DAY TEN

Unit Test 2

(Physical Chemistry I)

1 Heat released during mixing of 50 mL of 0.1 M H_2SO_4 with 50 mL of 0.2 M KOH is

(a) 57.3×10^3 J (b) 573 J
(c) 5.73×10^3 J (d) 57.3×10^2 J

2 Which one of the following statements is false?

(a) Work is a state function
(b) Temperature is a state function
(c) Change in the state is completely defined when the initial and final states are specified
(d) Work appears at the boundary of the system

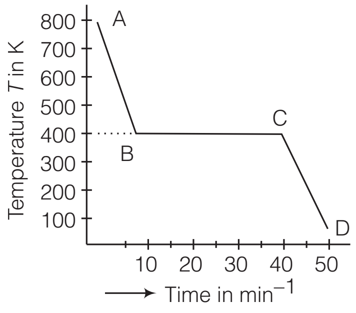
3 What is the entropy change (in $JK^{-1} mol^{-1}$) when one mole of ice is converted into water at 0°C?
(The enthalpy change for the conversion of ice to liquid water is 6.0 kJ mol^{-1} at 0°C)

(a) 20.13 (b) 2.013 (c) 2.198 (d) 21.98

4 Enthalpy of combustion of methane and ethane are –210 kcal/mol and –368 kcal/mol respectively. The enthalpy of combustion of decane is

(a) –158 kcal/mol (b) –1632 kcal/mol
(c) –1700 kcal/mol (d) data is incomplete

5 One mole of substance is cooled at the rate of 0.4 kJ min^{-1} as shown in graph. Curve *AB*, points *B* and *C* and curve *CD* represent respectively, the cooling of the liquid, start of freezing, completion of freezing and cooling of the solid. Based on this data the entropy of fusion in J mol K^{-1} is



(a) 10 (b) 20 (c) 30 (d) 40

6 The molar heat capacity of water at constant pressure *p*, is 75 $JK^{-1} mol^{-1}$. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand, the increase in temperature of water is

(a) 1.2 K (b) 2.4 K
(c) 4.8 K (d) 6.6 K

7 Consider the following reaction occurring in an automobile.

$$2C_8H_{18} + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

The sign of ΔH, ΔS and ΔG would be

(a) +, –, + (b) –, +, –
(c) –, +, + (d) +, +, –

8 The entropy change can be calculated by using the expression $\Delta S = \frac{q_{rev}}{T}$.
When water freezes in a glass beaker, choose the correct statement amongst the following. **→ [NCERT Exemplar]**

(a) ΔS (system) decreases but ΔS (surroundings) remains the same
(b) ΔS (system) increases but ΔS (surroundings) decreases
(c) ΔS (system) decreases but ΔS (surroundings) increases
(d) ΔS (system) decreases and ΔS (surroundings) also decreases

9 Standard enthalpy and standard entropy change for the oxidation of NH_3 at 298 K are – 382.64 kJ mol^{-1} and – 145.6 $kJmol^{-1}$ respectively. Standard Gibbs energy change for the same reaction at 298 K is

(a) –221.1 kJ mol^{-1} (b) – 339.3 kJ mol^{-1}
(c) –439.3 kJ mol^{-1} (d) –523.2 kJ mol^{-1}

10 For a general reaction,

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

The specific rate constant is $K_{forward} = 2.0 \times 10^{-3} mol^{-1} Ls^{-1}$ at a certain temperature. Reaction starts with equimolar amounts of *A* and *B*. Reaching at equilibrium, it is

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observed that A is twice that of C. The specific rate constant for the backward reaction is

(a) 1.5×10^{2} mol^{-1}Ls^{-1} (b) 5.0×10^{-4} mol^{-1}Ls^{-1}
(c) 8.0×10^{-3} mol^{-1}Ls^{-1} (d) None of these

11 $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$
If nitrosyl bromide is 34% dissociated at 25°C and a total pressure of 0.25 atm, K_p for the dissociation at this temperature is

