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## JF Physical Chemistry 2013-2014.

# JF CH 1101: Introduction to Physical Chemistry.

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## A compendium of past examination questions set on Physical Chemistry on the JF Chemistry paper and problem sheets associated with CH1101 Physical Chemistry (Lyons).

You will not fully understand Physical Chemistry if you cannot solve numerical problems on the material delivered in lectures. Formulating and solving problems is a key skill needed for success in this branch of Chemistry, which has the reputation of being difficult because of its intrinsic mathematical nature.

This booklet has been produced to provide JF Chemistry students with a full selection of problems in basic Physical Chemistry set by the author over the last few years. These problems have appeared in the Annual, and the Supplemental examination papers in Chemistry set by the Examination Board of the School of Chemistry, University of Dublin, Trinity College.

They are made available to Trinity College JF Chemistry students to assist them in their revision of the basic Physical Chemistry lectures on properties of Gases, Thermodynamics, Equilibria and Electrochemistry delivered by Professor Lyons in the first semester to students taking CH 1101. This document is not to be distributed widely.

I hope that you will find it a useful self learning and revision aid.

Professor Mike Lyons 15-10-2013

# JF Chemistry Module CH1101. 2009

## MCQ Semister 1 Test

- 1. Consider the synthesis of ammonia which proceeds according to the following reaction:  $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \rightarrow NH_3(g)$ . If the standard change in Gibbs energy for the reaction is given by  $\Delta_r G^0 = -16,370$  J mol<sup>-1</sup> at T = 298 K then the equilibrium constant K for the reaction is:
  - (a) 7.38 x 10<sup>2</sup> (Answer)
  - (b) 7.38 x 10<sup>-2</sup>
  - (c) 0.1
  - (d) 100
  - (e) there is insufficient data supplied to answer the question.

You may assume that the gas constant  $R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$ .

2. In air at 298 K which gas has the lowest average root mean square speed?

(a)  $H_2O(g)$ ; (b)  $CO_2(g)$  (Answer); (c) CO(g); (d) Ne(g); (e)  $CH_4(g)$ .

- 3. For ideal gases which of the following statements are correct?
  - i. At constant temperature, the volume of a fixed mass of gas is proportional to the external pressure.
  - ii. At constant external pressure and temperature, when 1L of  $N_2$  reacts with 2L of  $O_2$ , 2L of  $NO_2$  are formed
  - iii. At a given temperature and external pressure, equal volumes of any ideal gas contain the same number of molecules
  - iv. At a given temperature, the molecules in any ideal gas have the same average velocity
  - v. At a given pressure and temperature, the mean-free path of a gas is independent of the volume of the containing vessel
    - a) (ii) and (iii)
    - **b)** (i), (iii) and (v)
    - c) (ii) and (iii)

- **d)** (ii) and (v)
- e) (ii), (iii) and (v) (Answer)

## Section A Long Questions 2009

#### Annual

- Briefly discuss the concept of pH as applied to aqueous solutions paying attention to its definition and measurement.
- (b) Draw the shape expected for the titration curve expected for a titration of a strong acid by a strong base and between a weak acid and a strong base. You should describe features of interest associated with each of these titration curves.
  Consider the titration of 100 mL of 0.1 M acetic acid with 0.1 M NaOH. (i) What is the pH of the solution when 90 mL of 0.1 M NaOH has been added to 100 mL of 0.1 M acetic acid. (ii) Determine the pH at the equivalence point. (iii) What is the pH after 110 mL of 0.1 M NaOH has been added.

## **Supplemental**

- (a) Define the terms oxidation, reduction, galvanic cell, electrolysis cell.
- (b) Describe using a suitable example, with a labelled diagram and pertinent chemical equations, how a fuel cell operates.
- (c) Derive and state the relationship between the change in Gibbs free energy  $\Delta G$  and the open circuit cell potential  $E_{cell}$ .
- (d) Calculate the equilibrium constant at 298 K for the reaction  $Fe(s)+Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq)+Cd(s)$  given that the standard reduction potentials are E<sup>0</sup>(Cd<sup>2+</sup>,Cd) = -0.40 V and E<sup>0</sup>(Fe<sup>2+</sup>,Fe) =- 0.44 V. Is the reaction strongly product favoured?

## Section B MCQ 2009

## Annual

- 1. Consider the following reaction:  $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ . At equilibrium at a certain temperature the concentrations of NH<sub>3</sub> (g), H<sub>2</sub>(g) and N<sub>2</sub>(g) are 0.94 M, 1.60 M and 0.52 M respectively. The numerical value of the equilibrium constant K<sub>c</sub> for the reaction is: (a) 0.415 ; (b) 1.13; (c) 1.06; (d) 0.664; (e) 1.27. Correct answer: a.
- 2. Calculate the concentration of OH<sup>-</sup> ion for an aqueous solution with a pH of 9.45. Note that the ion product of water  $K_w = 1 \times 10^{-14}$ . (a)  $1.8 \times 10^{-10}$  M ; (b)  $1.0 \times 10^{-14}$  M ; (c)  $2.8 \times 10^{-5}$  M ; (d) 0.35 M ; (e)  $3.5 \times 10^{-10}$  M. Correct answer: c
- 3. A buffer contains equal concentrations of a weak acid HA and its conjugate base A<sup>-</sup>. If the value of K<sub>A</sub> for the weak acid is 1.0 x 10<sup>-9</sup>, what is the pH of the buffer? (a) 9.0 ; (b) 5.0 ; (c) 1.0; (d) 13.0 ; (e) 7.0. Correct answer: a.
- 4. If the standard potential E<sup>0</sup> is 0.56 V at 298 K for the cell reaction:  $Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$ calculate the equilibrium constant for the reaction. (a) 6.2 x 10<sup>56</sup> ; (b) 37.8 ; (c) 2.9 x 10<sup>9</sup> ; (d) 2.5 x 10<sup>28</sup> ; (e) 1.4 x 10<sup>3</sup>. Correct answer: a.

# Supplemental

- Consider the reaction: N<sub>2</sub>(g)+3H<sub>2</sub>(g) ⇒ 2NH<sub>3</sub>(g). If the standard molar free energy of formation of NH<sub>3</sub>(g) at 298 K is 16.45 kJ mol<sup>-1</sup>, calculate the equilibrium constant for this reaction at 298 K.
   (a) 3.62 x 10<sup>-2</sup>; (b) 1.66 x 10<sup>-3</sup>; (c) 5.26 x 10<sup>-14</sup>; (d) 1.71 x 10<sup>-6</sup>; (e) 2.29 x 10<sup>-7</sup>. Correct answer: d.
- 2. The pH of 0.1 M CH<sub>3</sub>COOH is 2.87. What is the value of K<sub>A</sub> for CH<sub>3</sub>COOH? (a) 1.3 x 10<sup>-3</sup>; (b) 1.8 x 10<sup>-6</sup>; (c) 1.8 x 10<sup>-5</sup>; (d) 0.037; (e) 2.7 x 10<sup>-6</sup>. Correct answer: c.
- 3. The conjugate base of  $HSO_4^-$  is: (a)  $OH^-$ ; (b)  $SO_4^{2-}$ ; (c)  $H_2SO_4$ ; (d)  $HSO_4^-$  (e)  $H_2O$ . Correct answer: b.

4. The standard potential of the  $Ag^+|Ag$  redox couple is + 0.80 V and the standard potential of the cell  $Fe(s)|Fe^{2+}(aq)||Ag^+(aq)|Ag(s)$  is + 1.24 V. What is the standard potential of the  $Fe^{2+}|Fe$  redox couple? (a) 2.04 V; (b) - 0.44 V; (c) - 2.04 V; (d) + 0.44 V; (e) - 0.88 V. Correct answer: b.

# JF Chemistry Module CH 1101 2010.

# Section A Long Questions 2010.

# Annual.

1.

Answer either : part (a) and part (b) or part (c) and part (d).

