

Second Semester BSc Degree examination may 2019

Complementary Course

CH1231.1/ CH1231.2 – Physical Chemistry I

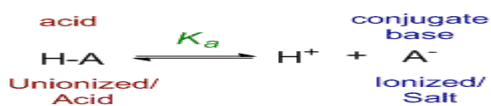
Common for Physics and Geology

(2017 Admission onwards ) Max Marks :80

| Q.No | Section A<br>Answer All questions, Each question carries 1 mark   | Marks |
|------|---|-------|
| 1    | Calculate the pH of 0.025 N HNO <sub>3</sub> assuming 100% ionization<br>pH=-log[H <sup>+</sup> ]= 1.6  | 1     |
| 2    | Calculate the degree of hydrolysis of 0.2M sodium acetate in solution. K <sub>a</sub> of acetic acid = 1.8x10 <sup>-5</sup> , K <sub>w</sub> = 1x10 <sup>-14</sup><br>$\alpha=(K_w/K_aC)^{1/2}=5.19 \times 10^{-5}$ | 1     |
| 3    | Give an example of endothermic reaction<br>Any example  | 1     |
| 4    | Define buffer solution<br>Solution which resist change in pH by the addition of small amount of acid or base  | 1     |
| 5    | Define the term spontaneous process<br>Process which take place without the help of any external agency   | 1     |
| 6    | Define free energy<br>Thermodynamic property whose decrease in magnitude in any process gives the useful work or<br>G=H-TS  | 1     |
| 7    | What is leveling effect<br>All strong acid are completely ionized in water and give same amount of H <sup>+</sup> ion concentration. So the relative strength of strong acids cannot be compared                    | 1     |

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|   | in aqueous solution. This effect of strength of an acid by a solvent is called leveling effect   |                       |
| 8   | Define chemical equilibrium<br>It is a state of reversible reaction at which the rate of forward reaction is equal to the rate of backward reaction and composition of the system remains constant   | 1                     |
| 9   | What is meant by reversible reaction<br>Reactions take place in both forward and backward directions   | 1                     |
| 10  | Define pH<br>$\text{pH} = -\log_{10}[\text{H}^+]$  | 1                     |
| <b>Section B</b>  |  |                       |
| <b>Answer any eight questions Each question carries 2 marks</b> |  |                       |
| 11  | Write the Henderson equation for acidic buffer and explain the terms<br>$\text{pH} = \text{pK}_a + \log\left[\frac{[\text{Salt}]}{[\text{Acid}]}\right]$ , $\text{pK}_a$ dissociation constant of acid, [Salt]- concentration of salt, [Acid]- concentration of acid   | 1+1                   |
| 12  | Calculate the hydronium and hydroxyl ion concentrations of a solution having pH 10.27<br><br>$\text{H}^+ = 1.95 \times 10^{-10}$<br>$\text{OH}^- = 5.3 \times 10^{-3}$   | 2                     |
| 13  | Calculate $K_p$ for the reaction<br>$\text{A}_{(g)} + \text{B}_{(g)} = \text{C}_{(g)} + \text{D}_{(g)}$<br>If $\Delta G^\circ$ for the reaction is $-3435 \text{ kJ mol}^{-1}$<br>$\Delta G^\circ = -2.303 RT \log K_p$<br>$\log K_p = \frac{3435 \times 1000}{2.303 \times 8.314 \times 273}$<br>Equation and correct substitution gives full marks |                       |
| 14  | $\Delta H$ and $\Delta S$ for the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ at 700K are respectively $-112.9 \text{ kJ}$ and $-145.5 \text{ JK}^{-1}$ , Calculate the free energy change and predict whether the reaction  | $1 \frac{1}{2} + 1/2$ |