(a) 1.37×10^{-3} (b) 9.78×10^{-3}
(c) 2.16×10^{-2} (d) 5.67×10^{-3}

12 The equilibrium constant K_p for the thermal dissociation of PCl_5 at 200°C is 1.6 atm. The pressure (in atm) at which it is 50% dissociated at that temperature is

(a) 4.8 (b) 4.2 (c) 3.2 (d) 2.4

13 The equilibrium constant (K_p) for the decomposition of gaseous reaction

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$$

is related to degree of dissociation (α) at a total pressure p is given by

(a) $K_p = \frac{\alpha^3 p^{1/2}}{(1+\alpha)(2+\alpha)^{1/2}}$ (b) $K_p = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$
(c) $K_p = \frac{\alpha^{3/2} p^{2}}{(1-\alpha)(2+\alpha)^{1/2}}$ (d) $K_p = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

14 $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$
equilibrium pressure is 3 atm for the above reaction. K for the reaction is

(a) 4 (b) 27 (c) $\frac{4}{27}$ (d) $\frac{1}{27}$

15 Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$?

→ **[NCERT Exemplar]**

(a) $\Delta G^\ominus = 0$ (b) $\Delta G^\ominus > 0$
(c) $\Delta G^\ominus < 0$ (d) $\Delta G^\ominus = -RT \ln 2$

16 0.1 M solution of three sodium salts NaX, NaY and Na Z have pH 7.0, 9.0 and 11.0 respectively. Which of the following is the correct order of increasing acidic strength for acids HX, HY and HZ?

(a) $HX < HY < HZ$ (b) $HZ < HY < HX$
(c) $HX = HY = HZ$ (d) $HY < HX < HZ$

17 A weak acid, HA has a K_a of 1.00×10^{-5}. If 0.100 mole of this acid is dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to

(a) 99.0% (b) 1.00%
(c) 99.9% (d) 0.100%

18 At 25°C, the dissociation constant of a base BOH, is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01 M aqueous solution of the base would be

(a) 2.0×10^{-6} mol L^{-1} (b) 1.0×10^{-5} mol L^{-1}
(c) 1.0×10^{-6} mol L^{-1} (d) 1.0×10^{-7} mol L^{-1}

19 The solubility product of PbI_2 is 7.47×10^{-9} at 15°C and 1.39×10^{-8} at 25°C. The molar heat of solution of PbI_2 is

(a) 21.15 kJ/mol (b) 29.37 kJ/mol
(c) 44.31 kJ/mol (d) 46.25 kJ/mol

20 The solubility product of a salt having formula M_2X_3 is 2.2×10^{-20}. If the solubility of an another salt having formula M_2X is twice the molar solubility of M_2X_3, the solubility product of M_2X is

(a) 3×10^{-12} (b) 9.16×10^{-5}
(c) 4.58×10^{-5} (d) 2.76×10^{-18}

21 The volume of water needed to dissolve 1g of $BaSO_4$ $(K_{sp} = 1.1 \times 10^{-10})$ at 25°C is

(a) 820 L (b) 205 L (c) 410 L (d) 100 L

22 Which of the following equilibrium can be described as an acid-base reaction using the Lewis acid-base definition, but not using Bronsted-Lowry definition?

(a) $NH_3 + CH_3COOH \rightleftharpoons CH_3COO^- + NH_4^+$
(b) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
(c) $4NH_3 + [Cu(H_2O)_4]^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$
(d) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$

23 Which of the following is pH of solution at 25°C, which is twice alkaline as twice as many hydroxide ions as in pure water?

(a) 14 (b) 9 (c) 6.699 (d) 7.301

24 The pH of 10^{-7} M HCl is

(a) 7 (b) 6.97 (c) 6.79 (d) 7.27

25 Which of the following buffer solution turns invalid on addition of 10 mL of 1.0 M HCl?

(a) 100 mL having 0.15 M NH_3 and NH_4Cl each
(b) 100 mL having 0.2 M NH_3 and NH_4Cl each
(c) 100 mL having 0.2 M NH_3 and 0.1 M NH_4Cl each
(d) 100 mL having 0.05 M NH_3 and NH_4Cl each