- a. What is the internal energy U and the enthalpy H of a system? Write down an expression for the First Law of Thermodynamics which relates the change in internal energy of a system to the work done on the system and the heat absorbed by the system. Hence derive a relationship between the change in internal energy  $\Delta$ U and the change in enthalpy  $\Delta$ H of a system.
- b. A gas absorbs 300 J of heat and at the same time expands by 1  $dm^3$  against a constant pressure of 1 atm. What is the change in internal energy  $\Delta U$  and change in enthalpy  $\Delta H$  of the system.
- c. Define the term heat capacity and briefly describe using a labelled diagram and any equations where pertinent how the bomb calorimeter can be used to measure the change in internal energy of combustion of a material.
- d. Inside in a bomb calorimeter, 1.0 g of octane  $C_8H_{18}$  combusts in oxygen to form carbon dioxide and water according to the expression  $C_8H_{18} + 25/2O_2 \rightarrow 8CO_2 + 9H_2O$ . The temperature was observed to rise from 25.00 to 33.20 °C. The calorimeter contained 1200 g of water (specific heat capacity of water =  $4.184 \text{ Jg}^{-1}\text{K}^{-1}$ ) and the heat capacity of the bomb is 837 JK<sup>-1</sup>. Calculate the internal energy of combustion of octane.
- 2. Answer all parts.
  - (a) Briefly explain using specific examples and clearly labelled diagrams how a Galvanic (Voltaic) cell and how a Polymer Membrane Electrolyte (PEM) fuel cell operates.
  - (b) The net reaction that occurs in a voltaic cell is  $Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$ . Write down the half reactions that occur at the anode and cathode. If the standard

reduction potentials at 298K are  $E^{0}(Ag^{+},Ag)=0.799V$  and  $E^{0}(Zn^{2+},Zn) = -0.763V$ , calculate the voltage developed by the cell, the change in reaction Gibbs energy  $\Delta G^{0}$  and the equilibrium constant K for the cell reaction. Is the reaction strongly product favoured?

(c) Consider a galvanic cell involving the following half-reactions:  $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s), E^{0}(Ni^{2+},Ni) = -0.25 V; Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s), E^{0}(Cr^{3+},Cr) = -0.74 V.$  Calculate the cell potential observed at a temperature of 298 K when  $[Ni^{2+}] = 1.0 \times 10^{-4} M$  and  $[Cr^{3+}] = 2.0 \times 10^{-3} M.$ 

## Supplemental 2010.

- 1.
- (a) A strip of magnesium metal of mass 12.5 g is dropped into a beaker of dilute hydrochloric acid. Given that the Mg is the limiting reactant, calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1 atm and the temperature is 293.2 K.
- (b) If the enthalpy of combustion of solid citric acid is 1986 kJ mol<sup>-1</sup>, calculate the heat liberated when 10 g of solid citric acid undergoes total combustion at 298 K: (i) at constant pressure, (ii) at constant volume. Note: citric acid has formula  $C_6H_8O_7$ . The molar mass M = 192 g mol<sup>-1</sup>. Total combustion means reaction with  $O_2$  and conversion to  $CO_2$  and  $H_2O$ .
- 2. Answer four parts.
  - (a) What do you understand by the terms weak acid and solution pH? Provide an example of a weak acid and indicate the way that the acid strength of a weak acid can be quantified.
  - (b) Calculate the pH of a 5.0 x  $10^{-2}$  M NaOH solution given the information that  $K_w = 1.0 \times 10^{-14}$ .
  - (c) Calculate the  $H_3O^+$  ion concentration and the pH of a 0.003 M  $Ba(OH)_2$  solution assuming that the ion product  $K_w = 1.0 \times 10^{-14}$ .
  - (d) Derive an expression for the pH of an aqueous solution of weak acid HA of concentration c and having an acid dissociation

constant  $K_A$ . If  $K_A$  is assumed to be very small derive an approximate expression for the solution pH mentioning any approximations which you make.

(e) Use the theoretical results derived in part (d) to calculate the pH of a weak acid solution of concentration 0.1 M and having an acid dissociation constant  $K_A = 3.5 \times 10^{-8}$ .

# Section B MCQ.

# Annual.

- Which of the following graphs does not give a straight line for an ideal gas? (a) V versus T, (b) T versus P, (c) P versus 1/V, (d) n versus 1/T, (e) n versus 1/P. (correct answer option (e)).
- 2. Which of the following statements is always true for an ideal gas?
  - (a) If the temperature and volume of a gas both increase at constant pressure, the amount of gas must also increase.
  - (b) If the pressure increases and the temperature decreases for a constant amount of gas, the volume must decrease.
  - (c) If the volume and the amount of gas both decrease at constant temperature, the pressure must decrease.

(Correct answer option (b)).

- 3. A solution has a hydrogen ion concentration of 0.001 M. Which of the following statements are correct? (i) The solution pH is 3.0. (ii) The solution is acidic. (iii) The hydroxide ion concentration is 1.0 x  $10^{-11}$ . Note that  $K_w = 10^{-14}$ .
  - (a) All statements are correct.
  - (b) (i) only.
  - (c) (i) and (ii) only.
  - (d) (iii) only.
  - (e) None of the statements are correct.

(Correct answer option (a)).

4. Given that  $K_a$  (acetic acid) = 1.80 x 10<sup>-5</sup> and  $K_W = 1.0 x 10^{-14}$  then the pH of an 0.89 M solution of sodium acetate is : (a) 9.35, (b) 7.0, (c) 5.0, (d) 13.0 and (e) 3.0. (Option (a) is correct).

- 5. The Galvanic cell Cu |Cu<sup>2+</sup>(aq) |Ag<sup>+</sup>(aq) |Ag is based on the following cell reaction: 2Ag<sup>+</sup>(aq) + Cu(s) → 2Ag(s) + Cu<sup>2+</sup>(aq). Note that T = 298 K and the standard electrode potentials are E<sup>0</sup>(Cu<sup>2+</sup>,Cu) = 0.34V and E<sup>0</sup>(Ag<sup>+</sup>,Ag) = 0.80V. Which of the following statements are correct?
  (i) The silver electrode is the cathode and the copper electrode is the anode. (ii) Two moles of electrons flow through the external circuit from anode to cathode when the cell operates. (iii) The observed cell potential is 0.46 V. (iv) The change in Gibbs energy for the cell reaction is -88,766 J mol<sup>-1</sup>.
  - (a) All statements are correct.
  - (b) (i) only.
  - (c) (i) and (ii) only.
  - (d) (iii) and (iv) only.
  - (e) None of the statements are correct.

(Option (a) is correct).

6. Which of the following statements pertaining to ideal gases are correct? (i) The average kinetic energy of a gas molecule is proportional to the absolute temperature T of the gas sample. (ii) The ratio of the velocities by which two different types of ideal gas

molecules A and B move is given by  $\frac{v_A}{v_B} = \sqrt{\frac{m_B}{m_A}}$  where m and v

denote the mass and velocity of the molecules. (iii) The average velocity of a  $H_2$  molecule at 273 K is 2000 ms<sup>-1</sup> if the average velocity of an  $O_2$  molecule at this temperature is 500 ms<sup>-1</sup>. (iv) The heavier the gas molecule is the quicker it travels through the container.

- (a) All statements are correct.
- (b) (i), (ii) and (iii) are correct.
- (c) (iv) is correct.
- (d) (iii) is correct.
- (e) None of the statements are correct.

(Option (b) is correct).

7. Which of the following is the correct expression for the equilibrium constant for the reaction:  $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ 

(a) 
$$K_c = \frac{[NO_2]}{[NO][O_2]}$$
, (b)  $K_c = \frac{[NO][O_2]}{[NO_2]}$ , (c)  $K_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$ ,

(d) 
$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$
, (e)  $K_c = \frac{[2NO]^2[O_2]}{[2NO_2]^2}$ 

(Option (d) is correct).

