{-5}	7.0	0.5%
(vi)	1.25	9.35	52.8%

5. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.

$$1.84 \times 10^{-5} = \frac{0.04}{0.06} \times [H^+].$$

$$[H^+] = \frac{3}{2} \times 1.84 \times 10^{-5} = 2.76 \times 10^{-5}\ M.$$

8. $pOH = pK_b + \log \frac{[n_{salt}]}{[n_{acid}]}$

Since, $pH = 5$; $pOH = 9$.

$$9 = 8.824 + \log \frac{[n_{salt}]}{0.2 mol}.$$

$$0.176 = \log \frac{[n_{salt}]}{0.2 mol}$$

$[n_{salt}] = 0.3$ mole.

DPP No. # 19

8. **(i)** The conc. of HCl is highest in this case.

(ii) This is actually a solution of weak acid HCN with salt NaCl (having spectator ions only)

(iii) $[H^+] = 10^{-10}$ M from Hendersen equation.

9. **(iii)**

	$NaOH$	$+ H_2SO_4 \longrightarrow$	$NaHSO_4 + H_2O$
initial m mole	10	5	0
reaction	5	0	5

	$NaOH$	$+ NaHSO_4 \longrightarrow$	$Na_2SO_4 + H_2O$
	5	5	0
	0	0	5

$$pH = 7 + \frac{1}{2}\left[2 + \log\frac{5}{200}\right] = 7 + \frac{1}{2}\left[2 + \log 5 - \log 200\right] = 7 + \frac{1}{2}[2 + 0.7 - 0.3 - 2] = \mathbf{7.2}.$$

DPP No. # 21

3. $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{-2}$

$\quad 2s' \quad (s' + 10^{-2}) \approx 10^{-2}$

$K_{sp} = (2s')^2\ (10^{-2}) = (2 \times 2 \times 10^{-8})^2\ (10^{-2}) = 16 \times 10^{-18}$.

DPP No. # 22

2. pH = 13 means $[H^+] = 10^{-13}$ mol L^{-1}

or $10^{-13} \times 6.023 \times 10^{23} / 1000$ H^+ ions/c.c $= 6.023 \times 10^7$

3. $K_W = 55.5 \times 3.6 \times 10^{-15} \times 0.1 = 2 \times 10^{-14}$

Hence temperature must be > 25°C.

4. $K_h = \dfrac{10^{-14}}{4 \times 10^{-13}} = 0.025$

$$\begin{array}{llllllll} & BH^+ & + & H_2O & \rightleftharpoons & B & + & H_3O^+ \\ t = 0 & C & & & & & & \\ t_{eq} & C(1-\alpha) & & & & C\alpha & & C\alpha \end{array}$$

$K_h = \dfrac{C\alpha^2}{(1-\alpha)} = 0.025 \quad \Rightarrow \quad \dfrac{0.01\,\alpha^2}{1-\alpha} = 0.025.$

$\Rightarrow \alpha^2 + 2.5\alpha - 2.5 = 0 \quad \Rightarrow \quad \alpha = 0.76$

$[H^+] = 7.6 \times 10^{-3} \quad \Rightarrow \quad pH = -\log [H^+] = 2.1.$

5. $pH = P_{KIn} + \log_{10}\left[\dfrac{In^-}{HIn}\right]$

$pH = [6 - \log_{10} 5] + \log_{10}\left[\dfrac{1}{20}\right] = 4$

$pH = P_{KIn} + \log_{10}\left[\dfrac{In^-}{HIn}\right]$

$= P_{KIn} + \log_{10}\left[\dfrac{40}{1}\right]$

$= 6 - \log_{10} 5 + \log_{10} 40$

$= 6 - 0.7 + 1.6 = 6.9$

6. If 10^{-3} mole $Zn(OH)_2$ go into $Zn(OH)_4^{2-}$.

$Zn(OH)_2\,(s) + 2OH^-\,(aq) \rightleftharpoons Zn(OH)_4^{2-}\,(aq)$

$10^{-2} = \dfrac{10^{-3}}{[OH^-]^2} \quad \Rightarrow \quad [OH^-] = 0.316\text{ M}$

7.* $pK_a\,(H_3O^+) = -1.74 = pK_b$ of OH^-

$pK_a + pK_b = 14$ only for conjugate acid base pair.

