DAY ELEVEN

Unit Test 2
(Physical Chemistry I)

1 The free energy for the following reactions are as follows:

$$C_2H_2(g)+\frac{5}{2}O_2(g)\longrightarrow 2CO_2(g)+H_2O(l);\Delta G^\circ=-1234\text{ kJ}$$

$$C(s)+O_2(g)\longrightarrow CO_2(g);\Delta G^\circ=-394\text{ kJ}$$

$$H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l);\Delta G^\circ=-237\text{ kJ}$$

The standard free energy change for the following reaction is ➜ NCERT Exemplar

$$H_2(g)+2C(s)\longrightarrow C_2H_2(g)$$

(a) –209 kJ
(b) –2259 kJ
(c) +209 kJ
(d) +2259 kJ

2 The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound ➜ NCERT Exemplar

(a) is always negative
(b) is always positive
(c) may be positive or negative
(d) is never negative

3 The internal energy change when a system goes from state A to B is 40 kJ mol^{-1}. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy?

(a) 40 kJ (b) > 40 kJ
(c) < 40 kJ (d) Zero

4 Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 JK^{-1} mol^{-1}, respectively. For the reaction, $\frac{1}{2}X_2+\frac{3}{2}Y_2 \longrightarrow XY_3; \Delta H=-30$ kJ, to be at equilibrium, the temperature will be

(a) 1250 K (b) 500 K
(c) 750 K (d) 1000 K

5 An ideal gas heat engine operates in Carnot cycle between 227°C and 127°C. It absorbs 6×10^4 cal of heat at high temperature. Amount of heat converted to work is

(a) 1.2×10^4 cal (b) 4.8×10^4 cal
(c) 6×10^4 cal (d) 2.4×10^4 cal

6 When one mole of anhydrous $FeSO_4$ is dissolved in excess of water, there in evolution of 58.2 kJ of heat. But when one mole of $FeSO_4\cdot5H_2O$ is dissolved in water, the heat change is + 8.6 kJ. Calculate the enthalpy of hydration of anhyd. $FeSO_4$.

(a) – 49.6 kJ (b) – 66.8 kJ (c) + 49.6 kJ (d) + 66.8 kJ

7 $A\longrightarrow B, \Delta H=+\text{ve}$. Graph between $\log_{10} p$ and $\frac{1}{T}$ is a straight line of slope $\frac{1}{4.606}$. Hence, ΔH is

(a) 1 (b) 2 (c) 4 (d) –1

8 The heat of atomisation of $PH_3(g)$ is 228 kcal mol^{-1} and that of $P_2H_4(g)$ is 355 kcal mol^{-1}. The energy of the P—P bonds (in kcal mol^{-1}) is

(a) 102 (b) 51 (c) 26 (d) 204

9 Match the following and choose the correct option.

Column I		Column II	
A.	$Q=K$	1.	Reaction is nearer to completion.
B.	$Q<K$	2.	Reaction is not at equilibrium.
C.	$Q>K$	3.	Reaction is fast in forward direction.
D.	$K>>>1$	4.	Reaction at equilibrium.
		5.	Reaction proceeds in backward direction.

	A	B	C	D
(a)	4	2,3	2,5	1
(b)	1	2,3	4	2
(c)	2	3	1,4	3,4
(d)	1	2	3	2,4

10 1 mole of non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95K) $\longrightarrow$ (4.0 atm, 5.0 L, 245 K) with a change in internal energy, $\Delta E = 30.0$ L atm. The change in enthalpy (ΔH) of the process in L atm is

(a) 40.0 (b) 42.3 (c) 44.0
(d) not defined because pressure is not constant

11 **Assertion** (A) Aqueous solution of ammonium carbonate is basic.

Assertion (R) Acidic/basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b value of the acid and the base forming it.

→ [NCERT Exemplar]

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct and Reason is incorrect
(d) Both Assertion and Reason are incorrect

12 The polymerisation of ethene to linear polythene is represented by the reaction.

$$n(CH_2{=}CH_2) \longrightarrow -\!\!(CH_2{-}CH_2)\!\!-_n$$

Given that the average enthalpies of bond dissociation for C=C and C—C at 298 K are + 590 and + 331 kJ mol^{-1} respectively. The enthalpy of polymerisation per mole of ethene at 298 K, is

(a) 72 kJ mol^{-1} (b) 27 kJ mol^{-1}
(c) 1144 kJ mol^{-1} (d) 172 kJ mol^{-1}

13 When 1 mole of an ideal gas is compressed to half its initial volume and simultaneously heated to twice its initial temperature, the change in entropy (ΔS) is