# Supplemental.

- Which of the following graphs does not give a straight line for an ideal gas? (a) P versus V, (b) P versus T, (c) V versus T, (d) Average kinetic energy vs T, (e) P versus n. (correct answer option (a)).
- 2. The equilibrium constant for the reaction of hydrogen gas and ethene to produce ethane under certain conditions is 9.8 x  $10^{18}$ .  $H_2(g) + C_2H_4(g) \rightleftharpoons C_2H_6(g)$  K = 9.8 x  $10^{18}$ . What is the equilibrium constant for the following reaction  $C_2H_6(g) \rightleftharpoons H_2(g) + C_2H_4(g)$  under the same conditions? (a) – 9.8 x  $10^{18}$ . (b) – 4.9 x  $10^{18}$ . (c) 1.9 x  $10^{19}$ . (d) 9.8 x  $10^{-18}$ . (e) 1.0 x  $10^{-19}$ . (Correct answer : option (e)).
- 3. The thermodynamic equilibrium constant for the following reaction
  2 SO<sub>2</sub>(g) + O<sub>2</sub>(g) = 2 SO<sub>3</sub>(g) is 0.15 at 1227°C. Which of the following statements are true? (i) The reaction is strongly product favoured. (ii) The reaction is reactant favoured. (iii) The change in Gibbs energy is negative. (iv) The change in Gibbs energy is 23.66 kJ mol<sup>-1</sup>.
  - (a) All statements are correct.
  - (b) (i) is correct.
  - (c) (ii) and (iv) are correct.
  - (d) (iii) is correct.
  - (e) None of the statements are correct.

(Correct option : answer (c)).

4. Which of the following statements pertaining to acids and bases are correct? (i) Acids are species which accept protons. (ii) Acid solutions have a pH value greater than 7. (iii) bases are species which donate protons. (iv) The pH of a base solution is less than 7. (v) The weaker the Bronsted Lowry acid the stronger is the conjugate base.

- (a) All statements are correct.
- (b) None of the statements are correct.
- (c) (i) and (ii) are correct.
- (d) (v) is correct.
- (e) (iii) and (iv) are correct.

(Correct answer: option (d)).

5. The Galvanic cell  $Zn|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu$  is based on the following cell reaction:  $2Cu^{2+}(aq) + Zn(s) \rightarrow 2Cu(s) + Zn^{2+}(aq)$ . Note that T = 298 K and the standard electrode potentials are  $E^0(Cu^{2+}, Cu) = 0.34V$  and  $E^0(Zn^{2+}, Zn) = -0.76V$ . Which of the following statements are correct? (i) The copper electrode is the cathode and the zinc electrode is the anode. (ii) Two moles of electrons flow through the external circuit from anode to cathode when the cell operates. (iii) The observed cell potential is 1.10 V. (iv) The change in Gibbs energy for the cell reaction is -212,300 J mol^{-1}.

- (a) All statements are correct.
- (b) (i) only.
- (c) (i) and (ii) only.
- (d) (iii) and (iv) only.
- (e) None of the statements are correct.

(Option (a) is correct).

6. Which of the following is the correct expression for the equilibrium constant for the reaction:  $2A(g) \rightleftharpoons 2B(g) + C(g)$ 

(a) 
$$K_c = \frac{[A]}{[B][C]}$$
, (b)  $K_c = \frac{[B][C]}{[A]}$ , (c)  $K_c = \frac{[A]^2}{[B]^2[C]}$ ,

(d) 
$$K_c = \frac{[B]^2[C]}{[A]^2}$$
, (e)  $K_c = \frac{[2B]^2[O_2]}{[2A]^2}$ . (Correct option = (d)).

7. On the space shuttle, the carbon dioxide produced by the astronauts is handled by an environmental control system that utilizes the following reaction.

 $CO_2(g)$  + 2LiOH(s)  $\longrightarrow$  Li<sub>2</sub>CO<sub>3</sub>(s) + H<sub>2</sub>O(l)

If the standard change in enthalpy and entropy for the reaction are  $\triangle H^{\circ} = -138.4 \text{ kJ}$  and  $\triangle S^{\circ} = -139 \text{ J/K}$ , then the standard change in Gibbs energy  $\triangle G^{\circ}$  at 298 K for this reaction is : (a) 4.13 x 10<sup>4</sup> kJ. (b) -135 kJ. (c) – 180 kJ. (d) – 97.0 kJ. (Correct answer option (d)).

### JF Chemistry Module CH 1101 2011.

# Annual 2011. Long Q

1.

- a. Discuss what is meant by the internal energy U and enthalpy H of a gas. Write down an expression for the first law of thermodynamics which relates the change in internal energy ΔU of a system and energy changes arising from transfers of heat q and work w. How may we interpret this expression when we specifically consider an isolated system?
- b. The temperature of 1 mol of a liquid is raised by heating it with 750 J of energy. It expands and does 200 J of work.
  Calculate the change in internal energy of the liquid.
- c. Derive a relationship between the change in enthalpy  $\Delta H$  and the change in internal energy  $\Delta U$  for a chemical reaction.
- d. Zinc metal reacts with dilute nitric acid according to the following equation:  $Zn(s) + 2 HNO_3(aq) \rightarrow H_2(g) + Zn(NO_3)_2(aq)$ . Calculate the difference between  $\Delta H$  and  $\Delta U$  for the latter reaction when T = 298 K.
- 2.
- a. Define (i) oxidation, (ii) reduction, (iii) Galvanic cell and (iv) standard electrode potential.
- b. Explain, using a carefully labelled diagram and chemical equations how the hydrogen/oxygen fuel cell operates. Why are fuel cells attractive as electricity sources?
- c. Derive, for a Galvanic cell, the relationship between the cell potential  $E^{0}_{cell}$  and the change in Gibbs energy  $\Delta G^{0}$  for the cell reaction. Indicate how you would calculate the equilibrium constant K from a knowledge of either  $\Delta G^{0}$  or  $E^{0}_{cell}$ .
- d. Calculate the equilibrium constant at 298 K for the reaction:

Sn(s) + 2 Cu<sup>2+</sup>(aq) → Sn<sup>2+</sup>(aq) + 2 Cu<sup>+</sup>(aq) given the following standard electrode potential values:  $E^0(Cu^{2+},Cu) = 0.15$  V and  $E^0(Sn^{2+},Sn) = -0.14$  V. Would this combination of redox couples form the basis of a good Galvanic cell?

# Annual 2011 MCQ

- The activation energy for the isomerization of cyclopropane to propene is 274 kJ/mol. By what factor does the rate of reaction increase as the temperature rises from 500°C to 550°C, assuming all else remains constant? (R = 8.314 J/mol K).
  - a. 1
  - b. 13
  - c. 2.6
  - d. 400
  - e. There is not enough information given to answer the question. (Correct option (b))
- 2. Which postulate of kinetic-molecular theory best accounts for the fact that gases can be compressed easily?
  - a. A gas is composed of molecules whose size is much smaller than the distances between them.
  - b. Gas molecules move randomly--at various speeds and in every possible direction.
  - c. Except when molecules collide, forces of attraction and repulsion between them are negligible.
  - d. When collisions occur, they are elastic.
  - e. The average kinetic energy of gas molecules is proportional to the absolute temperature. (Correct option: (a))
- 3. Given an aqueous solution of 0.30 M acetic acid ( $K_a = 1.8 \times 10^{-5}$ ), the pH is approximately
  - a. 0.52
  - b. 2.6
  - c. 4.7
  - d. 5.3
  - e. 6.1 (Correct option: (b))