$\alpha = 1.8 \times 10^{-9}$ or 1.8×10^{-7} % for H_2O.

8.* (A) Correct statement

(B) Due to common ion effect on $H_2O \rightleftharpoons H^+ + OH^-$

(D) relative strength of strong acids can not be determined in water due to levelling effect.

9. I.P. $\geq K_{sp}$

$[Mg^{2+}]\,[OH^-] \geq 10^{-11}$

$[OH^-]^2 \geq 10^{-10}$

$[OH^-] \geq 10^{-5}$

$P^{OH} \leq 5$

$P^{H} \geq 9$

10. 25 ml of 0.02 N acetic acid $= \dfrac{0.02}{1000} \times 25 = 5 \times 10^{-4}$ g eq.

2.5 ml of 0.1 N NaOH $= \dfrac{0.1}{1000} \times 25 = 2.5 \times 10^{-4}$ g eq.

After neutralization, CH_3COOH left is $(5 - 2.5) \times 10^{-4}$ g eq. $= 2.5 \times 10^{-4}$ g eq.

$pH = pK_a = -\log (10^{-5})$; $= 5$

11. Blue litmus turns red by acidic solution

(i) $Al_2(SO_4)_3$
(iv) H_3BO_3
(v) H_3PO_3
(vi) HIO_3
(vii) H_2PtCl_{16}

(All five acidic nature)

12. Na_2HPO_3 is the salt of H_3PO_3 which is dibasic in nature (as it contains two OH^- groups)

13. **(i)** $[H^+] = \sqrt{K_1C_0} = \sqrt{4\times10^{-7}\times0.1} = 2\times10^{-4}$ M.

(ii) $[H^+] = \sqrt{K_1K_2} = \sqrt{4\times10^{-7}\times4\times10^{-11}} = 4\times10^{-9}$ M

(iii) $[H^+] = \sqrt{K_1C_1+K_2C_2} = \sqrt{10^{-7}\times0.1+4\times10^{-7}\times0.2} = 3\times10^{-4}$ M

DPP No. # 23

1. Hydrolysis of cartion can form H^+. So Be^{+2}, $C_5H_6N^+$ forms acidic solution.

3. $BH^{2-} + H_2O \rightleftharpoons BH_2^- + OH^-$

$$K_b = \frac{K_w}{K_a(\text{of } BH_2^-)}$$

i.e. $K_b = \dfrac{K_w}{K_2}$

4. $[Ag^+]$ req for pptation of AgX$= \dfrac{K_{sp}}{[X^-]} = \dfrac{9\times10^{-14}}{10^{-6}} = 9\times10^{-8}$ M

$[Ag^+]$ req for pptation of $Ag_2Y = \sqrt{\dfrac{K_{sp}}{[y^-]}} = \sqrt{\dfrac{4.9\times10^{-21}}{10^{-6}}} = 7\times10^{-8}$ M

$[Ag^+]$ req for pptation of $Ag_3Z = \sqrt[3]{\dfrac{K_{sp}}{[z^-]}} = \sqrt[3]{\dfrac{5.12\times10^{-28}}{10^{-6}}} = 8\times10^{-8}$ M

clearly, $[Ag^+]$ req for pptation of Ag_2Y is minimum.
$\therefore$ Ag_2Y will be the first one to pricipitate out.