26 Which of the following acts as both reducing and oxidising agents?

(a) H_2SO_4 (b) H_2O_2 (c) KOH (d) $KMnO_4$

27 In the reaction,

$$H_2O_2 + Na_2CO_3 \longrightarrow Na_2O_2 + CO_2 + H_2O$$

the substance undergoing oxidation is

(a) H_2O_2 (b) Na_2CO_3
(c) Na_2O_2 (d) None of these

28 Which substance serves as a reducing agent in the following reaction,

$$14H^+ + Cr_2O_7^{2-} + 3Ni \longrightarrow 2Cr^{3+} + 7H_2O + 3Ni^{2+} ?$$

(a) H_2O (b) Ni (c) H^+ (d) $Cr_2O_7^{2-}$

29 Which of the following is a redox reaction?

(a) $NaCl + KNO_3 \longrightarrow NaNO_3 + KCl$
(b) $CaC_2O_4 + 2HCl \longrightarrow CaCl_2 + H_2C_2O_4$
(c) $Mg(OH)_2 + 2NH_4Cl \longrightarrow MgCl_2 + 2NH_4OH$
(d) $Zn + 2AgCN \longrightarrow 2Ag + Zn(CN)_2$

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30 When SO_2 is passed in a solution of potassium iodate, the oxidation state of iodine changes from?

(a) + 5 to 0 (b) + 5 to –1
(c) – 5 to 0 (d) –7 to –1

31 How many moles of electrons are involved in the reduction of one mole of MnO_4^- ion in alkaline medium to MnO_3^-?

(a) 2 (b) 1
(c) 3 (d) 4

32 The oxidation number of P in $P_2O_7^{4-}$ is

(a) +3 (b) + 4 (c) + 5 (d) + 6

33 The oxidation states of sulphur in the anions SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_6^{2-}$ follow the order

(a) $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$ (b) $S_2O_6^{-} < S_2O_4^{2-} < SO_3^{2-}$
(c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$ (d) $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

34 In which of the following compounds, the oxidation number of iodine is fractional?

(a) IF_7 (b) I_3^- (c) IF_5 (d) IF_3

35 For the redox reaction,

$$MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$$

the correct coefficients for the balanced reaction are

	MnO_4^-	$C_2O_4^{2-}$	H^+
(a)	2	5	16
(b)	16	5	2
(c)	5	16	2
(d)	2	16	5

Direction (Q. Nos. 36-37) *In the following questions more than one of the answers given may be correct. Select the correct answers and mark it according to the codes.*

Codes

(a) 1, 2 and 3 are correct (b) 1 and 2 are correct
(c) 2 and 4 are correct (d) 1 and 3 are correct

36 Select the correct relation.

1. $\Delta H_T = \Delta E_T + \Delta n_g RT$
2. $\log T + (\gamma - 1) \log V = \text{constant}$
3. $\Delta E_{T_2} = \Delta E_{T_1} + \Delta C_V (T_2 - T_1)$
4. $\log p - \gamma \log V = \text{constant}$

37 pH of the following solution is not affected by dilution

1. 0.01 M CH_3COONH_4
2. buffer of 0.01 M CH_3COONa and 0.01 M CH_3COOH
3. 0.01 M $NaHCO_3$
4. 0.01 M CH_3COONa

38 Match the effect of addition of 1 M NaOH to 100 mL 1 M CH_3COOH (in Column I) with pH (in Column II) and choose the correct code given below.

	Column I		Column II
A.	25 mL of NaOH	1.	pK_a
B.	50 mL of NaOH	2.	$pK_a + \log 3$
C.	75 mL of NaOH	3.	$pK_a - \log 3$
D.	100 mL of NaOH	4.	$\frac{1}{2}[pK_w + pK_a + 2]$

Codes

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

Direction (Q. Nos. 39-40) *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) Assertion is true, Reason is true; Reason is a correct explanation for Assertion
(b) Assertion is true, Reason is true; Reason is not a correct explanation for Assertion
(c) Assertion is true, Reason is false
(d) Assertion is false, Reason is true

39 **Assertion** Iodine is more soluble in CCl_4 than in water.