- 4. Calculate the mass of gold that could be plated from a solution with a current of 0.40 A for 22 min.
  - a. 0.0018 g
  - b. 0.0060 g
  - c. 0.36 g
  - d. 1.10 g
  - e. 3.20 g (Correct option: (c))
- 5. A large flask of water is placed on a heater and 100 J of energy is transferred reversibly to the water at 298 K. What is the change in entropy of the water?
  - a. + 0.336 J K<sup>-1</sup>
  - b.  $-0.336 \text{ J K}^{-1}$
  - c. + 3.36 J K<sup>-1</sup>
  - d.  $3.36 \text{ J K}^{-1}$
  - e. There is not enough information given to answer the question. (Correct option: (a)).
- 6. The pH of a 0.01 M aqueous solution of the antiseptic mandelic acid is 2.95. What is the  $K_A$  of this acid?
  - a. 1.40 x 10<sup>-4</sup>
  - b. 14 x 10<sup>4</sup>
  - c. 1.40 x 10<sup>-7</sup>
  - d. 140
  - e. There is not enough information provided to solve the problem. (Correct option: (a)).
- 7. The standard free energy of reaction  $\Delta_r G^0$  for the reaction:  $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$  is -141.74 kJ mol<sup>-1</sup> at 298K. What is the free energy of reaction  $\Delta_r G$  when the partial pressure of each gas is 100 bar?
  - a. 153.16 kJ mol<sup>-1</sup>

- b. 153.16 kJ mol<sup>-1</sup>
- c. 1532 kJ mol<sup>-1</sup>
- d. 153.16 J mol<sup>-1</sup>
- e. There is not enough information provided to solve the problem. (Correct option: (b)).
- 8. Consider the following Galvanic cell  $Zn(s)|Zn^{2+}(aq)|Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$ . If the standard potential  $E^{0}(Zn^{2+},Zn) = -0.76$  V and the standard cell potential  $E^{0}_{cell} = 0.91$  V, then the standard potential of the  $Sn^{4+/2+}$  redox couple is
  - a. 0.15 V
  - b. 0.15 V
  - c. 150 V
  - d. 1.67 V
  - e. 1.67 V (Correct option: (b)).

# Supplemental 2011. Long Questions

- 1.
- a. Define the terms weak acid, acid dissociation constant  $K_{\text{A}},$  and pH.
- b. Derive an expression for the pH of a solution of a weak acid HA involving the acid dissociation constant K<sub>A</sub> and the molar concentration c of the acid. Outline any approximations made in this derivation.
- c. The K<sub>A</sub> value of hypochlorous acid HCIO is  $3.5 \times 10^{-8}$ . Calculate the pH of a 0.0075 M concentration of this acid at 298 K.
- 2.
- a. Define the terms (i) reaction rate, (ii) reaction order, (iii)
   rate constant and (iv) activation energy, (v) half life.
- b. Describe using a suitable equation (the Arrhenius equation) how the rate constant for a chemical reaction varies with changes in solution temperature, and show

how the activation energy of a chemical reaction may be evaluated by examining rate constant versus temperature data and constructing a suitable graph.

c. Rate constants for the reaction CO(g) + NO<sub>2</sub>(g) → CO<sub>2</sub>(g)
+ NO(g) were measured at four different temperatures. The data is outlined in tabular form below. Use this data and the Arrhenius equation to evaluate the activation energy of the reaction.

Rate	0.0521	0.101	0.184	0.332
constant				
k/M <sup>-1</sup> s <sup>-1</sup>				
T/K	288	298	308	318

# Supplemental 2011 MCQ

1. Consider the electrochemical cell diagram shown below. As you observe the reaction in the cell, you notice that the tin electrode seems to be disappearing while there are deposits forming on the silver electrode. Which of the following is a correct statement?



- a. The silver electrode is the cathode and the tin electrode is the anode.
- b. Electrons are flowing from the silver electrode to the tin electrode.
- c. Nitrate ions are flowing through the salt bridge to the silver solution.
- e. The silver electrode is the anode and the tin electrode is the cathode. (Correct option: (a)).
- 2. Which of the following statements is a **true** statement concerning a reaction that has reached a state of equilibrium?
  - a. A system has reached equilibrium when the concentrations of reactants and products remain constant.
  - b. A system has reached equilibrium when the reaction has stopped and no more products are formed.
  - c. A system has reached equilibrium when the concentrations of reactants and products correspond to the stoichiometric ratios determined by the balanced equation.
  - A system has reached equilibrium when the rate constant for the forward reaction equals the rate constant of the reverse reaction. (Correct option: (a)).
- 3. For the reaction of A  $\rightarrow$  B, which of the following statements about the rates of forward and reverse reactions is true at time x?



- a. The rate of forward reaction is greater.
- b. The rate of reverse reaction is greater.
- c. The rates of forward and reverse reactions are equal.
- d. The relative rates of reaction cannot be determined from the graph.
- e. None of the options are correct. (Correct option: (c)).
- 4. Calculate the Gibbs free energy change for the following reaction which produces the metal zinc from its ore zinc(II) oxide.  $2 \operatorname{ZnO}(s) \rightarrow 2 \operatorname{Zn}(s) + O_2(g)$  given that  $\Delta G^0_f(Zn) = 0.0 \text{ kJ/mol}, \Delta G^0_f(O_2(g)) = 0.0 \text{ kJ/mol}, \Delta G^0_f(ZnO(s)) = -318.3 \text{ kJ/mol}.$ 
  - a. 318.3 kJ/mol
  - b. 636.6 kJ/mol
  - c. + 318.3 kJ/mol
  - d. + 636.6 kJ/mol
  - e. + 734.5 kJ/mol (correct option: (d)).
- 5. 25 mL of 0.5 M HCl is added to a coffee cup calorimeter containing 50 mL of 0.5 M NaOH at 25°C. After stirring, the final temperature of the solution in the calorimeter was measured as 27.21°C. Calculate the change in enthalpy  $\Delta H$  for the neutralization reaction. Assuming that the total volume is the same as the sum of the individual volumes and

that the final solution has the same density and specific heat capacity as water so density  $\rho = 1.0 \text{ g mL}^{-1}$  and specific heat capacity c is given by c= 4.184 J g<sup>-1</sup>K<sup>-1</sup>.

- a. 55.4 kJ mol<sup>-1</sup>
  b. + 55.4 kJ mol<sup>-1</sup>
  c. 693 J
  d. + 693 J
  e. 693 kJ mol<sup>-1</sup> (Option: (a) correct).
- 6. Which of the following statements referring to a Galvanic cell are correct?
  - (i) A Galvanic cell is an electrochemical energy generator.
  - (ii) Oxidation occurs at the anode.
  - (iii) Reduction occurs at the cathode.
  - (iv) Electrons flow from cathode to anode through the external circuit
  - (v) The relationship between cell potential  $E^{0}_{cell}$  and the change in Gibbs energy for the cell reaction under standard conditions is  $\Delta G^{0} = - nFE^{0}_{cell}$ , where F is the Faraday constant and n denotes the number of electrons flowing through the circuit.
    - a. All statements are correct
    - b. Statements (i), (ii), (iii), (v)
    - c. Statements (i), (ii), (iii), (iv)
    - d. Statements (ii), (iii), (iv) and (v)
    - e. None of the statements are correct. (Correct option(b)).
- 7. Propanoic acid  $CH_3CH_2COOH$  is a carboxylic acid whose salts are used to retard mould growth in foods. What is the hydrogen ion concentration of an 0.1 M propanoic acid solution given that  $K_A = 1.3 \times 10^{-5}$ .
  - a. 1.1 x 10<sup>-3</sup> M
  - b. 11 x 10<sup>-5</sup> M

- c. 110 x 10<sup>-3</sup> M
- d. 1.0 x 10<sup>-7</sup> M
- e. 1.0 x 10<sup>-9</sup> M (Option (a) correct).
- 8. In order to study hydrogen halide decomposition a researcher fills an evacuated 2.0 L flask with 0.20 mol HI gas and allows the following reaction to proceed at 453°C,  $2HI(g) = H_2(g) + I_2(g)$ . At equilibrium

[HI] = 0.078 M. The value of the equilibrium constant  $K_{\rm c}$  is

- a. 0.02
- b. 20.0
- c. 200
- d. 2000
- e. 0.0002 (Correct option: (a)).

