## DAY ELEVEN

# Unit Test 2 (Physical Chemistry I)

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

 $C_{2}H_{2}(g) + \frac{5}{2}O_{2}(g) \longrightarrow 2CO_{2}(g) + H_{2}O(I); \Delta G^{\circ} = -1234 \text{ kJ}$   $C(s) + O_{2}(g) \longrightarrow CO_{2}(g); \Delta G^{\circ} = -394 \text{ kJ}$   $H_{2}(g) + \frac{1}{2}O_{2}(g) \longrightarrow H_{2}O(I); \Delta G^{\circ} = -237 \text{ kJ}$ 

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<sup>-1</sup>. 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<sup>-1</sup> mol<sup>-1</sup>, respectively. For the reaction,

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \longrightarrow XY_3; \Delta H = -30 \text{ kJ, to be at equilibrium,}$$

the temperature will be

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

- **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  $FeSO_4 \cdot 5H_2O$  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**  $A \longrightarrow B$ ,  $\Delta H = +$  ve. Graph between  $\log_{10} p$  and  $\frac{1}{\tau}$  is a

straight line of slope  $\frac{1}{4.606}$ . Hence,  $\Delta H$  is

(b) 2 (c) 4

**8** The heat of atomisation of  $PH_3(g)$  is 228 kcal mol<sup>-1</sup> and that of  $P_2H_4(g)$  is 355 kcal mol<sup>-1</sup>. The energy of the P—P bonds (in kcal mol<sup>-1</sup>) is

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

**9** Match the following and choose the correct option.

		Colur	mn I			Column II
	А.	Q	=K		1.	Reaction is nearer to completion.
	В.	Q	) < K		2.	Reaction is not at equilibrium.
	C.	Q	) > K		3.	Reaction is fast in forward direction.
	D.	Κ	>>> 1		4.	Reaction at equilibrium.
					5.	Reaction proceeds in backward direction.
	А	в	С	D		ABCD
(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

CLICK HERE

(a) 1



(d) –1

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 ( $\Delta H$ ) of the process in L atm is (c) 44.0 (a) 40.0 (b) 42.3

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(d) not defined because pressure is not constant
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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<sup>--</sup> respectively. The enthalpy of polymerisation per mole of ethene at 298 K, is

(a) 72 kJ mol <sup>-1</sup>	(b) 27 kJ mol <sup>-1</sup>
(c) 1144 kJ mol <sup>-1</sup>	(d) 172 kJ mol <sup>-1</sup>

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 ( $\Delta S$ ) is

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

- 14 The enthalpy changes of formation of the gaseous oxides of nitrogen (N<sub>2</sub>O 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 HCI for complete reaction. The strength of the HCI 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<sub>2</sub>SO<sub>4</sub> 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<sub>3</sub> and CH<sub>3</sub>COOH 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)  $\frac{p_1}{p_1 + p_2} + \frac{p_2}{p_1 + p_2}$ 

(1.)

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

3.078 atm	(b) 4.078 atm
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 <sub>2</sub>
(c) Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	(d) KBr

(a)

(C)

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

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(a) 34.2
              (b) 68.4
                             (c) 136.2
                                            (d) 171.2
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22 Match the following and choose the correct option.

		(	Colun	nn I	Column II					
	Α.		Δ	3	1.	Δί	J + n	RT		
	В.		Δŀ	-	2.	Δ	H – T.	ΔS		
	C.		Δί	J	3.	r	nC v c	IT		
	D.		Δ\$	6	4.	2.303 <i>n</i>	Rlog	$10\left(\frac{1}{10}\right)$	$\left(\frac{\frac{2}{2}}{\frac{1}{1}}\right)$	
	Α	В	С	D			А	В	С	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<sub>4</sub>HS 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<sub>3</sub> and H<sub>2</sub>S 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<sub>4</sub>HS at this temperature, is

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

24 For the reaction,

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

- When  $K_{\rho}$  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)  $K_p = K_C$ 

**CLICK HERE** 

- (c)  $K_p$  is less than  $K_c$
- (d)  $K_{p}$  is greater than  $K_{C}$

25 For the equilibrium,

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

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

Hence, for the equilibrium,

 $AgCI + 2NH_3 \Longrightarrow Ag(NH_3)_2^+ + CI^-$ 

equilibrium constant is

(a) 0.32× 10 <sup>-2</sup>	(b) $0.31 \times 10^{-2}$
(c) 1.01 × 10 <sup>17</sup>	(d) $1.01 \times 10^{-1}$