(a) C_V ln 2 (b) C_p ln 2 (c) R ln 2 (d) $(C_V - R)$ ln2

14 The enthalpy changes of formation of the gaseous oxides of nitrogen (N_2O and NO) are positive because of

(a) the high bond energy of the nitrogen molecule
(b) the high electron affinity of oxygen atoms
(c) the high electron affinity of nitrogen atoms
(d) the tendency of oxygen to form O^{2-} ion

15 1.0 g of pure calcium carbonate was found to require 50 mL of dilute HCl for complete reaction. The strength of the HCl solution is given by

(a) 0.2 N (b) 0.4 N (c) 2.0 N (d) 4.0 N

16 What is the molarity of H_2SO_4 solution that has a density 1.84 g/cc at 35°C and contains solute 98% by weight ?

(a) 4.18 M (b) 1.84 M (c) 8.41 M (d) 18.4 M

17 The lowering in vapour pressure caused by the addition of 100 g of sucrose (molecular mass = 342) to 1000 g of lowering in water, if the vapour pressure of pure water at 25°C is 23.8 mm Hg, is

(a) 0.012 mm Hg (b) 0.125 mm Hg
(c) 1.15 mm Hg (d) 1.25 mm Hg

18 Two solutions of KNO_3 and CH_3COOH are prepared separately. Molarity of both is 0.1 M and their osmotic pressures are p_1 and p_2 respectively. The correct relationship between the osmotic pressures is

(a) $p_1 = p_2$ (b) $p_1 > p_2$
(c) $p_2 > p_1$ (d) $\frac{p_1}{p_1 + p_2} + \frac{p_2}{p_1 + p_2}$

19 The osmotic pressure of a 5% (w/V) solution of cane sugar at 150°C is

(a) 3.078 atm (b) 4.078 atm
(c) 5.071 atm (d) 2.45 atm

20 Which will show maximum depression in freezing point when concentration is 0.1 M?

(a) Urea (b) $BaCl_2$
(c) $Al_2(SO_4)_3$ (d) KBr

21 A 5% solution of sugarcane (mol wt. = 342) is isotonic with 1% solution of x. The mol. wt. of x is

(a) 34.2 (b) 68.4 (c) 136.2 (d) 171.2

22 Match the following and choose the correct option.

	Column I		Column II
A.	ΔG	1.	$\Delta U + nRT$
B.	ΔH	2.	$\Delta H - T\Delta S$
C.	ΔU	3.	$nC\,vdT$
D.	ΔS	4.	$2.303nR\log 10\left(\frac{V_2}{V_1}\right)$

	A	B	C	D
(a)	2	1	3	4
(b)	1	2	3	4
(c)	3	2	4	1
(d)	4	3	2	1

23 An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.5 atm pressure. Ammonium hydrogen sulphate decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches at equilibrium, the total pressure in the flask rises to 0.84 atm.
The equilibrium constant for the decomposition of NH_4HS at this temperature, is

(a) 0.11 (b) 0.17
(c) 0.18 (d) 0.30

24 For the reaction,

$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$; $K_C = 1.8 \times 10^{-6}$ at 184°C
$(R = 0.00831 \text{ kJ mol}^{-1} \text{ K}^{-1})$

When K_p and K_C are compared at 184°C, it is found that

(a) whether K_p is greater than, less than or equal to K_C depends upon the total gas pressure
(b) $K_p = K_C$
(c) K_p is less than K_C
(d) K_p is greater than K_C

25 For the equilibrium,

$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+; K_1 = 1.8 \times 10^7$$

and $Ag^+ + Cl^- \rightleftharpoons AgCl; K_2 = 5.6 \times 10^9$

Hence, for the equilibrium,

$$AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$$

equilibrium constant is

(a) 0.32×10^{-2} (b) 0.31×10^{-21}
(c) 1.01×10^{17} (d) 1.01×10^{-17}

26 Given pH of a solution *A* is 3 and it is mixed with another solution having pH 2. If both are mixed, resultant pH of the solution will be

(a) 3.21 (b) 1.96 (c) 3.42 (d) 3.58

27 For the reaction,

$$CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4 \cdot 3H_2O(s) + 2H_2O(g)$$

K_p at 298 K is 1.086×10^{-4} atm^2 and vapour pressure of water is 23.8 torr. The salt $CuSO_4 \cdot 5H_2O$ will be efforescent when the relative humidity is