# JF Science Chemistry CH 1101

# Annual 2012. Long Questions

 (a) What is internal energy? Write down an expression for the first law of thermodynamics which relates the change in internal energy of a system to the energy changes arising from transfers of heat q and work w. Explain in words what this expression tells us. Using this expression what can we conclude if the system is regarded as isolated? What are the units of internal energy?

(b) Explain what is meant by the term entropy in thermodynamics. Give a mathematical definition of entropy. What is the relationship between entropy and probability? What are the units of entropy?

(c) A 100 W electric heater is used to heat gas in a cylinder for 10 min. The gas expands from 500 cm<sup>3</sup> to 21.4 dm<sup>3</sup> against a pressure of 1.10 atm. What is the change in internal energy of the gas?

(d) Calculate the entropy change when 1.0 mol of water at 373 K vaporizes to steam. You may assume that the enthalpy change  $\Delta_{vap}H^0$  for water is 40.7 kJ mol<sup>-1</sup>.

2. (a) Discuss what is meant by the concept of the 'equilibrium constant' K of a chemical reaction and indicate how such a quantity may be formally defined for the general reaction  $aA + bB \rightarrow pP + qQ$  where A,B denote reactants and P,Q denote products. What is the thermodynamic definition of equilibrium in terms of the change in Gibbs energy  $\Delta G$ ?

(b) Write down the relationship between the equilibrium constant and the standard change in Gibbs energy  $\Delta G^0$ .

(c)The thermodynamic equilibrium constant K is 6.46 at 373 K for the reaction  $N_2O_4(g) \rightarrow 2NO_2(g)$ . 1 mol of  $N_2O_4$  is introduced into a sealed container at 373K. The final pressure in the container is 1.5 bar when the system comes to equilibrium. Find the composition of the mixture at equilibrium. Note that 1 bar =  $1 \times 10^5$  Pa.

## Annual 2012. MCQ

- 1. Which of the following statements is a **true** statement concerning a reaction that has reached a state of equilibrium?
  - a. A system has reached equilibrium when the concentrations of reactants and products remain constant.
  - b. A system has reached equilibrium when the reaction has stopped and no more products are formed.
  - c. A system has reached equilibrium when the concentrations of reactants and products correspond to the stoichiometric ratios determined by the balanced equation.
  - A system has reached equilibrium when the rate constant for the forward reaction equals the rate constant of the reverse reaction. (Correct option: (a)).
- 25 mL of 0.5 M HCl is added to a coffee cup calorimeter containing
   50 mL of 0.5 M NaOH at 25°C. After stirring, the final temperature of the solution in the calorimeter was measured as 27.21°C.

Calculate the change in enthalpy  $\Delta H$  for the neutralization reaction. Assuming that the total volume is the same as the sum of the individual volumes and that the final solution has the same density and specific heat capacity as water so density  $\rho = 1.0$  g mL<sup>-1</sup> and specific heat capacity c is given by c= 4.184 J g<sup>-1</sup>K<sup>-1</sup>.

- a. 55.4 kJ mol<sup>-1</sup>
- b. + 55.4 kJ mol<sup>-1</sup>
- c. 693 J
- d. + 693 J
- e. 693 kJ mol<sup>-1</sup> (**Option: (a) correct**).
- 3. Which of the following statements referring to a Galvanic cell are correct?
- (vi) A Galvanic cell is an electrochemical energy generator.
- (vii) Oxidation occurs at the anode.
- (viii) Reduction occurs at the cathode.
- (ix) Electrons flow from cathode to anode through the external circuit
- (x) The relationship between cell potential  $E^{0}_{cell}$  and the change in Gibbs energy for the cell reaction under standard conditions is  $\Delta G^{0} = - nFE^{0}_{cell}$ , where F is the Faraday constant and n denotes the number of electrons flowing through the circuit.
  - f. All statements are correct
  - g. Statements (i), (ii), (iii), (v)
  - h. Statements (i), (ii), (iii), (iv)
  - i. Statements (ii), (iii), (iv) and (v)
  - j. None of the statements are correct. (Correct option(b)).
- 4. An inflated balloon has a volume of 6 dm<sup>3</sup> at sea level where the pressure P = 1 atm. It is allowed to ascend until the pressure is 0.45 atm. Furing ascent, the temperature of the gas falls from 295 K to 252 K. The volume of the balloon at its final altitude is:

- a. 11.0 dm<sup>3</sup>
- b. 110 dm<sup>3</sup>
- c. 1.0 dm<sup>3</sup>
- d.  $0.11 \text{ dm}^3$
- e. There is not enough information supplied to solve the problem. (Correct option: (a)).
- 5. The pH of a 0.028 M solution of NaOH is (note that  $K_w = 1.0 \times 10^{-14}$ ) :
  - a. 12.45
  - b. 2.45
  - c. 14.0
  - d. 5.6
  - e. 7.0 (Correct option (a))
- 6. The pH of a buffer solution consisting of a weak acid HA and its conjugate base A<sup>-</sup> can be calculated by which of the following formulae ?
  - a.  $pH = pK_A + log([A^-]/[HA])$
  - b.  $pH = pK_A log([HA]/[A^-])$
  - c.  $pH = K_A + [A^-]/[HA]$
  - d.  $pH = K_A [A^-]/[HA]$
  - e.  $pH = K_A + [HA]/[A^-]$  (Correct option (a))
- 7. Consider the electrochemical cell diagram shown below. As you observe the reaction in the cell, you notice that the tin electrode seems to be disappearing while there are deposits forming on the silver electrode. Which of the following is a correct statement?



- f. The silver electrode is the cathode and the tin electrode is the anode.
- g. Electrons are flowing from the silver electrode to the tin electrode.
- h. Nitrate ions are flowing through the salt bridge to the silver solution.
- i. The half-reaction occurring at the tin electrode is  $Sn^{4+} + 2e^{-}$ -----S $n^{2+}$ .
- j. The silver electrode is the anode and the tin electrode is the cathode. (Correct option: (a)).

# Supplemental 2012.

 (a) Define what is meant by the term 'Ideal Gas'. Write down the equation of state of an ideal gas. Under what conditions does the behaviour of real gases conform to the behaviour expected of ideal gases?

(b) Calculate the volume occupied by 1.0 mol of an ideal gas at 298 K and 1 atm pressure. Note that 1 atm = 101325 Pa.

(c) Write down Dalton's law of partial pressures for a mixture of ideal gases. A mixture of nitrogen and carbon dioxide contains  $38.4\% N_2$  by mass. What is the mole fraction of  $N_2$  in the mixture ? Hence calculate the mole fraction of  $CO_2$  in the mixture. If the total pressure P is 1.2

atm, what is the partial pressure of each gas in Pa? Note that the molar masses of  $CO_2$  and  $N_2$  are 44.01 g mol<sup>-1</sup> and 28.0 g mol<sup>-1</sup> respectively.

2. (a) Define the term pH as applied to aqueous solutions. What is a weak acid ? How is the acidity of a weak acid quantified?

(b) Define what is meant by a buffer solution. Provide an example of a buffer solution and describe how such a solution works.

(c) Write down an expression for the pH of a buffer solution (the Henderson-Hasselbalch equation). Hence calculate the pH of a buffer solution containing 0.15 mol dm<sup>-3</sup> ethanoic acid and 0.205 mol dm<sup>-3</sup> sodium ethanoate given that the  $pK_A$  for ethanoic acid is 4.76 at 298 K.