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

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

27 For the reaction,

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

 $K_{\rho}$  at 298 K is 1.086  $\times$  10<sup>-4</sup> atm<sup>2</sup> and vapour pressure of water is 23.8 torr. The salt CuSO<sub>4</sub>  $\cdot$  5H<sub>2</sub>O 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<sub>3</sub> solution. If  $pK_a$  of NH<sub>4</sub><sup>+</sup> 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<sup>-5</sup> 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<sub>4</sub>) <sub>2</sub>SO<sub>4</sub> 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<sup>-4</sup> moles of solid NaCl are added, what will be the [Ag<sup>+</sup>] 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) <sub>2</sub>	(b) Ca(OH) <sub>2</sub>
(c)Ba(OH) <sub>2</sub>	(d) Be(OH) <sub>2</sub>

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

Heat obtained due to expansion of 1 mole of H<sub>2</sub> 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<sup>-1</sup>. The enthalpy of hydrogenation of 1,3-pentadiene is + 230 kJ mol<sup>-1</sup>. Hence, resonance (delocalisation) energy of 1,3-pentadiene is

  (a) 22 kJ
  (b) 104 kJ
  (c) 252 kJ
  (d) 11kJ
- 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[HA] is ionised 5% in 0.1 M aqueous solution. What is the equilibrium constant for its ionisation?

$HA(aq) + H_2O(l) \Longrightarrow H_3O^+$	$(aq) + A^{-}(aq)$	
(a) $9.5 \times 10^{-2}$	(b) $2.63 \times 10^{-4}$	
(c) $2.303 \times 10^{-3}$	(d) $5 \times 10^{-3}$	<b>→</b>

**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<sub>4</sub> 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,

**CLICK HERE** 

N<sub>2</sub>(g) + 3H<sub>2</sub>  $\longrightarrow$  2NH<sub>3</sub>(g);  $\Delta H = -95.4$  kJ and  $\Delta S = -198.3$ JK<sup>-1</sup>

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

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

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

**42**  $pK_b$  of NH<sub>3</sub> 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



**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 NH₄OH is a weak base. → NCERT Exemplar

- 46 Assertion (A) On mixing equal volumes of 1 M HCl and 2M CH<sub>3</sub>COONa, an acidic buffer solution is formed.
  Reason (R) Resultant mixture contains CH<sub>3</sub>COOH and CH<sub>3</sub>COONa 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

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

### **Hints and Explanations**

 $\begin{array}{l} \mathbf{1} \ \ \mathrm{C_2H_2}(g) + \frac{5}{2}\mathrm{O_2}(g) \rightarrow 2\mathrm{CO_2}(g) + \mathrm{H_2O}(l); \\ & \Delta G^\circ = -1234 \, \mathrm{kJ} \\ \mathrm{(b)} \ \ [\mathrm{C}(\mathrm{s}) + \mathrm{O_2} \ (g) \longrightarrow \mathrm{CO_2}(g); \\ & \Delta G^\circ = -394 \, \mathrm{kJ} \ ] \times 2 \\ \mathrm{(c)} \ \mathrm{H_2} \ (g) + \frac{1}{2} \ \mathrm{O_2}(g) \longrightarrow \mathrm{H_2O}(l); \\ & \Delta G^\circ - 237 \, \mathrm{kJ} \\ \mathrm{Add} \ \mathrm{Eq.} \ \mathrm{(b)} \ + \ \mathrm{(c)} \ \mathrm{and} \ \mathrm{then} \ \mathrm{subtract} \ \mathrm{from} \\ \mathrm{(a)}, \ \mathrm{to} \ \mathrm{get}, \\ & 2\mathrm{C}(\mathrm{s}) + \mathrm{H_2}(g) \longrightarrow \mathrm{C_2H_2} \ (g); \end{array}$ 

 $\Delta G^\circ = -209 \text{ kJ}$  **2** Combustion of elements to form a compound can be exothermic or endothermic e.g. C + O<sub>2</sub>  $\longrightarrow$  CO<sub>2</sub> is

whereas,  $C + 2S \longrightarrow CS_2$  is endothermic Hence, enthalpy of formation can be positive or negative.

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

exothermic.

