Solutions to 2009 prelim H2 Chemistry P 2

1 a i
$$P_e(CH_4) = 1.25$$
 atm; $P_e(H_2S) = 2.5$ atm; $P_e(CS_2) = 1.25$ atm; $P_e(H_2) = 5.0$ atm

ii

$$K_{p} = \frac{(P_{CS_{2}})(P_{H_{2}})^{4}}{(P_{CH_{4}})(P_{H_{2}S})^{2}} atm^{2}$$

- iii $K_p = 100 \text{ atm}^2$
- iv (I) Equilibrium shifts left.
 - (II) Equilibrium shifts right.

Q1b)(i)

pH = 5.13 (2 dec pl.)

(ii) amt of NH_4^+ to be neutralized to form buffer of max buffer capacity

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vol of NaOH required = 10 \text{ cm}^3
pH = pK<sub>a</sub>
= 9.26
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Q2a) (i) It is a polypeptide chain joined by amino acid units through peptide bonds.

(ii) Ile-Gly-Asp-Glu-Asn-Tyr

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(b) (i) $-CH_2SH + -CH_2SH + [O] \rightarrow -CH_2S-SCH_2 + H_2O$ $-CH_2SH + -CH_2SH \rightarrow -CH_2S-SCH_2 + H_2$ $-CH_2SH + -CH_2SH \rightarrow -CH_2S-SCH_2 + 2[H]$

- (ii) tdid : Valine phenylalanine:
 ionic interaction : lysine- glutamic, lysine- aspartic acid
 H-bonding: Serine Aspartic acid: (Serine- glutamic acid), (Aspartic glutamic acid)
- (c) (i) optimum working pH for this enzyme is 2.5. At pH lower or above 2.5, the existing ionic or H-bonding interactions are destroyed . changing the tertiary structure of protein rendering it inactive.

(ii) addition of heavy metal ions which will destroy the disulfide bonds by forming ppt with sulfur. Protein denatured therefore lost its activity.Supply of heat/ high temp also acceptable.

(ii) Both Lysine and compound A can react with alkali to form soluble salt. However, when compound A is formed, it loses its basic property as it forms the amide (not peptide) linkage. No reaction therefore insoluble in acid. However it is still soluble in alkaline medium as it still carries the COOH group that can react to form the soluble salt in alkaline solution.

3(a) (i) $AI_2O_3 + 6H^+ \rightarrow 2AI^{3+} + 3H_2O$ $AI_2O_3 + 2OH + 3H_2O \rightarrow 2[AI(OH)_4]$



(ii) Ionic Radius:

There are two isoelectronic series in period 3.

Within each series, an increasing number of protons results in increasingly stronger nuclear attraction experienced by the valence electrons.

Valence electrons are pulled closer to nucleus, leading to a decreasing trend in ionic radius. Anionic series has a larger size than cationic series as the valence electrons are in a higher principal quantum shell, experience weaker nuclear attraction and are less tightly held.

pH:

 Na_2O and MgO are ionic oxides that dissolve completely in water to form basic solution. Al₂O₃ and SiO₂ are insoluble in water \therefore pH of solution is that of water. P₄O₁₀ and SO₃ are covalent oxides that hydrolyse in water to give acidic solution.

(c) (i)
$$[Mg(H_2O)_6]^{2+} + H_2O \implies [Mg(H_2O)_5(OH)]^+ + H_3O^+$$

- (ii) $\Delta H = +4336 \text{ kJ mol}^{1}$
- (iii) Formation of both MgCl₂ and MgCl₃ give rise to negative ΔS as there is a decrease in the amount of gaseous particles in the system after the reaction. $\Delta G = \Delta H - T\Delta S$ Comparing ΔH of both reactions, formation of MgCl₃ will result in a positive ΔG whereas formation of MgCl₂ will result in a negative ΔG as ΔG is more dependent on magnitude and sign of ΔH of the reactions since both reactions have a small difference in ΔS .

So formation of $MgCl_3$ will be less feasible than that of $MgCl_2$.

- 4. (a) (i) $K_2Cr_2O_7$, dil. H_2SO_4 , heat with distillation
 - (ii) 2,4-dinitrophenylhydrazine. Positive observation: orange ppt
 - (iii) Cyanide ions can attack the trigonal planar carbonyl carbon from top and bottom with equal probabilities. Hence a racemic mixture is formed. The optical activity of one enantiomer cancels out the optical activity of the other hence the product mixture does not exhibit any optical activity.
- (b) (i) $(CH_3)_2CHCH_2CH_2OCOCH_3 + NaOH$ $\rightarrow (CH_3)_2CHCH_2CH_2OH + CH_3CO_2Na$
 - (ii) I. The change in concentration of NaOH per unit time can be tracked by the change in pH of the solution using a pH meter.

II. To determine the order wrt to NaOH, measure the change in [NaOH] vs time with large excess of ester. [Ester] is much higher than [NaOH]. Plot [NaOH] vs time graph. From the half-life, order wrt [NaOH] can be determined. To determine the order wrt ester, conduct a second experiment with double [ester], but same [NaOH]. Plot [NaOH] vs time. Compare the ratio is of initial rate of first and second experiment and the ratio of the [ester] in both experiment to determine the order wrt ester.

- (iii) The intermolecular forces in acid is hydrogen bonding while in ester is permanent dipoledipole interaction. Since hydrogen bonding is stronger than permanent dipole-dipole interaction, more energy is required to break the intermolecular forces in acid to change it from liquid to gas.
- (iv) Stage I: LiAlH₄, dry ether
 Stage II: excess con. H₂SO₄, 170°C
 Stage III: Cold KMnO₄, NaOH
 Compound C: (CH₃)₂CHCH=CH₂