# Supplemental 2012. MCQ

- The equilibrium constant for the reaction H<sub>2</sub>(g) + I<sub>2</sub>(g) → 2 HI(g) at 698 K is K = 54.3. If 0.50 mol of H<sub>2</sub> and 0.50 mol of I<sub>2</sub> are present initially in the vessel which has a volume of 5.25 dm<sup>3</sup> then the composition of the gas at equilibrium is:
  - a. [H<sub>2</sub>] = [I<sub>2</sub>] = 0.0203 M, [HI] = 0.15 M
  - b.  $[H_2] = [I_2] = 0.0406 \text{ M}, [HI] = 0.15 \text{ M}$
  - c.  $[H_2] = [I_2] = 0.0609 \text{ M}, [HI] = 0.30 \text{ M}$
  - d.  $[H_2] = [I_2] = 0.0203 \text{ M}, [HI] = 0.30 \text{ M}$

(Correct option (a))

- A balloon indoors, where the temperature is 300 K, has a volume of 2.0 dm<sup>3</sup>. What will its volume be outdoors where the temperature is 250 K. You may assume that the pressure remains constant.
  - a. 1.67 dm<sup>3</sup>
  - b. 167 dm<sup>3</sup>
  - c.  $0.167 \text{ dm}^3$

d. 16.7 dm<sup>3</sup> (Correct answer option (a))

- e.
- 3. Propanoic acid  $CH_3CH_2COOH$  is a carboxylic acid whose salts are used to retard mould growth in foods. What is the hydrogen ion concentration of an 0.1 M propanoic acid solution given that  $K_A = 1.3 \times 10^{-5}$ .
  - a. 1.1 x 10<sup>-3</sup> M
  - b. 11 x 10<sup>-5</sup> M
  - c. 110 x 10<sup>-3</sup> M
  - d. 1.0 x 10<sup>-7</sup> M
  - e.  $1.0 \times 10^{-9}$  M (Option (a) correct).
- 4. Consider the following Galvanic cell  $Zn(s)|Zn^{2+}(aq)|Sn^{4+}(aq),Sn^{2+}(aq)|Pt(s)$ . If the standard potential  $E^{0}(Zn^{2+},Zn) = -0.76$  V and the standard cell potential  $E^{0}_{cell} = 0.91$  V, then the standard potential of the Sn<sup>4+/2+</sup> redox couple is
  - a. 0.15 V
  - b. 0.15 V
  - c. 150 V
  - d. 1.67 V
  - e. 1.67 V (Correct option: (b)).
  - f.
- 5. The pH of a 0.01 M aqueous solution of the weak acid HA is 2.95. What is the  $K_{A}$  of this acid?
  - a. 1.40 x 10<sup>-4</sup>
  - b. 14 x 10<sup>4</sup>
  - c. 1.40 x 10<sup>-7</sup>
  - d. 140
  - e. There is not enough information provided to solve the problem. (Correct option: (a)).
  - f.
- 6. A large flask of water is placed on a heater and 200 J of energy is transferred reversibly to the water at 298 K. What is the change in entropy of the water?

- b. 0.671 J K<sup>-1</sup>
  c. + 3.36 J K<sup>-1</sup>
  d. 3.36 J K<sup>-1</sup> (Correct option (a))
  e.
- 7. The change in Gibbs Energy  $\Delta G^0$  under standard conditions for a chemical reaction is 200 kJ mol<sup>-1</sup>. At a temperature of 298 K the corresponding equilibrium constanmt will be:
  - a. 80.71
  - b. 807
  - c. 8.71
  - d. 0.871 (correct option (a))

# JF Science Chemistry CH 1101

## Annual 2013. Long Questions

- 1.
- a. Describe what you understand by the terms closed, open and isolated system. Write down a mathematical expression for the first law of thermodynamics explaining each of the terms involved. Why can we state that the total internal energy of an isolated system is constant?
- b. Define the terms specific and molar heat capacities  $C_s$  and  $C_m$  and write down mathematical expressions which can be used to calculate a numerical value for these quantities.
- c. The specific heat capacity of liquid water is 4.18 JK<sup>-1</sup>g<sup>-1</sup>.
   Calculate the energy required to heat 1.0 mol of water from 298 K to 363 K.
- d. The standard enthalpy change of vaporization of ethanol  $C_2H_5OH$  is 43.5 kJmol<sup>-1</sup>. Calculate the enthalpy change when 0.5 g of ethanol vaporizes at its boiling point at 1 bar pressure.
- e. Derive a mathematical relationship between the enthalpy and the internal energy of a chemical reaction assuming that any gas phase reactants or products obey the ideal gas equation. The change in internal energy for the combustion of naphthalene at 298 K which proceeds according to  $C_{10}H_8(s) + 12 O_2(g) \rightarrow 10 CO_2(g) + 4 H_2O$  (I) was measured in a bomb calorimeter as  $\Delta U^0 = -5142$  kJ mol<sup>-1</sup>. Calculate the enthalpy of combustion of naphthalene  $\Delta H^0$  at 298 K.
- 2.
- a. What do you understand by the terms equilibrium constant K and reaction quotient Q ? What is the relationship between Q and K for a (i) spontaneous reaction and (ii) a reaction at equilibrium?

- b. Write down the mathematical relationship between the change in Gibbs energy  $\Delta G$  and the reaction quotient Q. Show that this expression reduces to  $\Delta G^0 = -RT \ln K$  when the reaction is at equilibrium.
- c. Industrially methanol is prepared via the following reaction:  $CO(g) + 2 H_2(g) \rightarrow CH_3OH(g)$ . Calculate the equilibrium constant for the reaction at 298 K given the following data for the Gibbs energy of formation  $DG^0$  at 298 K (units: kJ mol<sup>-1</sup>) : CO(g) = -137.2;  $H_2(g) = 0$ ;  $CH_3OH(g) = -162.0$ .

# Annual MCQ

- The density of O<sub>2</sub> gas at 273 K and 1 atm pressure (assuming that the universal gas constant R = 0.08206 dm<sup>3</sup> atm mol<sup>-1</sup>K<sup>-1</sup> and the molar mass of molecular oxygen is 32 g mol<sup>-1</sup>) is (a) 1.43 g dm<sup>-3</sup>; (b) 0.143 g dm<sup>-3</sup>; (c) 14.3 g dm<sup>-3</sup>; (d) 0.0143 g dm<sup>-3</sup>; (e) There is not enough data provided to answer the question. {correct answer: option (a)}
- Kinetic theory states that two gases at the same temperature must have the same average kinetic energy. Determine the average velocity of a H<sub>2</sub> molecule at 273 K if the average velocity of an O<sub>2</sub> molecule at this temperature is 500 ms<sup>-1</sup>. (a) 2000 ms<sup>-1</sup>; (b) 200 ms<sup>-1</sup>; (c) 20 ms<sup>-1</sup>; (d) 2 ms<sup>-1</sup>; (e) 0.2 ms<sup>-1</sup>. [Correct answer: option (a)].
- 3. The pH of an 0.10 M solution of the weak acid hypochlorous HOCI ( $K_A = 2.9 \times 10^{-8}$ ) is : (a) 4.27; (b) 11.0 ; (c) 7.0; (d) 1.0; (e) 3.5. [Correct answer: option (a)]
- 4. A reaction decays via first order kinetics with a rate constant given by 5 x 10<sup>-2</sup> s<sup>-1</sup>. The half life of the reaction is (a) 13.8 s; (b) 138 s;
  (c) 138 hours; (d) 1.38 s; (e) 0.138 s. [correct answer: option (a)].
- 5. The change is standard Gibbs energy ∆G<sup>0</sup> at 298 K for the reaction N<sub>2</sub>(g) + 3 H<sub>2</sub>(g) →2 NH<sub>3</sub>(g) is 32.96 kJ. The equilibrium constant K for this reaction at 298 K is (a) 60 x 10<sup>5</sup>; (b) 6.0 x 10<sup>5</sup>; (c) 600; (d) 6 x 10<sup>-5</sup>; (e) 1.0. [Correct answer: option (b)].