(a) 80% (b) 60%
(c) 50% (d) less than 33.1%

28 50.0 mL of 0.3 M HCl is mixed with 50 mL of 0.4 M NH_3 solution. If pK_a of NH_4^+ is 9.26, pH of the mixture is

(a) 5.22 (b) 1.30 (c) 8.78 (d) 12.70

29 pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be

(a) unionised in the small intestine and in the stomach
(b) completely ionised in the small intestine and in the stomach
(c) ionised in the stomach and almost decrease in the small intestine
(d) ionised in the small intestine and almost unionised in the stomach

30 A weak acid H*X* has the dissociation constant 1×10^{-5} M. It forms a salt Na*X* on reaction with alkali. The degree of hydrolysis of 0.1 M solution of Na*X* is

(a) 0.0001% (b) 0.01%
(c) 0.1% (d) 0.15%

31 A sample of $Na_2CO_3 \cdot H_2O$ weighing 0.62 g is added to 100 mL of 0.1 N $(NH_4)_2SO_4$ solution. What will be the resulting solution?

(a) Acidic (b) Neutral
(c) Basic (d) None of these

32 At infinite dilution, the percentage ionisation for both strong and weak electrolyte is

(a) 1% (b) 20%
(c) 50% (d) 100%

33 A litre of solution is saturated with AgCl. To this solution if 1.0×10^{-4} moles of solid NaCl are added, what will be the $[Ag^+]$ assuming no volume change?

(a) More (b) Less (c) Equal (d) Zero

34 Which hydroxide will have lowest value of solubility product at normal temperature (25°C)?

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) $Be(OH)_2$

35 When solid potassium cyanide is added in water, the

(a) pH will increase
(b) pH will decrease
(c) pH will remain same
(d) electrical conductivity will not change

36 Heat obtained due to expansion of 1 mole of H_2 gas at 1000 K from 10 L to 100 L under isothermal reversible condition is absorbed by an engine having a sink at 300 K. Useful work obtained is

(a) – 1382 cal (b) – 3224 cal
(c) 1382 cal (d) 3224 cal

37 The enthalpy of hydrogenation of 1-pentene is + 126 kJ mol^{-1}. The enthalpy of hydrogenation of 1,3-pentadiene is + 230 kJ mol^{-1}.Hence, resonance (delocalisation) energy of 1,3-pentadiene is

(a) 22 kJ (b) 104 kJ
(c) 252 kJ (d) 11 kJ

38 An aqueous solution of liquid '*X*' [mol. weight 56] 28% by weight has a vapour pressure 150 mm. Find the vapour pressure of '*X*' if vapour pressure of water is 155 mm of Hg.

(a) 110 mm (b) 150 mm
(c) 220 mm (d) 125 mm

39 A monoprotonic weak acid[H*A*] is ionised 5% in 0.1 M aqueous solution. What is the equilibrium constant for its ionisation?

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

(a) 9.5×10^{-2} (b) 2.63×10^{-4}
(c) 2.303×10^{-3} (d) 5×10^{-3}

Direction (Q. Nos. 40-42) *Aqueous calcium chloride solution is mixed with sodium oxalate and precipitate of calcium oxalate formed is filtered and dried. Its saturated solution was prepared and 250 mL of this solution was titrated with 0.001 M $KMnO_4$ solution, when 6.0 mL of this was required.*

40 100 mL of pH = 6 (acidic) is diluted to 1000 mL by H_2O. pH will increase approximately by

(a) 9 unit (b) 1 unit (c) 0.7 unit (d) – 0.7 unit

41 Consider the following reaction,

$$N_2(g) + 3H_2 \longrightarrow 2NH_3(g);$$
$$\Delta H = -95.4 \text{ kJ and } \Delta S = -198.3 \text{ JK}^{-1}$$

Find the temperatures at which Gibbs energy change (ΔG) is zero and predict if the reaction below this temperature would be spontaneous or non-spontaneous.