5. $\Delta T_f = i\times k_f\times m$
$0.2 = i\times1.8\times0.1$
$\Rightarrow$ $i = 1.11$
$\Rightarrow$ $\alpha = 0.11$

$$k_a = \frac{c\alpha^2}{1-\alpha} = \frac{0.1\times(0.11)^2}{(1-0.11)}$$

$= 1.35\times10^{-3}$ **Ans.**

6. Let the solubility of AgCl, AgBr and Ag_2CrO_4 be xM, yM and zM, then we get

$K_{sp(AgCl)} = x^2 \Rightarrow x = \sqrt{1.8\times10^{-10}} \Rightarrow x = 10^{-5}\sqrt{1.8}$

Similarly, $y = 10^{-7}\sqrt{50}$

$K_{sp}\ Ag_2CrO_4 = 4z^3 = 2.4\times10^{12}$
$\Rightarrow$ $z = (60)^{1/3}\times10^{-4}$
$\therefore$ More (Ag^+) is needed to precipitate it.

7. In $AgNO_3$ solution, the solubility of AgCN will decrease as compared to pure water because of common ion effect of Ag^+ ion.
In NH_3 solution and buffer of pH = 5, the solubility of AgCN will increase due to complex formation in case of NH_3 solution and hydrolysis of CN^- ions in case of buffer of pH = 5.

8. In a given mixture, the ionisation of two acids can be written as: Let α, β be degree of ionisation at same concentration.

$$\underset{1-\alpha}{CH_3COOH} \rightleftharpoons \underset{\beta}{CH_3COO^-} + \underset{\alpha+\beta-x}{H^+} \qquad \underset{1-\beta}{C_2H_5COOH} \rightleftharpoons \underset{\beta}{C_2H_5COO^-} + \underset{\alpha+\beta-x}{H^+}$$

$$\therefore \qquad K_{A.A} = \frac{[\alpha][\alpha+\beta-x].c}{[1-\alpha]} \qquad K_{P.A} = \frac{[\beta][\alpha+\beta-x].c}{[1-\beta]}$$

(where 'x' is equivalents of NaOH droped).

$$\therefore \qquad \frac{K_{A.A}}{K_{P.A}} = \frac{\alpha}{1-\alpha} \times \frac{1-\beta}{\beta} \qquad \text{or} \qquad \frac{\alpha}{1-\alpha} = \frac{1.75}{1.3} \times \left[\frac{\beta}{1-\beta}\right]$$

Hence, A,C,D.

9. m. moles of HCl = 0.1 × 20 = 2
m. moles of CH_3COOH = 0.1 × 20 = 2
After titration of HCl by NaOH

$$[CH_3COOH] = \frac{2}{40} = \frac{1}{20}\,M$$

$$\therefore \text{pH} = \frac{1}{2}(pK_a - \log C) = \frac{1}{2}\left[5 - \log 2 - \log\left(\frac{1}{20}\right)\right] = \mathbf{3.}$$

10. When 10 ml of NaOH is added, it reacts with CH_3COOH to produce salt and water. The solution is then an acidic buffer. So, for acidic buffer,

$$\text{pH} = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

$$= 4.7 + \log\frac{10 \times 0.1}{60 \times 0.1 - 10 \times 0.1}$$

$$= 4.7 + \log\frac{1}{5} = \mathbf{4}$$

11. $C_6H_5NH_3^+Cl^-$, $FeCl_3$, $Al(NO_3)_3$.

DPP No. # 24

1. **(a)** In polymerisation of ethene gas forming polyethene and condensation of dew on leaves in winters, entropy of the system decreases.
(b) Δn_g is most – ve
(c) Polymerisation leads to more ordered structure.