- 6. Calculate the equilibrium constant at 298 K for the reaction between Zn metal and acid which can be written as: Zn(s) + 2  $H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$  given that the standard reduction potentials are  $E^0(H^+,H_2) = 0.0$  V and  $E^0(Zn^{2+}, Zn) = -0.76$  V. You may assume that F = 95,500 Cmol<sup>-1</sup> and R = 8.314 Jmol<sup>-1</sup>K<sup>-1</sup>. (a) 5.53 x 10<sup>25</sup>; (b) 5.53 x 10<sup>-25</sup>; (c) 5.53; (d) 100; there is not enough data given to answer the question. [Correct answer: option (a)].
- 7. A small cylinder of oxygen gas has a volume of 5 dm<sup>3</sup>. The cylinder is stored at 293 K and the pressure inside is 56 bar. Assuming that oxygen behaves as an ideal gas under these conditions, calculate the mass of oxygen in the cylinder. Note that 1 bar = 1 x 10<sup>5</sup> Pa. (a) 370 g; (b) 37 g; (c) 3700 g; (d) 0.37 g; (e) 0.037 g. [Correct answer: option (a)].

# Supplemental

- 1.
- a. Explain the terms anode, cathode, electrolytic and Galvanic cell.
- b. Using a clearly labelled diagram explain how the hydrogen/oxygen fuel cell operates.
- c. Derive the relationship between the change in Gibbs energy for the cell reaction  $\Delta G^0$  and the equilibrium cell potential difference between cathode and anode  $E^0_{cell}$ .
- d. Calculate the cell potential  $E^{0}_{cell}$ , the change in Gibbs energy  $\Delta G^{0}$  at 298 K and the equilibrium constant K for the following cell reaction Fe<sup>2+</sup>(aq) + Ag<sup>+</sup>(aq)  $\rightarrow$ Fe<sup>3+</sup>(aq) + Ag(s) assuming the following values for the standard reduction potentials:  $E^{0}(Ag^{+},Ag) = 0.80 \text{ V}$  and  $E^{0}(Fe^{3+},Fe^{2+}) = 0.77 \text{ V}.$

2.

a. Provide a definition for the pH of an aqueous solution and describe mathematically how it can be related to the hydrogen ion activity present in the solution.

b. What is the difference between a strong and a weak acid? How can the strength of a series of different weak acids be compared?

c. Make labelled diagrams of the titration curves expected when (i) a strong base is added to a strong acid and (ii) a strong base is added to a weak acid. You should point out features of interest in both of these curves. How could these experiments be best monitored experimentally?

d. Describe, using chemical equations, how a buffer solution such as the acetic acid/sodium acetate system works in maintaining the solution pH constant over a defined region.

#### Supplemental

- A balloon occupies a volume of 600 cm<sup>3</sup>. What volume will it occupy if the surrounding pressure is reduced so that the pressure in the balloon is reduced to one third of its starting value? (a) 200 cm<sup>3</sup>; (b) 900 cm<sup>3</sup>; (c) 1800 cm<sup>3</sup>; (d) 2400 cm<sup>3</sup>; (e) 100 cm<sup>3</sup>.
- 2. The root mean square speed of an ideal gas molecule is given by  $v = \sqrt{3RT/M}$  where M denotes the molar mass of the molecule. At 293 K the root mean square speed of butane gas C<sub>4</sub>H<sub>10</sub> is (a) 355 ms<sup>-1</sup>; (b) 35.5 ms<sup>-1</sup>; (c) 3,500 ms<sup>-1</sup>; (d) 3.55 ms<sup>-1</sup> (e) 400 ms<sup>-1</sup>. Assume that R = 8.314 Jmol<sup>-1</sup>K<sup>-1</sup>.
- The rate constant of a reaction which obeys first order kinetics is 6.6 x 10<sup>-4</sup> s<sup>-1</sup>. Then the half life of the reaction is : (a) 17.5 min; (b) 20 min; (c) 175 min; (d) 1750 min; (e) 17.5 s. [Correct answer: option: option (a)].
- 4. The standard enthalpy change of vaporization of ethanol C<sub>2</sub>H<sub>5</sub>OH is + 43.5 kJ mol<sup>-1</sup>. Calculate the enthalpy change when 0.5 g of ethanol vaporizes at its boiling point at 1 bar. (a) 0.5 kJ; (b) 0.05 kJ; (c) 5 kJ; (d) 15 kJ; (e) 50 kJ. [Correct answer: option (a)].
- The specific heat capacity of liquid water is 4.18 JK<sup>-1</sup>g<sup>-1</sup>. Calculate the energy required to heat 1.0 mol of water from 298 K to 363 K. (a) 4.9 kJ; (b) 1.0 kJ; (c) 49 kJ; (d) 42 kJ; (e) 0.49 kJ. [correct answer: option (a)].
- 6. Calculate the change in Gibbs energy □G<sup>0</sup> when 1.0 mol ice melts at 283 K given that □H<sup>0</sup><sub>fus</sub>(H<sub>2</sub>O) = + 6.01 kJmol<sup>-1</sup> and □S<sup>0</sup><sub>fus</sub>(H<sub>2</sub>O) = + 22 JK<sup>-1</sup>mol<sup>-1</sup>. (a) 0.22 kJmol<sup>-1</sup>; (b) + 0.22 kJmol<sup>-1</sup>; (c) 2.2 kJmol<sup>-1</sup>; (d) 0.22 Jmol<sup>-1</sup>; + 22 kJmol<sup>-1</sup>. [Correct answer: option (a)].

7. The relationship between the change in Gibbs energy under standard conditions  $\Delta G^0$  and the equilibrium constant K of a reaction is: (a)  $\Delta G^0 = RTK$ ; (b)  $\Delta G^0 = RT \ln K$ ; (c)  $\Delta G^0 = -RT \ln K$ ; (d)  $\Delta G^0 = K/RT$ ; (e)  $\Delta G^0 = -RTK$ . [Correct answer: option (c)].

## JF Chemistry Module CH1101.

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## Miscellaneous Problems.

## Problem Sheet 1.

# Introduction to Physical Chemistry: Gas Laws and Chemical Thermodynamics.

- A 1x10<sup>3</sup> L steel storage tank contains 88.5 kg of methane CH<sub>4</sub>. If the temperature of the gas is 298 K determine the pressure inside the tank.
- 2. A sample of helium gas is held at constant temperature inside a cylinder of volume 0.80 L, where a piston exerts a pressure of 1.5 x 10<sup>5</sup>Pa. If the external pressure on the piston is increased to 2.1 x 10<sup>5</sup> Pa, what will the new volume of the gas be?
- Calculate the work done by a system in which a reaction results in the formation of 1 mol CO<sub>2</sub> gas at 298 K and 100 kPa. Assume that CO<sub>2</sub> behaves as an ideal gas.
- 4. Calculate the work done when 1 mol Ar gas confined in a cylinder of volume 1 dm<sup>3</sup> at 298 K expands isothermally and reversibly to 2 dm<sup>3</sup>.
- 5. A strip of magnesium metal of mass 12.5 g is dropped into a beaker of dilute hydrochloric acid. Given that the Mg is the limiting reactant, calculate the work done by the system as a result of the reaction. The atmospheric pressure is 1 atm and the temperature is 293.2 K.

- 6. A system absorbs 300 J of heat and at the same time expands by 1  $dm^3$  against a constant pressure of 1 atm. Determine the change in internal energy and enthalpy in the system. Note that 1 atm =  $1.013 \times 10^5 \text{ Nm}^{-2}$ .
- If the enthalpy of combustion of solid citric acid is 1986 kJ mol<sup>-1</sup>, calculate the heat liberated when 10 g of solid citric acid undergoes total combustion at 298 K: (i) at constant pressure, (ii) at constant volume. Note: citric acid has formula C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>. The molar mass M = 192 g mol<sup>-1</sup>. Total combustion means reaction with O<sub>2</sub> and conversion to CO<sub>2</sub> and H<sub>2</sub>O.

