

**UNIVERSITY OF ZAMBIA**  
**SCHOOL OF NATURAL SCIENCES**  
**FINAL EXAMINATIONS 2016/2017 ACADEMIC YEAR, SEPTEMBER 2017**  
**C2615: BASIC PHYSICAL CHEMISTRY**

**Duration: Three (3) Hour**

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**Instructions:**

Answer any **four (4)** questions.

Answer each question in a **separate answer booklet**.

All questions carry equal marks. **(20 Marks)**

You are reminded to answer questions in a clear and logical manner.

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**Useful Information and Constants:**

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

Molar volume of gas at STP =  $22.4 \text{ dm}^3 \text{ mol}^{-1}$ , STP = 273 K and 1 atm, 1 cal = 4.18 J

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 1.01325 \times 10^5 \text{ Nm}^{-2}$$

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**Question 1**

- (a)
- (i) Dalton's law of partial pressures states that the total pressure of a mixture of gases is the sum of the partial pressures of the components of the mixture. Which assumption of the kinetic molecular theory justifies this law? Explain in brief.
  - (ii)  $200 \text{ cm}^3$  of oxygen is collected over water at  $25 \text{ }^\circ\text{C}$  and 1 atm. If the oxygen obtained is dried at constant temperature of  $25 \text{ }^\circ\text{C}$  and 1 atm, what volume will it occupy?
  - (iii) What volume will be occupied by the water removed from the oxygen if maintained at  $25 \text{ }^\circ\text{C}$  and 1 bar? (The equilibrium vapour pressure of water at  $25 \text{ }^\circ\text{C}$  is 0.04 bar)
- (b) Suppose 0.167 g of ethanol,  $\text{C}_2\text{H}_5\text{OH}$ , was injected into  $100 \text{ cm}^3$  a gas syringe. The syringe placed in a boiling water bath for several minutes. The atmospheric pressure was 0.99 bar and the temperature of the bath was  $100 \text{ }^\circ\text{C}$ .
- (i) What volume of ethanol would have been produced under these conditions?
  - (ii) Make comment on the suitability of the syringe used.

### Question 2

- (a) Define the term *internal energy* as used to describe chemical systems.
- (b) Calculate the change in internal energy for the reaction given below using the data provided at 25 °C.



Substance	NaCl (s)	H <sub>2</sub> SO <sub>4</sub> (l)	HCl(g)	Na <sub>2</sub> SO <sub>4</sub> (s)
$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	- 410	- 810	- 92	-1383

- (c) Explain how water freezing at -10 °C can be thermodynamically spontaneous, even though entropy decreases.
- (d) Determine the amount of heat required to convert 10 g of ice at 0 °C to vapour at 100 °C. For water  $\Delta_{\text{fus}} H = 334 \text{ J g}^{-1}$ ,  $\Delta_{\text{vap}} H = 2, 257 \text{ J g}^{-1}$  and  $C_p = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$ .

### Question 3

- (a) A CHE2615 student studying kinetics of a reaction  $\text{A} + \text{B} \rightarrow \text{C}$  collected following data:

$$[\text{B}] = 10.00 \text{ mol dm}^{-3}$$

Time	[A] mol dm <sup>-3</sup>
0	0.1000
10	0.0900
20	0.0800
30	0.0700
40	0.0600
50	0.0500

Then she repeats the experiment with  $[\text{B}] = 5.0 \text{ mol dm}^{-3}$

Time	[A] mol dm <sup>-3</sup>
0	0.1000
10	0.0975
20	0.0950
30	0.0925
40	0.0900
50	0.0875

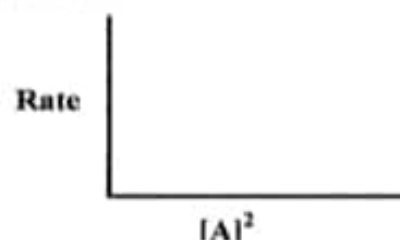
- (i) Plot concentration time graph for the results with  $[B] = 5.0 \text{ mol dm}^{-3}$ .
- (ii) What is the order of reaction with respect to A.
- (iii) What is the concentration of B at 50 minutes in each experiment?
- (iv) What is the pseudo rate constant ( $k$ ) when  $[B] = 5.00 \text{ mol dm}^{-3}$ . Calculate the pseudo rate constant when  $[B]$  is  $10 \text{ mol dm}^{-3}$ .
- (v) Calculate the order with respect to B.
- (vi) Write the rate law with the value of rate constant with its unit.

