COLÁISTE NA TRÍONÓIDE, BAILE ÁTHA CLIATH | TRINITY COLLEGE DUBLIN
Ollscoil Átha Cliath | The University of Dublin

JF Physical Chemistry 2010-2011.

JF CH 1101: Introduction to Physical Chemistry.

Dr Mike Lyons.

School of Chemistry
Trinity College
Dublin 2.

melyons@tcd.ie

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

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 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 Dr Lyons in the first semester to students taking CH 1101.

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

Mike Lyons
1 September 2010

JF Chemistry Module CH1101. 2009

MCQ Semister 1 Test

1. Consider the synthesis of ammonia which proceeds according to the following reaction: ½ $N_2(g)$ + 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^{-1} at T = 298 K then the equilibrium constant K for the reaction is:

   (a) 7.38 x 10^2 **(Answer)**

   (b) 7.38 x 10^{-2}

   (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 J $mol^{-1}K^{-1}$.

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

(a) 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 ΔG 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 $E^0(Cd^{2+},Cd) = -0.40$ V and $E^0(Fe^{2+},Fe) = -0.44$ 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_3 (g), H_2(g) and N_2(g) are 0.94 M, 1.60 M and 0.52 M respectively. The numerical value of the equilibrium constant K_c 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^- ion for an aqueous solution with a pH of 9.45. Note that the ion product of water K_w = 1 x 10^{-14}. (a) 1.8 x 10^{-10} M ; (b) 1.0 x 10^{-14} M ; (c) 2.8 x 10^{-5} M ; (d) 0.35 M ; (e) 3.5 x 10^{-10} M. Correct answer: c
3. A buffer contains equal concentrations of a weak acid HA and its conjugate base A^-. If the value of K_A for the weak acid is 1.0 x 10^{-9}, 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^0 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^{56} ; (b) 37.8 ; (c) 2.9 x 10^{9} ; (d) 2.5 x 10^{28} ; (e) 1.4 x 10^{3}. Correct answer: a.

Supplemental

1. Consider the reaction: $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$. If the standard molar free energy of formation of NH_3(g) at 298 K is – 16.45 kJ mol^{-1}, calculate the equilibrium constant for this reaction at 298 K. (a) 3.62 x 10^{-2} ; (b) 1.66 x 10^{-3} ; (c) 5.26 x 10^{-14} ; (d) 1.71 x 10^{-6} ; (e) 2.29 x 10^{-7}. Correct answer: d.
2. The pH of 0.1 M CH_3COOH is 2.87. What is the value of K_A for CH_3COOH? (a) 1.3 x 10^{-3} ; (b) 1.8 x 10^{-6} ;(c) 1.8 x 10^{-5} ; (d) 0.037; (e) 2.7 x 10^{-6}. 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. Dr Mike Lyons

Section A Long Questions 2010.

Annual.

1.

Answer **<u>either</u>** : part (a) and part (b) **<u>or</u>** 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 ΔU and the change in enthalpy ΔH 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 ΔU and change in enthalpy ΔH 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 $Jg^{-1}K^{-1}$) and the heat capacity of the bomb is 837 JK^{-1}. 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 ΔG^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^{-1}, 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^{-1}. 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 5.0×10^{-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.

1. 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 1.0×10^{-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) = 1.80×10^{-5} and $K_W = 1.0 \times 10^{-14}$ 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 $Cu\left|Cu^{2+}(aq)\right\|Ag^{+}(aq)\left|Ag\right.$ is based on the following cell reaction: $2Ag^{+}(aq)+Cu(s)\rightarrow 2Ag(s)+Cu^{2+}(aq)$. Note that T = 298 K and the standard electrode potentials are $E^{0}(Cu^{2+},Cu)=0.34V$ and $E^{0}(Ag^{+},Ag)=0.80V$. 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^{-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 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^{-1} if the average velocity of an O_2 molecule at this temperature is 500 ms^{-1}. (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.

1. 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 9.8×10^{18}. $H_2(g) + C_2H_4(g) \rightleftharpoons C_2H_6(g)$ $K = 9.8 \times 10^{18}$. 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) – 9.8×10^{18} . (b) – 4.9×10^{18}. (c) 1.9×10^{19}. (d) 9.8×10^{-18}. (e) 1.0×10^{-19}.
   (Correct answer : option (e)).
3. The thermodynamic equilibrium constant for the following reaction $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$ 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^{-1}.
   (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 $Zn\left|Zn^{2+}(aq)\right\|Cu^{2+}(aq)\left|Cu\right.$ 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.

$$CO_2(g) + 2LiOH(s) \longrightarrow Li_2CO_3(s) + H_2O(l)$$.

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

JF Chemistry Module CH1101.

Dr Mike Lyons, School of Chemistry, Trinity College Dublin.
Email: melyons@tcd.ie

Problem Sheet 1.

Introduction to Physical Chemistry: Gas Laws and Chemical Thermodynamics.

1. A 1×10^3 L steel storage tank contains 88.5 kg of methane CH_4. 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 1.5×10^5Pa. If the external pressure on the piston is increased to 2.1×10^5 Pa, what will the new volume of the gas be?

3. Calculate the work done by a system in which a reaction results in the formation of 1 mol CO_2 gas at 298 K and 100 kPa. Assume that CO_2 behaves as an ideal gas.

4. Calculate the work done when 1 mol Ar gas confined in a cylinder of volume 1 dm^3 at 298 K expands isothermally and reversibly to 2 dm^3.

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 = 1.013×10^5 Nm^{-2}.

7. If the enthalpy of combustion of solid citric acid is – 1986 kJ mol^{-1}, 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^{-1}. Total combustion means reaction with O_2 and conversion to CO_2 and H_2O.

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 = 0.4 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_2H_5OH 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^{-1}. Estimate its value at 373 K. Note that the molar heat capacities at constant pressure for H_2O(g), H_2(g) and O_2(g) are 33.58 JK^{-1}mol^{-1}, 28.84 JK^{-1}mol^{-1}, and 29.37 JK^{-1}mol^{-1} respectively.

7. Calculate the change in molar entropy when a sample of hydrogen gas expands isothermally to twice its initial volume.

8. 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^{-1}mol^{-1}.

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 $A \overset{K}{\rightleftharpoons} B$ at 37°C assuming that Δ_rG^0 = - 2.2 kJmol^{-1}.

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 $kJmol^{-1}$.

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 5.0×10^{-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 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 x 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^-. Use this expression to calculate the pH of a solution containing 0.75 M lactic acid (K_A = 1.4 x 10^{-4}) 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 ΔG 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 ΔG (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^{-1}. Determine the equilibrium constant of the reaction.

d. The following equation $N_2(g)+O_2(g)\rightleftarrows 2NO(g)$ 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^{-3} and $[O_2]$ = 0.20 mol dm^{-3} before any reaction occurs. Calculate the equilibrium concentrations of reactants and products after the mixture has been heated to 1500K.

3.

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 ΔG^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.

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 $AgNO_3$, 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 $CuSO_4$ for a period of 20 min.