Reason Non-polar solutes are more soluble in non-polar solvents.

40 **Assertion** A buffer solution has a capacity to resist the change in pH value on addition of small amount of acid or base to it.

Reason pH value of buffer solution does not change on dilution or on keeping for long.

ANSWERS

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

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Hints and Explanations

1. M_{eq} of $H_2SO_4 = 2 \times 0.1 \times 50 = 10$

M_{eq} of $KOH = 0.2 \times 50 = 10$

$$\text{Heat released} = \frac{10 \times 57.3 \times 10^3}{1000} = 573\ \text{J}$$

2. Work is not a state function. State functions are path dependent.

3.
$$\Delta S_f = \frac{\Delta H_f}{T} = \frac{6 \times 10^3}{273} = 21.98\ \text{JK}^{-1}\text{mol}^{-1}$$

4. Given, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;$

$$\Delta H = -210\ \text{kcal/mol} \quad ..(i)$$

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O;$$

$$\Delta H = -368\ \text{kcal/mol} \quad ...(ii)$$

On subtracting Eq. (ii) from Eq. (i), we get

$$CH_2 + \frac{3}{2}O_2 \rightarrow CO_2 + H_2O;$$

$$\Delta H = -158\ \text{kcal/mol} \quad ...(iii)$$

$\therefore$ Enthalpy of combustion of one CH_2 unit $= -158$ kcal/mol

$$\Delta H_{comb}(C_{10}H_{22}) = \Delta H_{comb}(CH_4) + 9 \times \Delta H_{comb}(CH_2)$$
$$= -210 + (9 \times -158)$$
$$= -1632\ \text{kcal/mol}$$

5. The cooling shows fusion process for 30 min (40 – 10) at 400 K.

$$\Delta S = \frac{q}{T} = \frac{0.4 \times 10^3 \times 30}{400} = 30\ \text{J}$$

6.
$$q = mC_V\Delta T$$
$$1000 = \frac{100}{18} \times 75 \times \Delta T$$
$$\Rightarrow \quad \Delta T = 2.4\ \text{K}$$

7. The given reaction is combustion reaction, so it takes place by evolution of heat and hence, the sign of $\Delta H = -$ ve and there is a increase in the number of moles of gaseous products, so entropy also increases and hence, $\Delta S = +$ ve

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

$$= -\text{ve} - T(+\text{ve})$$
$$= -\text{ve at any temperature}$$

8. Freezing is exothermic process. The heat released increases the entropy of surrounding.

9. $\Delta G° = \Delta H° - T\Delta S°$

$$= -382.64 - 298 \times (-145.6 \times 10^{-3})$$
$$= -339.3\ \text{kJ mol}^{-1}$$

10.
$$A + B \rightleftharpoons C + D$$

Initial conc. $\quad a \quad a \quad 0 \quad 0$

Conc. at eq. $\quad (a - x) \quad (a - x) \quad x \quad x$

Given, $(a - x) = 2x$ or $a = 3x$

$$x = \frac{a}{3}$$

$$K_C = \frac{x^2}{(a - x)(a - x)} = \frac{a^2}{9 \cdot (2x)^2} = \frac{(3x)^2}{9(4x^2)}$$

$$K_C = \frac{1}{4} = 0.25 \text{ but } K_C = \frac{K_f}{K_b}$$

$$K_b = \frac{K_f}{K_C} = \frac{2 \times 10^{-3}}{0.25} = 8 \times 10^{-3}$$

11.
$$\underset{\text{At eq.}\ (1-x)}{2NOBr(g)} \rightleftharpoons \underset{x}{2NO(g)} + \underset{x/2}{Br_2(g)}$$