(a) 481 K ; non-spontaneous (b) 281 K ; spontaneous
(c) 281 K ; non-spontaneous (d) 481 K ; spontaneous

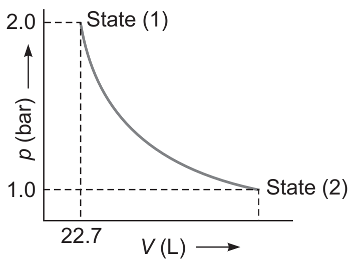
42 pK_b of NH_3 is 4.74 and pK_b of A^-, B^- and C^- are 4, 5 and 6, respectively. Aqueous solution of 0.01 M has pH in the increasing order

(a) $NH_4A < NH_4B < NH_4C$
(b) $NH_4C < NH_4B < NH_4A$
(c) $NH_4C < NH_4A < NH_4B = 7$
(d) All have equal pH being salt of weak acid and weak base

43 Given that $dE = TdS - pdV$ and $H = E + pV$. Which one of the following relations is true?

(a) $dH = TdS + Vdp$ (b) $dH = SdT + Vdp$
(c) $dH = -SdT - Vdp$ (d) $dH = dE - pdV$

44 1.0 mole of a monoatomic idea gas is expanded from state (1) to state (2) as shown in the figure. Calculate the work done for the expansion of gas from state (1) to state (2) at 298 K → NCERT Exemplar



(a) −1717.46 J (b) +1717.46 J
(c) −1908.2 J (d) +1908.2 J

Direction (Q. Nos. 45-50) *Each of these questions contains two statements: Assertion and* Reason. *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.*

(a) Both A and R are true and R is correct explanation of A
(b) Both A and R are true but R is not correct explanation of A
(c) A is true but R is false
(d) Both A and R are false

45 **Assertion** (A) An aqueous solution of ammonium acetate can act as a buffer.

Assertion (R) Acetic acid is a weak acid and NH_4OH is a weak base. → NCERT Exemplar

46 **Assertion** (A) On mixing equal volumes of 1 M HCl and 2M CH_3COONa, an acidic buffer solution is formed.

Reason (R) Resultant mixture contains CH_3COOH and CH_3COONa which are parts of acidic buffer.

47 **Assertion** (A) A liquid crystallises into a solid and is accompanied by decrease in entropy.

Reason (R) In crystals, molecules organise in an ordered manner.

48 **Assertion** (A) The pK_a of a weak acid becomes equal to pH of the solution at the mid point of its titration.

Reason (R) The molar concentrations of proton acceptor and proton donor become equal at the mid point of titration of a weak acid.

49 **Assertion** (A) Heat of neutralisation is always less than zero.

Reason (R) Neutralisation involves reaction between an acid and a base.

50 **Assertion** (A) The molality of the solution does not change with change in temperature.

Reason (R) The molality is expressed in units of moles per 1000 g of solvent.

ANSWERS

1. (a)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (a)	**6.** (b)	**7.** (a)	**8.** (b)	**9.** (a)	**10.** (b)
11. (a)	**12.** (a)	**13.** (d)	**14.** (a)	**15.** (b)	**16.** (d)	**17.** (b)	**18.** (b)	**19.** (c)	**20.** (c)
21. (b)	**22.** (a)	**23.** (a)	**24.** (d)	**25.** (a)	**26.** (b)	**27.** (d)	**28.** (c)	**29.** (d)	**30.** (b)
31. (a)	**32.** (d)	**33.** (b)	**34.** (d)	**35.** (a)	**36.** (d)	**37.** (a)	**38.** (a)	**39.** (b)	**40.** (c)
41. (d)	**42.** (b)	**43.** (a)	**44.** (a)	**45.** (b)	**46.** (a)	**47.** (a)	**48.** (a)	**49.** (b)	**50.** (a)

Hints and Explanations

1 $C_2H_2(g)+\frac{5}{2}O_2(g)\rightarrow 2CO_2(g)+H_2O(l);$

$$\Delta G^\circ = -1234\ \text{kJ}$$

(b) $[C(s)+O_2(g)\longrightarrow CO_2(g);$

$$\Delta G^\circ = -394\ \text{kJ}\ ]\times 2$$

(c) $H_2(g)+\frac{1}{2}O_2(g)\longrightarrow H_2O(l);$

$$\Delta G^\circ - 237\ \text{kJ}$$

Add Eq. (b) + (c) and then subtract from (a), to get,

$2C(s)+H_2(g)\longrightarrow C_2H_2(g);$

$$\Delta G^\circ = -209\ \text{kJ}$$

2 Combustion of elements to form a compound can be exothermic or endothermic e.g. $C+O_2\longrightarrow CO_2$ is exothermic.

whereas, $C+2S\longrightarrow CS_2$ is endothermic

Hence,enthalpy of formation can be positive or negative.