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|    | <p>is spontaneous or not at 700K</p> $\Delta G = \Delta H - T \Delta S$ $= -112900 + 700 \times 145.5$ $= -11.05 \text{ kJ/mol, since } \Delta G \text{ is negative the reaction is spontaneous}$  |           |
| 15 | <p>Define heats of reaction at constant volume and at constant pressure</p> <p>When a chemical reaction takes place at constant volume, the heat change is called heat of a reaction at constant volume. It is the internal energy change.</p> <p>When the reaction takes place at constant pressure, the heat change is called heat of reaction at constant pressure. It is the enthalpy change</p>   | 1+1       |
| 16 | <p>What are exothermic reactions? Give example</p> <p>A chemical reaction proceeds with the evolution of heat is called exothermic reaction. Eg: combustion</p>  | 2         |
| 17 | <p>What is meant by the term standard state</p> <p>It is the condition of a substance at 25°C and at one atmospheric pressure</p>  | 2         |
| 18 | <p>State Hess's law</p> <p>Enthalpy change of a reaction is same whether the reaction takes place in one step or several steps</p>   | 2         |
| 19 | <p>Define enthalpy of hydration</p> <p>It is the change in enthalpy when one mole of an anhydrous substance combines with requisite number of water molecules to form a hydrate.</p>   | 2         |
| 20 | <p>Write the equation for calculation of pH from EMF measurements</p> <ol style="list-style-type: none"> <li>Using calomel electrode and hydrogen electrode <math>\text{pH} = \frac{E_{\text{cell}} - E_{\text{calomel}}}{0.0591}</math>,</li> <li>Using quinhydrone electrode and calomel electrode <math>E_{\text{cell}} = E_{\text{calomel}} - E_{\text{QH}}</math>,<br/> <math>E_{\text{cell}} = E_{\text{calomel}} - (E_{\text{QH}}^0 + 0.0591 \text{pH})</math>, <math>E_{\text{calomel}} = 0.2425</math>, <math>E_{\text{QH}}^0 = 0.699</math>,<br/> <math>\text{pH} = \frac{E_{\text{cell}} + 0.4575}{0.0591}</math></li> <li>Using calomel and glass electrode <math>\text{pH} = \frac{E_{\text{cell}} - 0.2415 - E_{\text{G}}^0}{0.0591}</math></li> </ol> | Any one 2 |

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| 21   | <p>Define degree of hydrolysis. Write an example of a salt of strong base and weak acid.</p> <p>It is the fraction of total amount of salt undergoing hydrolysis</p> <p>Sodium acetate, Sodium carbonate</p>  | 2 |
| 22   | <p>Define standard free energy change of a reaction</p> <p>It is the free energy change when the reactant and product are at standard state and the reaction takes place at standard condition. <math>\Delta G^0</math></p>   | 2 |
| <p><b>Section C</b></p> <p><b>Answer any six questions, each question carries 4marks</b></p> |   |   |
| 23   | <p>State and explain the second law of thermodynamics</p> <p>It is impossible to convert heat into work without compensation or the entropy of the universe always increase in the course of every spontaneous process.</p> <p>For a spontaneous process entropy change is positive. i.e <math>\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} &gt; 0</math>. i.e <math>\Delta S_{total}</math> is positive and entropy of the universe increases.</p>  |   |
| 24   | <p>Define enthalpy. How is the enthalpy change in a process related to free energy change</p> <p>It is the total heat content of a system. It is equal to the internal energy of the system plus the product of pressure and volume. <math>H = E + PV</math> (2marks)</p> <p><math>\Delta G = \Delta H - T\Delta S</math> or <math>\Delta G = \Delta H + T[(\delta(\Delta G)/\delta T)_p]</math> (Any one equation with explanation of terms 2 marks)</p>   |   |
| 25   | <p>Derive Henderson equation for acidic buffer. Name any two applications</p> <p><b>For Acids</b></p> <div style="text-align: center;">  <p style="text-align: center;">Acid Dissociation</p> </div> <p>According to the law of dissociation, the acid dissociation constant <math>K_a</math> can be defined by the equation:</p> $K_a = \frac{[H^+][A^-]}{[HA]}$ <p>where <math>[H^+]</math> and <math>[A^-]</math> are the concentrations of the ionized form of the acid, while <math>[HA]</math> is the concentration of the unionized form. Taking log</p> |   |