## Problem Sheet 2.

# Introduction to Physical Chemistry: Gas Laws and Chemical Thermodynamics.

- 1. Calculate the mole fraction of  $N_2$ ,  $O_2$  and Ar in dry air at sea level, given that 100g of air consists of 75.5 g of  $N_2$ , 23.2 g  $O_2$  and 1.3 g Ar.
- 2. Determine the mean free path of oxygen molecules in a sample of oxygen at SATP (298K, 1 bar) given that the collision cross section of oxygen is  $\sigma = 0.4 \text{ nm}^2$ .
- 3. In an experiment to measure the heat released by the combustion of a sample of nutrient, the compound was burned in a calorimeter and the temperature was observed to rise by 3.22°C. When a current of 1.23 A from a 12 V source flows through a heater in the same calorimeter for a time of 156 s, the temperature rose by 4.47°C. What is the heat released by the combustion reaction?

- 4. Show that the difference in molar heat capacities for a perfect gas is given by:  $C_{P,m} C_{V,m} = R$ .
- 5. Ethanol C<sub>2</sub>H<sub>5</sub>OH is brought to the boil at 1 atm. When an electric current of 0.682 A from a 12 V supply is passed for 500s through a heating coil immersed in the boiling liquid, it is found that the temperature remains constant but 4.33 g of ethanol is vaporized. What is the enthalpy of vaporization of ethanol at its boiling point at 1 atm?
- 6. The standard enthalpy of formation of gaseous water at 298 K is -241.82 kJ mol<sup>-1</sup>. Estimate its value at 373 K. Note that the molar heat capacities at constant pressure for H<sub>2</sub>O(g), H<sub>2</sub>(g) and O<sub>2</sub>(g) are 33.58 JK<sup>-1</sup>mol<sup>-1</sup>, 28.84 JK<sup>-1</sup>mol<sup>-1</sup>, and 29.37 JK<sup>-1</sup>mol<sup>-1</sup> respectively.
- 7. Calculate the change in molar entropy when a sample of hydrogen gas expands isothermally to twice its initial volume.
- Calculate the change in molar entropy when hydrogen gas is heated from 293K to 303K at constant volume. The molar heat capacity at constant volume for hydrogen is 22.44 JK<sup>-1</sup>mol<sup>-1</sup>.
- 9. Suppose a certain small bird has a mass of 30g. what is the minimum mass of glucose that it must consume to fly to a branch 10 m above the ground? The change in Gibbs energy the oxidation of 1 mol glucose ( $C_6H_{12}O_6$ ) to carbon dioxide and water vapour at 298K is 2828 kJ.
- 10. Estimate the composition of a solution in which two isomers A and B are in equilibrium  $A \xleftarrow{\kappa} B$  at 37°C assuming that  $\Delta_r G^0 = -2.2$  kJmol<sup>-1</sup>.

- 11. Calculate the equilibrium constant of the reaction  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$  at 298K given that the change in standard Gibbs energy for the reaction is 32.90 kJmol<sup>-1</sup>.
- 12. Suppose that in an industrial process  $N_2$  at 1.00 bar is mixed with  $H_2$  at 3.00 bar and the two gases are allowed to come to equilibrium with the product ammonia in a reactor at constant volume in the presence of a catalyst. At the temperature of the reaction it has been determined experimentally that the equilibrium constant K = 977. What are the partial pressures of the three gases at equilibrium?

# Problem Sheet 3.

## **Chemical Equilibria and Electrochemistry**

1.

- a. What do you understand by the terms weak acid and solution pH? Provide an example of a weak acid and indicate the way that the acid strength of a weak acid can be quantified.
- b. Calculate the pH of a 5.0 x  $10^{-2}$  M NaOH solution given the information that  $K_w = 1.0 \times 10^{-14}$ .
- c. Calculate the  $H_3O^+$  ion concentration and the pH of a 0.003 M  $Ba(OH)_2$  solution assuming that the ion product  $K_w = 1.0 \times 10^{-14}$ .
- d. Derive an expression for the pH of an aqueous solution of weak acid HA of concentration c and having an acid dissociation constant K<sub>A</sub>. If K<sub>A</sub> is assumed to be very small derive an approximate expression for the solution pH mentioning any approximations which you make.
- e. Use the theoretical results derived in part c to calculate the pH of a weak acid solution of concentration 0.1 M and having an acid dissociation constant  $K_A = 3.5 \times 10^{-8}$ .
- f. Explain using chemical equations where pertinent, the observation that the pH of an aqueous sodium acetate solution

is alkaline whereas the pH of an ammonium chloride solution is acidic.

- g. Explain using an example how a buffer solution works and derive an expression for the pH of a buffer solution containing a weak acid HA and its conjugate base A<sup>-</sup>. Use this expression to calculate the pH of a solution containing 0.75 M lactic acid ( $K_A =$ 1.4 x 10<sup>-4</sup>) and 0.25 M sodium lactate.
- 2.
- a. What do you understand by the terms equilibrium constant K and reaction quotient Q.
- b. Derive an expression which relates the change in reaction Gibbs energy  $\Delta G$  to the equilibrium constant K and the reaction quotient Q according to:  $\Delta G = RT \ln\left(\frac{Q}{K}\right)$ . Indicate how this expression may be used to relate the sign of  $\Delta G$  (and hence to the question of whether the reaction occurs in a spontaneous or non spontaneous manner) to the relative magnitudes of Q and K.
- c. The standard change in Gibbs energy for a chemical reaction at a temperature of 298 K is – 150 kJ mol<sup>-1</sup>. Determine the equilibrium constant of the reaction.
- d. The following equation  $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$  describes the formation of NO which contributes to air pollution whenever a fuel is burnt in air in a closed container at a high temperature as in a gasoline engine. At 1500K the equilibrium constant K = 1 x  $10^{-5}$ . Suppose that a sample of air has  $[N_2] = 0.80$  mol dm<sup>-3</sup> and  $[O_2] = 0.20$  mol dm<sup>-3</sup> before any reaction occurs. Calculate the equilibrium concentrations of reactants and products after the mixture has been heated to 1500K.
- 3.
- Briefly explain using specific examples and clearly labelled diagrams how a Galvanic (Voltaic) cell and how a Polymer Membrane Electrolyte (PEM) fuel cell operates.

- b. The net reaction that occurs in a voltaic cell is  $Zn(s)+2Ag^+(aq) \rightarrow Zn^{2+}(aq)+2Ag(s)$ . Write down the half reactions that occur at the anode and cathode. If the standard reduction potentials at 298K are  $E^0(Ag^+,Ag)=0.799V$  and  $E^0(Zn^{2+},Zn) = -0.763V$ , calculate the voltage developed by the cell, the change in reaction Gibbs energy  $\Delta G^0$  and the equilibrium constant K for the cell reaction. Is the reaction strongly product favoured?
- c. Consider a galvanic cell involving the following half-reactions:  $Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s), E^{0}(Ni^{2+},Ni) = -0.25 \text{ V}; Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s), E^{0}(Cr^{3+},Cr) = -0.74 \text{ V}.$  Calculate the cell potential observed at a temperature of 298 K when  $[Ni^{2+}] = 1.0 \times 10^{-4} \text{M}$ and  $[Cr^{3+}] = 2.0 \times 10^{-3} \text{M}.$
- d. In a large number of samples of water in which the copper ion concentration is expected to be quite small, the  $[Cu^{2+}]$  was measured using an electrochemical cell. This setup consisted of a silver electrode dipping into a 1.0 M solution of AgNO<sub>3</sub>, which was connected by a salt bridge to a second compartment containing a copper electrode. The copper compartment was then filled with one water sample after another and the cell potential was measured for each sample. In the analysis of one particular sample the cell potential at 298 K was measured as 0.62 V, with the copper electrode being the anode. What was the concentration of  $Cu^{2+}$  ion in this sample. Note that the relevant reduction potentials are  $E^0(Cu^{2+}, Cu) = 0.34$  V and  $E^0(Ag^+, Ag) = 0.80$  V.
- e. What mass of copper is deposited on the cathode of an electrolytic cell if an electric currentof 2A is passed through a solution of CuSO<sub>4</sub> for a period of 20 min.