3 In case of cyclic process, $\Delta E = 0$.

4 $\Delta S = S(XY_3)-\frac{1}{2}S(X_2)-\frac{3}{2}S(Y_2)$

$= 50-30-60$

$= -40\ \text{J mol}^{-1}\ \text{K}^{-1}$

$\Delta H = -30\ \text{kJ} = -30000\ \text{J}$

$\Delta G = \Delta H - T\Delta S$

At equilibrium, $\Delta G = 0$

$$T=\frac{\Delta H}{\Delta S}=\frac{-30000}{-40}=750\ \text{K}$$

5 $\eta=\frac{T_2-T_1}{T_2}=\frac{500-400}{500}=\frac{1}{5}$

$$W=\eta\times Q=\frac{1}{5}\times 6\times 10^4=1.2\times 10^4$$

6 The hydration of $FeSO_4$ in depicted as

$FeSO_4 + 5H_2O \longrightarrow FeSO_4\cdot 5H_2O$;

$$\Delta_{hyd}H^- = ?$$

We have,

$FeSO_4(\text{anhyd})+H_2O(\text{excess})$

$\longrightarrow FeSO_4(aq);$

$\Delta H_1 = -58.2\ \text{kJ}$

$FeSO_4\cdot 5H_2O+H_2O(\text{excess})$

$\longrightarrow FeSO_4(aq);$

$\Delta H_2 = +8.6\ \text{kJ}$

Thus, we can calculate,

$$\Delta_{hyd}H = \Delta H_1 - \Delta H_2$$

$$= -58.2-8.6 = -66.8\ \text{kJ}$$

7 By Clapeyron – Clausius equation

$$\log p = -\frac{\Delta H}{2.303\,RT} + \text{constant}$$

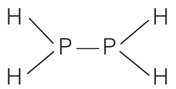
$$\frac{\Delta H}{2.303\,R}=\frac{1}{4.606}$$

$$\Delta H=\frac{2.303\times 2}{4.606}=1\ \text{cal}$$

8 Bond dissociation energy of $PH_3 = 228\ \text{kcal mol}^{-1}$

P—H bond energy

$$=\frac{228}{3}=76\text{kcal mol}^{-1}$$

Structure of P_2H_4 is 

$\therefore$ Bond dissociation energy of P_2H_4 can be given as

$4(P—H)+(P—P) = 355\ \text{kcal mol}^{-1}$

$4\times 76+(P—P) = 355\ \text{kcal mol}^{-1}$

$\therefore$ P—P bond energy $= 51\ \text{kcal mol}^{-1}$

9 $A\rightarrow 4,\ B\rightarrow 2,3,\ C\rightarrow 2,5\ D\rightarrow 1$

10 $\Delta H = \Delta E + \Delta n_g RT,\quad \Delta n_g = 1$ mol,

$\Delta T = 245-95 = 150\ \text{K},$

$R = 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1}$

$\Delta E = 30.0\ \text{L atm}$

$\Delta H = 30+1\times 0.0821\times 150 = 42.3\ \text{L atm}$

11 $(NH_4)_2CO_3\longrightarrow 2\overset{+}{N}H_4+CO_3^{2-}$

$2H_2O\longrightarrow 2OH^- + 2H^+$

$OH^- \downarrow NH_4OH$ Weak base; $H^+ \downarrow H_2CO_3$ Weak acid

If K_b of $NH_4OH > K_a$ of H_2CO_3. The solution is basic

or, if K_a of $H_2CO_3 > K_b$ of NH_4OH; the solution is acidic.

12 In this polymerisation reaction, every molecule of ethene involves breaking of one C ═ C (double bond) and formation of two C—C single bonds.

The amount of energy required to break one mole of >C ═ C< (double bond) into >C — C< (single bond) = 590 kJ.

The energy released in the formation of two moles of >C—C< single bond

$= 2\times 331 = 662$ kJ

Net energy released per mole of ethene

$= 662-590 = 72$ kJ

Enthalpy of polymerisation per mole of ethene at 298 K,

$$\Delta H = 72\ \text{kJ mol}^{-1}$$

13 When there is simultaneously change in temperature and volume (or pressure)

$$\Delta S = nC_V\ln\left(\frac{T_2}{T_1}\right)+nR\ln\left(\frac{V_2}{V_1}\right)$$

$$=C_V\ln\left(\frac{2}{1}\right)+R\ln\frac{1}{2}$$

$$=C_V\ln 2 - R\ln 2 = (C_V-R)\ln 2$$

14 The enthalpy changes of formation of the gaseous oxides of nitrogen are positive due to high bond energy of the nitrogen molecule.