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|    | <p><math>\log K_a = \log ([H^+][A^-]/[HA])</math><br/> Splitting the log terms into separate components gives you:<br/> <math>\log K_a = \log [H^+] + \log ([A^-]/[HA])</math><br/> Since <math>pK_a = -\log_{10} K_a</math> and <math>pH = -\log_{10} [H^+]</math>, therefore:<br/> <math>-pK_a = -pH + \log ([A^-]/[HA])</math><br/> Rearranging the terms we get the Henderson-Hasselbalch equation for acids as:<br/> <b><math>pH = pK_a + \log ([A^-]/[HA])</math></b><br/> This equation can also be written as:<br/> <math>pH = pK_a + \log [(salt)/(acid)]</math><br/> Application 1 Determination of pH of buffer solution</p>  |   |
| 26 | <p>Derive the equation for the relation between <math>K_w</math> and <math>K_h</math> of a salt of strong acid and weak base.</p> $B^+ + H_2O \rightleftharpoons BOH + H^+$ <p style="text-align: center;">Weak base</p> <p>Consider, for example, <math>NH_4Cl</math>. It ionises in water completely into <math>NH_4^+</math> and <math>Cl^-</math> ions. ions react with water to form a weak base (<math>NH_4OH</math>) and <math>H^+</math> ions.</p> $NH_4^+ + Cl^- + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$ <p>The equilibrium constant <math>K_h = [NH_4OH][H^+]/[NH_4^+]</math>-----(i)</p> <p>Thus, hydrogen ion concentration increases and the solution becomes acidic.</p> <p>Other equilibria which exist in solution are</p> $NH_4OH \rightleftharpoons NH_4^+ + OH^-$ $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \dots (ii)$ $H_2O \rightleftharpoons H^+ + OH^-$ $K_w = [H^+][OH^-] \dots (iii)$ <p>From I, ii and iii <math>K_h = K_w/K_b</math></p> |   |
| 27 | <p>Write short note on hydrolysis of salts</p> <p>Salt hydrolysis is the interaction of cation or anion or both of salt with <math>H^+</math> and <math>OH^-</math> of water to form acidic, basic or neutral solution.</p> <p>salts are classified into four categories.</p> <ul style="list-style-type: none"> <li>• Salt of a strong acid and a weak base.<br/> Examples: <math>FeCl_3</math>, <math>CuCl_2</math>, <math>AlCl_3</math>, <math>NH_4Cl</math>, <math>CuSO_4</math>, etc.</li> <li>• Salt of a strong base and a weak acid.<br/> Examples: <math>CH_3COONa</math>, <math>NaCN</math>, <math>NaHCO_3</math>, <math>Na_2CO_3</math>, etc.</li> </ul>  | <p>Definition<br/> with types<br/> 4 marks<br/> Or<br/> definition<br/> with<br/> explanation</p> |

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|    | <ul style="list-style-type: none"> <li>Salt of a weak acid and a weak base.<br/>Examples: <math>\text{CH}_3\text{COONH}_4</math>, <math>(\text{NH}_4)_2\text{CO}_3</math>, <math>\text{NH}_4\text{HCO}_3</math>, etc.</li> <li>Salt of a strong acid and a strong base.<br/>Examples: <math>\text{NaCl}</math>, <math>\text{K}_2\text{SO}_4</math>, <math>\text{NaNO}_3</math>, <math>\text{NaBr}</math>, etc.</li> </ul>  | of any one<br>type 4<br>marks   |
| 28 | <p>Write short note on bond energy</p> <p>Bond energy of a particular type of bond in a compound is defined as the average amount of energy required to break one mole of bonds of that type present in the compound. Or it is the average of bond dissociation energies of that type of bonds.</p> <p><math>\text{HO-H} \rightarrow \text{OH} + \text{H}; \Delta H = E_1</math></p> <p><math>\text{O-H} \rightarrow \text{O} + \text{H}; \Delta H = E_2</math></p> <p>Bond energy of O-H bond is <math>(E_1 + E_2)/2</math></p>   | Definition 2<br>marks<br>Any<br>relevant<br>point 2<br>marks                |
| 29 | <p>Explain any two applications of Hess's law.</p> <ol style="list-style-type: none"> <li>Determination of enthalpy of formation of substances which cannot be measured experimentally. Eg: methane, CO benzene etc</li> <li>Determination of enthalpy of transition. For eg: diamond to graphite</li> <li>Determination of enthalpy of reaction</li> </ol>  | Explanation<br>of any two<br>4 marks  |
| 30 | <p>Write short note on buffer capacity and buffer action</p> <p>The <b>buffer capacity</b> of a buffer solution is defined as the number of moles of acid or base added per liter of the solution to change the pH by one unit.</p> <p>Consider the acidic buffer solution containing acetic acid and sodium acetate. They dissociate as</p> <p><math>\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+</math></p> <p><math>\text{CH}_3\text{COONa} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{Na}^+</math></p> <p>When a few drops of an acid, HCl is added to this buffer solution, the <math>\text{H}^+</math> ions combine with <math>\text{CH}_3\text{COO}^-</math> ions to form weakly ionized molecules of <math>\text{CH}_3\text{COOH}</math>.</p> <p><math>\text{CH}_3\text{COO}^- + \text{H}^+ \rightleftharpoons \text{CH}_3\text{COOH}</math></p> <p>Thus <math>\text{H}^+</math> ion concentration does not change and hence the pH of the solution remains constant.</p> <p>When a few drops of base, NaOH is added to the buffer solution, hydroxyl ions of the base neutralize the acid, forming salt and water</p> | Buffer<br>capacity 1<br>mark<br>Buffer<br>action any<br>one type 3<br>marks |