3. For a reversible adiabatic process, $\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$

4. $$\Delta S_{gas} = n\,C_{V,m} \ln\frac{T_2}{T_1} = 2 \times \frac{3}{2} R \ln\frac{573}{473} = 3R \ln\left(\frac{573}{473}\right).$$

5. $$\Delta S = mS \ln\frac{T_2}{T_1} = 2.5 \times 4.2 \ln\left(\frac{360}{300}\right) = 1.89 \text{ J/K}$$

6. $$\Delta S_{(system)} = \frac{1 \times -436.8}{368} = -1.19 \text{ JK}^{-1}$$

The ice-water bath absorbs the 436.8 J mol^{-1} at temperature 273 K.

$$\therefore \qquad \Delta S_{surrounding} = \frac{1 \times 436.8}{273} = 1.6 \text{ JK}^{-1} \text{ and } \qquad \Delta S_{(universe)} = -1.19 + 1.6 = 0.41 \text{ JK}^{-1}$$

7. (A) For isoentropic process $\Delta S_{system} = 0$

$$\therefore nC_{p,\,m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = 0 \quad \Rightarrow \ln (P_2) = \frac{5}{2} \times \ln \left(\frac{600}{300}\right)$$

$= 1.75$ atm.

8. **(a)** For isothermal free expansion of an ideal gas,
$\Delta T = 0$ Therefore, $\Delta H = \Delta E = 0$
Also, W = 0 (since $P_{ext.} = 0$)
Therefore, from first law, q = 0. Therefore, $\Delta S_{surr.} = 0$.
Since gas is expanding, $\Delta S_{sys.} > 0$.

9.* $H_2O(\ell, 1bar, 373K) \longrightarrow H_2O(g, 1bar, 373\ K)$
$\Delta S > 0$
$\Delta H > 0$
$\Delta G = 0$

10. $W = -P_{ext}(V_f - V_i) = -(1\ atm)(8-2)\ L$
$= -6$ L atm
as q = 0 so

$$\Delta E = W = n\left(\frac{6}{2}R\right)\left(\frac{P_fV_f}{nR} - \frac{P_iV_i}{nR}\right) \qquad \text{Here } \Delta E = nC_V\Delta T$$

$3(8P_f - 12) = -6$

$$8P_f = 12 - \frac{6}{3} = 10 \quad \Rightarrow \quad P_f = \frac{5}{4}\ atm$$

$$\text{so,} \quad \frac{T_f}{T_i} = \frac{\frac{5}{4}\times 3}{6\times 2} = \frac{10}{12}$$

$$\text{so} \quad \Delta S = 3\,\frac{12}{300} \ln\left(\frac{10}{12}\right) + \frac{12}{300} \ln 8$$

$$= \frac{3\times 12}{300} \ln\left(\frac{5}{6}\times 2\right) \qquad = \frac{12}{100} \ln\left(\frac{5}{3}\right) \times 100\ J$$

$= 12(\ln 5 - \ln 3) = 12 \times 2.3 \times (0.7 - 0.48)$
$= 12 \times 2.3 \times 0.22 = 6.072$ J/K

Ans. 6 J/K

11. **(a) (i)** $\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T} = \frac{26\times 10^3}{308} = 84.41\ JK^{-1}\ mol^{-1}$.

(ii) $\Delta S_{cond.} = \frac{\Delta H_{cond}}{T} = -84.41\ JK^{-1}\ mol^{-1}$.

(b) Using $\Delta G = \Delta H - T\Delta S = -11.50$ KJ/mol.

12. **(a)** $T < \frac{\Delta H}{\Delta S} = \frac{-95.4\times 10^3}{-198.3} = 481.0$ K. (Since ΔS and ΔH both are negative)

(b) For $\Delta H_{min.}$, $\Delta G = 0$

$\therefore$ $\Delta H_{min} = T\Delta S = 36.06$ KJ.

13. Spontaneity of a reaction is decided by
$\Delta S_{total} = (\Delta S_{Sys} + \Delta S_{surr.}) > 0$

$$\Delta S_{surr} = \frac{-1648\times 10^3\ J/mol}{298} = 5530\ JK^{-1}\ mol^{-1}$$

$\therefore$ $\Delta S_{total} = 4980.6\ JK^{-1}\ mol^{-1} > 0$ (Hence, spontaneous).