4 
$$\Delta S = S (XY_3) - \frac{1}{2} S (X_2) - \frac{3}{2} S (Y_2)$$
  
= 50 - 30 - 60  
= -40 J mol<sup>-1</sup> K<sup>-1</sup>  
$$\Delta H = -30 \text{ kJ} = -30000 \text{ J}$$
  
$$\Delta G = \Delta H - T\Delta S$$
  
At equilibrium,  $\Delta G = 0$   
$$T = \frac{\Delta H}{\Delta S} = \frac{-30000}{-400} = 750 \text{ K}$$
  
**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<sub>4</sub> in depicted as  
FeSO<sub>4</sub> + 5H<sub>2</sub>O  $\longrightarrow$  FeSO<sub>4</sub> · 5H<sub>2</sub>O;

$$\Delta_{hyd}H^{-} = ?$$
We have,  
FeSO<sub>4</sub>(anhyd) + H<sub>2</sub>O(excess)  
 $\longrightarrow$  FeSO<sub>4</sub>(aq);  
 $\Delta H_1 = -58.2 \text{ kJ}$   
FeSO<sub>4</sub> · 5H<sub>2</sub>O + H<sub>2</sub>O(excess)  
 $\longrightarrow$  FeSO<sub>4</sub>(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<sub>3</sub> = 228 kcal mol<sup>-1</sup>  
P—H bond energy  

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

Structure of  $P_2H_4$  is  $H P - P H_4$ 

... 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 kcal mol^{-1}

**9** A  $\rightarrow$  4, B  $\rightarrow$  2,3, C  $\rightarrow$  2, 5 D  $\rightarrow$  1 **10**  $\Delta H = \Delta E + \Delta n_g RT$ ,  $\Delta n_g = 1$  mol,  $\Delta T = 245 - 95 = 150$  K.

$$\begin{array}{c} (\mathsf{NH}_4)_2\mathsf{CO}_3 \longrightarrow \mathsf{2NH}_4 + \mathsf{CO}_3^-\\ & \mathsf{2H}_2\mathsf{O} \longrightarrow \mathsf{2OH}^- + \mathsf{2H}^+\\ & \downarrow \\ & \mathsf{NH}_4\mathsf{OH} & \downarrow \\ & \mathsf{Weak base} & \mathsf{H}_2\mathsf{CO}_3\\ & \mathsf{Weak acid} \end{array}$$

If  $K_b$  of NH<sub>4</sub>OH >  $K_a$  of H<sub>2</sub>CO<sub>3</sub>. The solution is basic or, if  $K_a$  of H<sub>2</sub>CO<sub>3</sub> >  $K_b$  of NH<sub>4</sub>OH; 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  $>C--C \le$  single bond = 2 × 331 = 662 kJ

CLICK HERE

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  $CaCO_3$ 

$$V \times 50 = \frac{1}{50} \times 1000$$
$$N = \frac{1 \times 1000}{50 \times 50} = 0.41$$

**16** 98% H<sub>2</sub>SO<sub>4</sub> means 98 g H<sub>2</sub>SO<sub>4</sub> in 100 g solution.

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

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

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

Μ

**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 mm Hg

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**18** KNO<sub>3</sub> dissociates completely while CH<sub>3</sub>COOH dissociates to a smaller extent, hence  $p_1 > p_2$ .

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**19** 
$$C = \frac{5 \times 1000}{342 \times 100} = \frac{50}{342} \text{ mol } \text{L}^{-1}$$
  
 $\pi = \frac{50}{342} \times 0.082 \times 423 = 5.07 \text{ atm}$   
**20** KBr = K<sup>+</sup> + Br<sup>-</sup> = 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,  $AI_2(SO_4)_3$  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  $\rightarrow$  2, B  $\rightarrow$  1, C  $\rightarrow$  3, D  $\rightarrow$  4

**23** 
$$\operatorname{NH}_4\operatorname{HS}(s) \rightleftharpoons \operatorname{NH}_3(g) + \operatorname{H}_2\operatorname{S}(g)$$
  
Initially 1 0.5 0  
At equilibrium  $(1-x)$   $(0.5+x)$ 

Total pressure at equilibrium

$$= \rho_{\text{NH}_{3}} + \rho_{\text{H}_{2}\text{S}}$$
  
= 0.5 + x + x = 0.84  
x = 0.17 atm  
$$p_{\text{NH}_{3}} = 0.50 + 0.17 = 0.67 \text{ atm}$$
$$p_{\text{H}_{2}\text{S}} = 0.17 \text{ atm}$$
$$K_{p} = \rho_{\text{NH}_{3}} \cdot \rho_{\text{H}_{2}\text{S}}$$
  