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|   | <p><math>\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}</math>.</p> <p>Similarly, in a basic buffer solution of <math>\text{NH}_4\text{OH}</math> and <math>\text{NH}_4\text{Cl}</math>, they dissociates as</p> <p><math>\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-</math>.</p> <p><math>\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-</math>.</p> <p>When a few drops of a base added, the <math>\text{OH}^-</math> ions given by it combine with <math>\text{NH}_4^+</math> ions to form the weakly ionized <math>\text{NH}_4\text{OH}</math>.</p> <p><math>\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_4\text{OH}</math></p> <p>Thus the <math>\text{OH}^-</math> ion concentration or the pH of the solution remains unaffected.</p> <p>When a small amount of an acid is added, the <math>\text{H}^+</math> ions given by it combines with the <math>\text{OH}^-</math> ions already produced by <math>\text{NH}_4\text{OH}</math>.</p> <p><math>\text{NH}_4\text{OH} + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{NH}_4^+</math></p> <p>Therefore the <math>\text{H}^+</math> ions concentration or the pH of the solution remains unaffected.</p> |                               |
| 31  | <p>State the first law of thermodynamics and give the mathematical expression of the law. Energy can neither be created nor be destroyed. It can transfer from one form to other</p> <p><math>\Delta E = q + w</math></p>   | 2+2 with explanation of terms |
| <p><b>Section D</b></p> <p><b>Answer any two questions, Each question carries 15marks</b></p> |   |                               |
| 32  | <p>Define equilibrium constant. What are the factors which influence the value of equilibrium constant. Derive the relation between <math>K_p</math> and <math>K_c</math></p> <p>Equilibrium constant- it is the ratio of product of concentrations of product to that of reactants raised to the power equal to its coefficient in the balanced chemical equation(2marks)</p> <p>Equation of <math>K_c</math>, <math>K_p</math>, <math>K_x</math> (3marks)</p> <p>Factors: temperature</p> <p>Variation of <math>K_p</math> with temperature-van't Hoff equation</p> <p><math>d \ln K_p / dT = \Delta H^0 / RT^2</math> or <math>\ln K_{p1} / K_{p2} = \Delta H^0 / R [(T_2 - T_1) / T_2 T_1]</math> (2 marks)</p> <p>Pressure</p> <p><math>K_p</math> and <math>K_c</math> are independent of pressure(2 marks)</p> <p><math>K_x</math> depend on pressure <math>d \ln K_x / dp = -\Delta n / P</math> (2 marks)</p>  |                               |

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|    | <p>Relation between Kp and Kc<br/> <math>K_p = K_c(RT)^{\Delta n}</math> Derivation (4marks)</p>  |  |
| 33 | <p>(a) Discuss any four concepts of acids and bases. What are conjugate acid base pair.</p> <p>b. Derive the equation for hydrolytic constant of a salt of weak acid and weak base</p> <p>a) 1. Arrhenius concept of acid and base with one examples each (2+1)</p> <p>2. Lowry Bronsted Concept with examples (3 marks)</p> <p>3. Lewis concept with examples (3 marks)</p> <p>Conjugate acid base pair with one example (3 marks)</p> <p>b) Derivation of the relation (4 marks)</p> $\text{CH}_3\text{COO}^- + \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$ $\begin{matrix} C(1-h) & C(1-h) & Ch & Ch \end{matrix}$ $K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]}$ <p>Other equilibria which exist in solution are:</p> $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ $K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \dots (i)$ $\text{NH}_4\text{OH} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_4\text{OH}]} \dots (ii)$ $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ $K_w = [\text{H}^+][\text{OH}^-] \dots (iii)$ <p>From Eqs. (i), (ii) and (iii),</p> $K_h = K_w / K_a \cdot K_b = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \dots (iv)$ <p>Let C be the concentration and h be the degree of <b>hydrolysis</b></p> $K_h = h^2 / (1-h)^2$ |  |
| 34 | <p>(a) Write short note on enthalpy of neutralization</p> <p>(b) Derive Kirchoff equation</p> <p>(a) If attempted give 5 marks</p>  |  |

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|    | <p>(b) Derivation of <math>[\delta(\Delta H)/\delta T]_p = \Delta C_p</math> (3marks)</p> <p>Derivation of <math>[\delta(\Delta E)/\delta T]_v = \Delta C_v</math> (3 marks)</p> <p>Derivation of <math>\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)</math> (2 marks)</p> <p>Derivation of <math>\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)</math> (2 marks)</p>                             |  |
| 35 | <p>(a) Write short note on (i) entropy (ii) spontaneous process</p> <p>(b) State and explain the Chatlier's principle</p> <p>i) Entropy and its significance (5 marks)</p> <p>ii) Definition of spontaneous process, example and its criteria in terms of <math>\Delta G</math> ( using the equation <math>\Delta G = \Delta H - T\Delta S</math>) (5 marks)</p> <p>iii) If attempted give 5 marks</p> |  |