15 Meq. of HCl = M eq. of $CaCO_3$

$$N\times 50=\frac{1}{50}\times 1000$$

$$N=\frac{1\times 1000}{50\times 50}=0.4\text{N}$$

16 98% H_2SO_4 means 98 g H_2SO_4 in 100 g solution.

Volume of solution $=\frac{100}{1.84}$ cc $= 54.3$ cc

Number of moles of solute $=\frac{98}{98}=1$ mol

Molarity $=\frac{1}{54.3}\times 1000 = 18.4$ M

17 Molecular mass of sucrose = 342

Moles of sucrose $(x)=\frac{100}{342}=0.292$ mol

Moles of water $(N)=\frac{1000}{18}=55.5$ mol

Vapour pressure of pure water $p^\circ = 23.8$ mm Hg

$$\frac{\Delta p}{p^\circ}=\frac{n}{n+N}$$

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

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

$$= 0.125\ \text{mm Hg}$$

18 KNO_3 dissociates completely while CH_3COOH dissociates to a smaller extent, hence $p_1 > p_2$.

19 $C = \frac{5\times1000}{342\times100} = \frac{50}{342}$ mol L^{-1}

$\pi = \frac{50}{342}\times0.082\times423 = 5.07$ atm

20 $KBr = K^+ + Br^- = 2$ ions

$BaCl_2 = Ba^{2+} + 2Cl^- = 3$ ions

$Al_2(SO_4)_3 = 2Al^{3+} + 3SO_4^{2-} = 5$ ions

Urea does not get ionised.

Hence, $Al_2(SO_4)_3$ shows maximum depression in freezing point.

21 For isotonic solutions,

$$\frac{w_1}{m_1} = \frac{w_2}{m_2}$$

$$\frac{5}{342} = \frac{1}{m_2}$$

$$m_2 = 68.4$$

22 A → 2, B → 1, C → 3, D → 4

23 $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

	$NH_4HS(s)$	$NH_3(g)$	$H_2S(g)$
Initially	1	0.5	0
At equilibrium	$(1-x)$	$(0.5+x)$	x

Total pressure at equilibrium

$= p_{NH_3} + p_{H_2S}$

$= 0.5 + x + x = 0.84$

$x = 0.17$ atm

$p_{NH_3} = 0.50 + 0.17 = 0.67$ atm

$p_{H_2S} = 0.17$ atm

$K_p = p_{NH_3}\cdot p_{H_2S}$

$= 0.67\times0.17$

$= 0.114$ atm ≈ 0.11 atm

24 $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$K_C = 1.8\times10^{-6}$ at 184°C (= 457 K)

$R = 0.00831$ kJ mol^{-1} K^{-1}

$K_p = K_C(RT)^{\Delta n_g}$

where, Δn_g = gaseous products – gaseous reactants = 3 – 2 = 1

$K_p = 1.8\times10^{-6}\times0.00831\times457$

$= 6.836\times10^{-6}$

Thus, $K_p > K_C$

25 $Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+$; $K_1 = 1.8\times10^7$

$AgCl \rightleftharpoons Ag^+ + Cl^-$; $K_2' = \frac{1}{K_2} = \frac{1}{5.6\times10^9}$

$\therefore AgCl + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+ + Cl^-$

$K = K_1K_2' = \frac{K_1}{K_2}$

$= \frac{1.8\times10^7}{5.6\times10^9}$

$= 0.32\times10^{-2}$

26 pH of the solution $A = 3$

$[H^+]_A = 10^{-3}$ M

pH of the solution $B = 2$

$[H^+]_B = 10^{-2}$ M

$[H^+] = 10^{-3} + 10^{-2} = 11\times10^{-3}$

$pH = -\log(11\times10^{-3})$

$= 3 - \log 11 = 3 - 1.04 = 1.96$

27 An efflorescent salt is one that loses water to the atmosphere. This will occur if in the equilibrium water vapour pressure, with the salt is greater than the water vapour pressure in the atmosphere. For the given hydrated salt, equilibrium is

$$CuSO_4\cdot5H_2O(s) \rightleftharpoons CuSO_4\cdot3H_2O(s) + 2H_2O(g)$$

$K_p = p_{H_2O}^2 = 1.086\times10^{-4}$ atm^2

$\therefore p_{H_2O} = 1.042\times10^{-2}$ atm = 7.89 torr

Since, p_{H_2O} is less than the vapour pressure of water in air at the same temperature, $CuSO_4\cdot5H_2O$ will not always efflorescence. It will efflorescence only on a dry day, when the partial pressure of moisture in the air is less than 7.89 torr.