Initial pressure of NOBr $= p°$

After 34% dissociation, $p_{(NOBr)} = 0.66\,p°$

$$p_{(NO)} = 0.34p° \Rightarrow p_{(Br_2)} = 0.17\,p°$$

Total $= p_{NOBr} + p_{NO} + p_{(Br_2)}$

$= 0.25$ atm

$$0.66p° + 0.34\,p° + 0.17\,p° = 0.25\ \text{atm}$$
$$1.17\,p° = 0.25\ \text{atm}$$
$$p° = \frac{0.25}{1.17} = 0.214\ \text{atm}$$

$$K_p = \frac{p^2_{(NO)} \cdot p_{(Br_2)}}{p^2_{(NOBr)}}$$
$$= \frac{(0.34 \times 0.214)^2\,(0.17 \times 0.214)}{(0.66 \times 0.214)^2}$$
$$= 9.78 \times 10^{-3}$$

12. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$1 \quad 0 \quad 0$

$(1 - \alpha) \quad \alpha \quad \alpha$

$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} \Rightarrow K_p = \frac{\alpha^2 p}{(1-\alpha)}$$

$$1.6 = \frac{0.5 \times 0.5 \times p}{(1 - 0.5)} \Rightarrow 1.6 = \frac{0.25 \times p}{0.75}$$

$p = 4.8$ atm

13.
$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$$

Initial $\quad 1 \quad 0 \quad 0$

At equil $\quad (1 - \alpha) \quad \alpha \quad \alpha/2$

$$\text{Total moles} = (1 - \alpha) + \alpha + \frac{\alpha}{2} = 1 + \frac{\alpha}{2}$$

$$\text{Partial pressure of } H_2O = p\left(\frac{1 - \alpha}{1 + \frac{\alpha}{2}}\right)$$

$$\text{Partial pressure of } H_2 = p\left(\frac{\alpha}{1 + \frac{\alpha}{2}}\right)$$

$$\text{Partial pressure of } O_2 = p\left(\frac{\alpha}{2 + \alpha}\right)$$

$$K_p = \frac{p_{H_2} \cdot p_{O_2}^{1/2}}{p_{H_2O}}$$

$$\Rightarrow \quad K_p = \frac{\alpha^{3/2} \cdot p^{1/2}}{(1 - \alpha)(2 + \alpha)^{1/2}}$$

14. $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

$$\therefore \quad K_p = \frac{p^2_{NH_3} \times p_{CO_2}}{p_{NH_4COONH_2}(s)}$$

But, $p_{NH_4COONH_2}(s) = 1$ ($\because$ p of solids is taken as one)

$$\therefore \quad K_p = p^2_{NH_3} \times p_{CO_2}$$
$$= (3)^2 \times 3 = 27$$

15. $\Delta G^{\ominus} = 0$

We know that, $\Delta G^{\ominus} = -RT \ln K$

At the state of half completion of reaction

$[A] = [B]$, Therefore, $K = 1$. Thus, $\Delta G^{\ominus} = 0$

16. pH = 7 (NaX)

No hydrolysis as the salt of strong acid and strong base

pH = 9 (NaY)

$$pK_a = 2pH - pK_w - \log c$$
$$= 18 - 14 + 1$$

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$$pK_a = 5$$

$$pH = 11\ (NaZ)$$

$$pK_a = 22 - 14 + 1$$

$$pK_a = 9$$

Hence, the order of increasing acidic strength is

$$HZ < HY < HX$$

17. $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]^2}{[HA]}$$

$$[H^+] = \sqrt{K_a[HA]}$$

$$= \sqrt{1 \times 10^{-5} \times 0.1}$$

$$= \sqrt{1 \times 10^{-6}} = 1 \times 10^{-3}$$

$$\alpha = \frac{\text{actual ionisation}}{\text{molar concentration}}$$

$$= \frac{10^{-3}}{0.1} = 10^{-2}$$

% of acid dissociated

$$= 10^{-2} \times 100 = 1.00\%$$

18. Base BOH is dissociated as follows

$$BOH \rightleftharpoons B^+ + OH^-$$

So, the dissociation constant of BOH base

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

At equilibrium, $[B^+] = [OH^-]$

$$K_b = \frac{[OH^-]^2}{[BOH]}$$

Thus, $1.0 \times 10^{-12} = \dfrac{[OH^-]^2}{0.01}$

$$[OH^-]^2 = 1 \times 10^{-14}$$

$$[OH^-] = 1.0 \times 10^{-7}\ \text{mol L}^{-1}$$

19. $\log \dfrac{(K_{sp})_2}{(K_{sp})_1} = \dfrac{\Delta H}{2.303\,R}\left(\dfrac{T_2 - T_1}{T_1 \cdot T_2}\right)$