= 0.67 × 0.17  
= 0.114 atm ~ 0.11 atm  
**24** 2NO\_{2}(g) \implies 2NO(g) + O\_{2}(g)
$$K_{C} = 1.8 \times 10^{-6} \text{ at } 184^{\circ}\text{C} (= 457 \text{ K})$$
$$R = 0.00831 \text{ kJ mol}^{-1} \text{ K}^{-1}$$
$$K_{p} = K_{C}(RT)^{\Delta n_{g}}$$
where,  $\Delta n_{g}$  = gaseous products -  
gaseous reactants = 3-2 = 1  
$$K_{p} = 1.8 \times 10^{-6} \times 0.00831 \times 457$$
$$= 6.836 \times 10^{-6}$$
Thus,  $K_{p} > K_{C}$   
**25** Ag<sup>+</sup> + 2NH\_{3}  $\implies \text{Ag}(\text{NH}_{3})_{2}^{+}$ ;  
 $K_{1} = 1.8 \times 10^{7}$ AgCl  $\implies \text{Ag}^{+} + \text{Cl}^{-}$ ;  
 $K_{2}' = \frac{1}{K_{2}} = \frac{1}{5.6 \times 10^{9}}$ 
$$\therefore \text{ AgCl} + 2\text{NH}_{3} \implies \text{Ag}(\text{NH}_{3})_{2}^{+} + \text{Cl}^{-}$$

$$K = K_1 K_2' = \frac{K_1}{K_2}$$
$$= \frac{1.8 \times 10^7}{5.6 \times 10^9}$$
$$= 0.32 \times 10^{-2}$$

**26** pH of the solution 
$$A = 3$$
  
 $[H^+]_A = 10^{-3} \text{ M}$   
pH of the solution  $B=2$   
 $[H^+]_B = 10^{-2} \text{ M}$   
 $[H^+] = 10^{-3} + 10^{-2} = 11 \times 10^{-3}$   
pH = -log (11×10<sup>-3</sup>)  
= 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

$$CuSO_4 \cdot 5H_2O(s) \longrightarrow CuSO_4 \cdot 3H_2O(s)$$

+  $2H_2O(g)$  $K_p = p_{H_2O}^2 = 1.086 \times 10^{-4} \text{ atm}^2$ 

:.  $p_{H_{2}O} = 1.042 \times 10^{-2}$  atm = 7.89 torr

Since,  $p_{H_2O}$  is less than the vapour pressure of water in air at the same temperature,  $CuSO_4 \cdot 5H_2O$  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<sub>a</sub>(NH<sub>4</sub><sup>+</sup>) = 9.26

:.  $pK_b(NH_3) = 14 - 9.26 = 4.74$ 50 mL of 0.3 M HCl = 15 millimol 50 mL of 0.4 M NH<sub>3</sub> = 20 millimol

> $NH_3 + HCI \longrightarrow NH_4CI$ millimol 20 15 0

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)

∴ 
$$pOH = pK_b + \log \frac{[NH_4]}{[NH_3]}$$
  
= 4.74 + log 3  
∴  $pH = 14 - pOH = 9.26 - \log 3$   
= 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.** 
$$X^- + H_2O \implies HX + OH^-$$
  
 $K_h = \frac{10^{-14}}{10^{-5}}$   
So,  $x = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$   
 $= 100 \times 10^{-4} = 10^{-2} = 0.01$ 

So, degree of hydrolysis = 0.01%.

**31.** Gram equivalent of  $(NH_4)_2SO_4 = \frac{100}{1000} \times \frac{1}{10} \times 66 = 0.66$ Gram equivalent of  $Na_2CO_3 \cdot H_2O = \frac{0.62}{62} = 0.01$ 

Left (NH<sub>4</sub>)  $_2$ SO<sub>4</sub> = 0.66 – 0.01 = 0.65 Since, (NH<sub>4</sub>) $_2$ SO<sub>4</sub> 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<sup>+</sup> + Cl<sup>-</sup> x xAfter adding NaCl x x + 1×10<sup>-4</sup> [Ag<sup>+</sup>] decreases due to common ion

- effect. **34** Be(OH)<sub>2</sub> has lowest solubility and hence,
  - lowest solubility product.
- 35 KCN + H<sub>2</sub>O → 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** 
$$-W = q = 2.303 nRT \log \frac{V_2}{V_1}$$
  
 $= 2.303 \times 1 \times 2 \times 1000 \log \frac{100}{10}$   
 $= 4606 \text{ cal}$   
 $\eta = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$   
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  $\frac{300}{1000} = \frac{q_1}{4606}$ ,  
 $q_1 = 13818 = 1382 \text{ cal}$   
 $W = q_2 - q_1$   
 $= 4606 - 1382 = 3224 \text{ cal}$ 