Relative humidity

$= \frac{7.89}{23.8} = 0.331 = 33.1\%$

Thus, this salt will efflorescence when the relative humidity is less than 33.1%.

28. (*c*) $pK_a(NH_4^+) = 9.26$

$\therefore pK_b(NH_3) = 14 - 9.26 = 4.74$

50 mL of 0.3 M HCl = 15 millimol

50 mL of 0.4 M NH_3 = 20 millimol

$NH_3 + HCl \rightleftharpoons NH_4Cl$

	NH_3	HCl	NH_4Cl
Initial millimol	20	15	0
At equilibrium	5	0	15

Mixture is a buffer containing 5 millimol of NH_3 (base) and 15 millimol of NH_4^+ (conjugate acid)

$\therefore pOH = pK_b + \log\frac{[NH_4^+]}{[NH_3]}$

$= 4.74 + \log 3$

$\therefore pH = 14 - pOH = 9.26 - \log 3$

$= 9.26 - 0.48 = 8.78$

29. Aspirin is a weak acid. Due to common ion effect, it is unionised in acidic medium i.e. stomach but completely ionised in alkaline medium i.e. small intestine.

30. $X^- + H_2O \rightleftharpoons HX + OH^-$

$K_h = \frac{10^{-14}}{10^{-5}}$

So, $x = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$

$= 100\times10^{-4} = 10^{-2} = 0.01$

So, degree of hydrolysis = 0.01%.

31. Gram equivalent of

$(NH_4)_2SO_4 = \frac{100}{1000}\times\frac{1}{10}\times66 = 0.66$

Gram equivalent of

$Na_2CO_3\cdot H_2O = \frac{0.62}{62} = 0.01$

Left $(NH_4)_2SO_4 = 0.66 - 0.01 = 0.65$

Since, $(NH_4)_2SO_4$ is a salt of strong acid and weak base therefore solution will be acidic in nature.

32. According to Ostwald's dilution law, Degree of ionisation ∝ dilution

∴ At infinite dilution, strong and weak both electrolytes will be 100% ionised.

33 $AgCl \longrightarrow Ag^+ + Cl^-$

	Ag^+	Cl^-
	x	x
After adding NaCl	x	$x + 1\times10^{-4}$

$[Ag^+]$ decreases due to common ion effect.

34 $Be(OH)_2$ has lowest solubility and hence, lowest solubility product.

35 $KCN + H_2O \rightleftharpoons KOH + HCN$; KOH is a strong base and HCN is a weak acid, due to which solution will be basic in nature. Therefore, pH of the solution will increase.

36 $-W = q = 2.303nRT\log\frac{V_2}{V_1}$

$= 2.303\times1\times2\times1000\log\frac{100}{10}$

$= 4606$ cal

$\eta = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$

or $1 - \frac{T_1}{T_2} = 1 - \frac{q_1}{q_2}$

or $\frac{T_1}{T_2} = \frac{q_1}{q_2}$ or $\frac{300}{1000} = \frac{q_1}{4606}$,

$q_1 = 1381.8 = 1382$ cal

$W = q_2 - q_1$

$= 4606 - 1382 = 3224$ cal

37 $CH_2 {=} CHCH_2CH_2CH_3 + H_2$

$$\longrightarrow CH_3CH_2CH_2CH_2CH_3; \quad \Delta H = 126 \text{ kJ mol}^{-1}$$

$$H_2C{=}CH{-}CH_2{-}CH{=}CH_2 + 2H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3; \quad \Delta H = 230 \text{ kJ mol}^{-1}$$

Theoretical value of hydrogenation of two $[C{=}C]$ bonds = 252 kJ mol^{-1}. Thus, resonance energy = 252 − 230 = 22 kJ

38 According to Raoult's law for liquid mixtures,

$$p_t = p_A + p_B$$

$$\therefore \quad p_t = p^\circ_A \times \left[\frac{\frac{w_A}{M_A}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}\right] + p^\circ_B \times \left[\frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A} + \frac{w_B}{M_B}}\right]$$