$$\log \frac{1.39 \times 10^{-8}}{7.47 \times 10^{-9}} = \frac{\Delta H}{2.303 \times 8.314}\left(\frac{298 - 288}{288 \times 298}\right)$$

$$\Delta H = 44.318\ \text{kJ/mol}$$

20. $M_2X_3 \rightleftharpoons 2M^{3+} + 3X^{2-}$

$2S \qquad 3S$

(where, S = solubility)

$$K_{sp} = (2S)^2 \cdot (3S)^3 = 108\,S^5$$

or $2.2 \times 10^{-20} = 108\,S^5$

$\therefore \quad S = 4.59 \times 10^{-5}$

For M_2X,

$$M_2X \rightleftharpoons 2M^+ + X^{2-}$$

$2S \qquad S$

$$K_{sp} = (2S)^2 \cdot (S)$$

$$K_{sp} = 4S^3$$

$$K_{sp} = 4(2 \times 4.59 \times 10^{-5})^3$$

[$\because$ Solubility of $M_2X = 2 \times$ solubility of M_2X_3]

$$= 3 \times 10^{-12}$$

21. Solubility of $BaSO_4 = \sqrt{K_{sp}}$

$$= \sqrt{1.1 \times 10^{-10}} = 1.05 \times 10^{-5}\ \text{M}$$

Weight of $BaSO_4 = 1.05 \times 10^{-5} \times 233$

$$= 244.37 \times 10^{-5}\ \text{g/L}$$

Volume of water needed to dissolve 1 g $BaSO_4$

$$= \frac{1}{244.37 \times 10^{-5}} = 410\ \text{L}$$

22. The pair of electrons present at nitrogen (in NH_3 : Lewis base) is donated to Cu^{2+} (Lewis acid).

23. Solution contains

$$2[OH^-]_{\text{water}} = 2 \times 1 \times 10^{-7}$$

$$pOH = -\log(2 \times 10^{-7})$$

$$= 7 - 0.301 = 6.699$$

$$pH = 14 - pOH = 14 - 6.699 = 7.301$$

24. $[H^+]$ from water is significant here

$$[H^+] = \frac{K_w}{[H^+]} + [HCl]$$

HCl is completely ionised

$$[HCl] = [H^+]_{HCl}$$

$$[H^+]^2 = K_w + [HCl]\,[H^+]$$

$$[H^+]^2 - [HCl]\,[H^+] - K_w = 0$$

$$[H^+] = \frac{[HCl] \pm \sqrt{[HCl]^2 + 4\,K_w}}{2}$$

$$[H^+] = 1.62 \times 10^{-7}$$

$$pH = -\log(1.62 \times 10^{-7})$$

$$= 6.79$$

25. Millimoles of $NH_3 = 100 \times 0.05 = 5$ m moles

Added HCl $= 10 \times 1.0$ m $= 10$ m moles

NH_3 gets completely neutralised, solution turns acidic that's now it is not the buffer solution.

26. Hydrogen peroxide, H_2O_2 can act both as reducing and oxidising agents.

27. $\overset{+1}{H_2}\overset{-1}{O_2} + \overset{+1}{Na_2}\overset{+4}{C}\overset{-2}{O_3} \longrightarrow \overset{+1}{Na_2}\overset{-1}{O_2} + \overset{+4}{C}\overset{-2}{O_2} + \overset{+1}{H_2}\overset{-2}{O}$

$\therefore$ No change in oxidation number in any species.

28. $Ni \longrightarrow Ni^{2+} + 2e^-$

Here, Ni is oxidised and thus, serves as a reducing agent.

29. $\overset{0}{Zn} + 2\overset{+1}{Ag}CN \longrightarrow 2\overset{0}{Ag} + \overset{+2}{Zn}(CN)_2$

Zinc (Zn) is oxidised and silver (Ag) is reduced.