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$$\begin{array}{l} \textbf{37} \ \text{CH}_2 = \text{CHCH}_2\text{CH}_2\text{CH}_3 + \text{H}_2 \\ & \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3; \\ & \Delta H = 126 \ \text{kJ} \ \text{mol}^{-1} \\ & \text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2 + 2\text{H}_2 \\ & \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3; \\ & \Delta H = 230 \ \text{kJ} \ \text{mol}^{-1} \end{array}$$

Theoretical value of hydrogenation of two [C==C] bonds = 252 kJ mol<sup>-1</sup>. Thus, resonance energy = 252 - 230 = 22 kJ

**38** According to Raoult's law for liquid mixtures,

$$p_t = p_A + p_B$$

$$\therefore \quad p_t = p_A^{\circ} \times \left[ \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right] + p_B^{\circ}$$

$$\times \left[ \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right]$$

Given that,  $w_A = 28 \text{ g}$ ,  $w_{H_2O} = 72 \text{ g}$   $p^{\circ}_A = ?$   $p^{\circ}_{H_2O} = 155$ ,  $M_A = 56 \text{ g}$ ,  $M_{H_2O} = 18 \text{ g}$ and  $p_t = 150 \text{ mm}$ ∴  $150 = p^{\circ}_A \times \left[\frac{28}{56}\right]$ 

$$\begin{bmatrix} \frac{28}{56} + \frac{72}{18} \end{bmatrix} + 155 \times \begin{bmatrix} \frac{72}{18} \\ \frac{28}{56} + \frac{72}{18} \\ \frac{28}{56} + \frac{72}{18} \end{bmatrix}$$
$$150 = p_A^{\circ} \times \frac{1}{2} \times \frac{2}{9} + 155 \times 4 \times \frac{2}{9}$$

$$p^{\circ}_{A} = 110 \text{ mm}$$

**39** H<sub>2</sub>O(*I*) is taken as pure liquid, hence is not included in equilibrium.

 $HA(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$ 0 Initial 0.1 M 0 + <u>0.1 × 5</u>  $0.1 \times 5$  $0.1 \times 5$ Equilibrium 0.1 -+ 100 100 100 0.005 M Conc 0.095 M 0.005 M

$$K_{\rm C} = \frac{[{\rm H}_3{\rm O}^+][{\rm A}^-]}{[{\rm H}{\rm A}]} = \frac{0.005 \times 0.005}{0.095}$$
$$= 2.63 \times 10^{-4}$$

**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  $[H^+] = [H^+]_{Acid} + [H^+]_{Water}$  $= 10^{-7} + 10^{-7} = 2 \times 10^{-7} \text{ N}$  $\therefore \text{ pH} = -\log [H^+] = -\log (2 \times 10^{-7})$  $= 7 - \log 2 = 6.7$ Thus, change in pH = 0.7 unit

**41** 
$$\Delta G = \Delta H - T\Delta S$$
$$\Delta G = 0$$
$$\Delta H - T\Delta S = 0 \text{ or } \Delta H = T\Delta S$$
$$T = \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ JK}^{-1}} = 481 \text{ K}$$

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,  $\Delta G$ 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.

$$pK_b(A^-, B^-, C^-) = A^- < B^- < C^-$$
  
4 5 6

 $pK_a(HA, HB, HC) = HC < HB < HA$ 8 9 10 Greater the  $pK_a$ , greater is the value of pH

Thus, increasing order of pH NH<sub>4</sub>C < NH<sub>4</sub>B < NH<sub>4</sub>A

**13** Given, 
$$dE = TdS - pdV$$
  
 $H = E + pV$   
Differentiating Eq. (ii)

dH=dE + pdV + Vdp ...(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,  $p_1V_1 = p_2V_2$   
⇒  $\frac{V_2}{V_1} = \frac{p_1}{p_2} = \frac{2}{1} = 2$   
∴  $W = -2.303 nRT \log \frac{p_1}{p_2}$   
= -2.303 × 1 mol × 8.314 Jmol<sup>-1</sup>K<sup>-1</sup>

× 298K×log 2

= -2.303 × 8.314 × 298 × 0.3010 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<sub>3</sub>COOH and CH<sub>3</sub>COONa is known as acidic buffer. When a equal volume of 1 M HCl is added, the pH of the solution

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<sup>+</sup> and OH<sup>−</sup> 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.



...(i)

...(ii)