Given that, $w_A = 28$ g, $w_{H_2O} = 72$ g

$p^\circ_A = ?$

$p^\circ_{H_2O} = 155$, $M_A = 56$ g, $M_{H_2O} = 18$g

and $p_t = 150$ mm

$$\therefore \quad 150 = p^\circ_A \times \left[\frac{\frac{28}{56}}{\frac{28}{56} + \frac{72}{18}}\right] + 155 \times \left[\frac{\frac{72}{18}}{\frac{28}{56} + \frac{72}{18}}\right]$$

$$150 = p^\circ_A \times \frac{1}{2} \times \frac{2}{9} + 155 \times 4 \times \frac{2}{9}$$

$$\therefore \quad p^\circ_A = 110 \text{ mm}$$

39 $H_2O(l)$ is taken as pure liquid, hence is not included in equilibrium.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

	$HA(aq)$	$H_3O^+(aq)$	$A^-(aq)$
Initial	0.1 M	0	0
Equilibrium	$0.1 - \frac{0.1 \times 5}{100}$	$+\frac{0.1 \times 5}{100}$	$+\frac{0.1 \times 5}{100}$
Conc.	0.095 M	0.005 M	0.005 M

$$K_C = \frac{[H_3O^+][A^-]}{[HA]} = \frac{0.005 \times 0.005}{0.095}$$

$$= 2.63 \times 10^{-4}$$

40 On dilution, $N_1V_1 = N_2V_2$

$$10^{-6} \times 100 = N_2 \times 1000$$

$$N_2 = 10^{-7} \text{ N}$$

Since, acid solution has pH < 7, it will remain acidic even after dilution.

Hence, total $[H^+] = [H^+]_{Acid} + [H^+]_{Water}$

$$= 10^{-7} + 10^{-7} = 2 \times 10^{-7} \text{ N}$$

$$\therefore \quad pH = -\log [H^+] = -\log (2 \times 10^{-7})$$

$$= 7 - \log 2 = 6.7$$

Thus, change in pH = 0.7 unit

41

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = 0$$

$$\Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ JK}^{-1}} = 481 \text{ K}$$

At this temperature, the reaction would be in equilibrium and with the increase in temperature the opposing factor $T\Delta S$ would become more and hence, ΔG would become positive and the reaction would become non-spontaneous. The reaction would be spontaneous at the temperature below 481 K.

42 Salts (NH_4A, NH_4B, NH_4C) are of weak acid and weak base.

$$pH = 7 + \frac{pK_a}{2} - \frac{pK_b}{2}$$

Thus, greater the value of pK_a of HA, greater the pH.

$$pK_b(A^-, B^-, C^-) = \underset{4}{A^-} < \underset{5}{B^-} < \underset{6}{C^-}$$

$$pK_a(HA, HB, HC) = \underset{8}{HC} < \underset{9}{HB} < \underset{10}{HA}$$

Greater the pK_a, greater is the value of pH

Thus, increasing order of pH

$NH_4C < NH_4B < NH_4A$

43 Given, $dE = TdS - pdV$ …(i)

$$H = E + pV \quad \text{…(ii)}$$

Differentiating Eq. (ii)

$$dH = dE + pdV + Vdp \quad \text{…(iii)}$$

From Eq. (i) and (iii), we get

$$dH = TdS + Vdp$$

44 It is clear from the figure that the process has been carried out in infinite steps, hence it is isothermal reversible expansion.

$$W = -2.303 nRT \log \frac{V_2}{V_1}$$

But, $p_1V_1 = p_2V_2$

$$\Rightarrow \quad \frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$$

$$\therefore \quad W = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$= -2.303 \times 1 \text{ mol} \times 8.314 \text{ Jmol}^{-1}\text{K}^{-1} \times 298\text{K} \times \log 2$$

$$= -2.303 \times 8.314 \times 298 \times 0.3010 \text{ J}$$

$$= -1717.46 \text{ J}$$

45 Ammonium acetate is a salt of weak acid (CH_3COOH) and weak base (NH_4OH). Hence, Both *A* and *R* are true but *R* is not the correct explanation of *A*.

46 A buffer solution containing mixture of CH_3COOH and CH_3COONa is known as acidic buffer. When a equal volume of 1 M HCl is added, the pH of the solution almost remained unchanged and acidic buffer is formed.

47 When liquid crystalises, entropy decreases because in crystalline form the molecules are more ordered as campared to the liquid.

48 Both Assertion and Reason are correct and Reason is the correct explanation of the assertion.

49 Heat of neutralisation refers to the amount of heat liberated in the combination of H^+ and OH^- ions in the solution to form one mole of water. Hence, Reason is not the correct explanation of Assertion.

50 The molality of solution is expresed in terms of moles per 1000 g of solvent, i.e. depends only on masses and hence. remains unaffected by the temperature.