30. $S^{4+} \longrightarrow S^{6+} + 2e^- \times 5$

$10e^- + 2I^{5+}$ (i.e. KIO_3) $\longrightarrow I_2^0$

31. $Mn^{7+} + 2e^- \longrightarrow Mn^{5+}$

32. $P_2O_7^{4-} = 2 \times x + 7 \times (-2) = -4$

$\Rightarrow \quad x = +5$

33. Let oxidation state of S in SO_3^{2-}, $S_2O_4^{2-}$, $S_2O_6^{2-}$ is x.

In SO_3^{2-}; $\quad x + (-2 \times 3) = -2$

$$x = -2 + 6 = +4$$

In $S_2O_4^{2-}$; $\quad 2x + (-2 \times 4) = -2$

$$2x = -2 + 8 = +6$$

$\Rightarrow \quad x = \dfrac{+6}{2} = +3$

In $S_2O_6^{2-}$; $\quad 2x + (-2 \times 6) = -2$

$$2x = -2 + 12 = 10$$

$\Rightarrow \quad x = +5$

$\therefore$ Increasing order of oxidation state of S is

$$S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$$

34. I_3^-, $3 \times x = -1$

$\Rightarrow \quad x = -\dfrac{1}{3}$

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35. The balanced equation is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

36. (1) $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$

(2) $T \propto \left(\frac{1}{V}\right)^{\gamma-1}$ or $T = k\left(\frac{1}{V}\right)^{\gamma-1}$

$$\therefore \quad \log T = \log k + (\gamma - 1)\log\frac{1}{V}$$

$$\log T = \log k - (\gamma - 1)\log V$$

or $\log T + (\gamma - 1)\log V = \log k$ (constant)

(3) At constant volume, variation of heat of reaction with temperature is given by Kirchhoff's equation.

(4) $p \propto \left(\frac{1}{V}\right)^{\gamma}$ or $p = k\left(\frac{1}{V}\right)^{\gamma}$

$$\log p = \log k + \gamma\log\frac{1}{V} = \log k - \gamma\log V$$

$$\log p + \gamma\log V = \log k$$

37. pH of

1. salts of weak acid and weak base as $RCOONH_4$
2. buffer solutions
3. amphiprotic ions as HCO_3^-, HS^- are not affected by dilution.

38. 100 mL of 1 M
CH_3COOH = 100 millimoles

(A) 25 mL of 1 M
NaOH = 25 millimoles

$\therefore$ Resulting mixture will be a buffer containing
$CH_3COOH + CH_3COONa$.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

Initially	100	25	0	0
At equil.	75	0	25	

$$\therefore \quad pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$= pK_a + \log\frac{25}{75} = pK_a - \log 3$$

(B) 50 mL of 1 M NaOH = 50 millimoles

$$\therefore \quad CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

Initially	100	50	0	0
At equil.	50	0	50	

$$\therefore \quad pH = pK_a + \log\frac{50}{50} = pK_a$$

(C) 75 mL of NaOH = 75 millimoles

$$\therefore \quad CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

Initially	100	75	0	0
At equil.	25	0	75	

$$\therefore \quad pH = pK_a + \log\frac{[salt]}{[acid]} = pK_a + \log\frac{75}{25} = pK_a + \log 3$$

(D) 100 mL of NaOH = 100 millimoles of NaOH

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

Initially	100	100	0	0
At equil	0	0	100	

$$\therefore \quad pH = \frac{1}{2}[pK_w + pK_a + \log C]$$

$$= \frac{1}{2}[pK_w + pK_a + \log 100] = \frac{1}{2}[pK_w + pK_a + 2]$$

39. Iodine and CCl_4 are both the non-polar solvents and they do not ionise into ions but water is a polar solvent and change into ions H^+ and OH^-. So, iodine is more soluble in CCl_4 than H_2O.

40. If a strong acid is added, the H^+ ion added neutralised by the base. If a strong base is added, the OH^- ion added are neutralised by cation forming very slightly dissociated base. Thus, the pH of buffer is reserved.

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