(b) The reaction



is a second order with respect to NOBr. If  $[\text{NOBr}]_0 = 7.5 \times 10^{-3} \text{ M}$ .

- (i) How much NOBr will be left after a reaction time of 10 minutes?
- (ii) Determine the half-life of this reaction.
- (iii) Complete the sketch given for the reaction with a rate constant,  $k = 0.810 \text{ M}^{-1} \text{ s}^{-1}$  at  $10^\circ \text{C}$



#### Question 4

A saturated solution of silver chloride AgCl has a specific conductance of  $2.28 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$  at  $25^\circ \text{C}$ . The specific conductance of the water used to make up this solution is  $0.116 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$ . The limiting molar ionic conductance of the two ions are  $\Lambda_{\text{Ag}^+}^\circ = 0.00619$  and  $\Lambda_{\text{Cl}^-}^\circ = 0.00763 \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ .

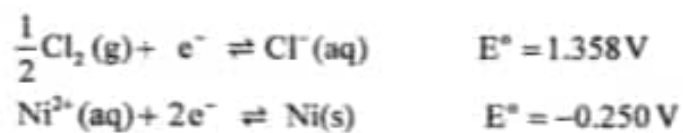
- (a)
  - (i) Calculate molar solubility,  $s$ , of AgCl in  $\text{mol L}^{-1}$
  - (ii) Determine the  $K_{\text{sp}}$  of AgCl.
- (b) From the following data calculate the molar conductance at infinite dilution of  $\text{NH}_4 \text{OH}$ .  
Molar conductance at infinite dilution of  $\text{Ba(OH)}_2$ ,  $\text{Ba(Cl)}_2$ , and  $\text{NH}_4 \text{Cl}$  are  $0.05254$ ,  $0.02799$ , and  $0.014985 \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$  respectively. Hint : balance the ions and simplify.
- (c) A  $0.00100 \text{ M}$  acetic acid has a resistance of  $21605 \Omega$  when measured in a conductance cell of cell constant  $105.0 \text{ m}^{-1}$ . The molar conductance at infinite dilution of acetic acid is  $0.03905 \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ .
  - (i) Calculate the specific conductance of the electrolyte.
  - (ii) Determine the degree of dissociation of acetic acid.

### Question 5

Consider a cell



The reduction potentials of the cell at 25 °C are given below.



- Using an appropriate ionic strength of the electrolyte, calculate the mean activity coefficient of  $\text{NiCl}_2$ , using the Debye- Hückel limiting law.
- Write the cell reaction.

**END OF EXAMINATION**

**SECTION A: Answer all questions**

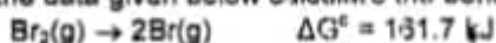
- A1.** Cement is a vital material in the construction industry. An important chemical reaction in the manufacture of Portland cement is the high temperature decomposition of calcium carbonate to give calcium oxide and carbon dioxide.



Suppose that 1.25 g  $\text{CaCO}_3$  is decomposed by heating, what volume of  $\text{CO}_2$  is evolved if it is measured at 740 torr and 25 °C?

- A2.** The concentration of a drug in the body is often expressed in units of milligram per kilogram of body weight. The initial dose in an animal was 25 mg/kg body weight. After 2 hours, this concentration dropped to 15 mg/kg body weight. If the drug is eliminated metabolically by a first order process, what is the rate constant for the process  $\text{min}^{-1}$ ?

- A3.** (a) Define bond dissociation enthalpy.  
(b) The entropies of  $\text{Br}_2(\text{g})$  and  $\text{Br}(\text{g})$  are 245.4 and 174.9  $\text{J mol}^{-1} \text{K}^{-1}$  respectively at 298 K. Using the data given below calculate the bond energy of  $\text{Br}_2$ .

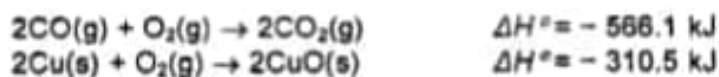


- A4.** A hydrocarbon is burned in a container with a movable piston with a cross-section area of  $0.5 \text{ m}^2$ . If the piston moved a distance of 30 cm against a pressure of 1 atm, how much work is done in the expansion?

- A5.** (a) Copper metal can be obtained by heating copper oxide in the presence of carbon monoxide according to the equation



Calculate  $\Delta H^\circ$  in kJ given the following thermochemical equations.



- (b) Construct an enthalpy diagram for the reaction between  $\text{CuO}(\text{s})$  and  $\text{CO}(\text{g})$  consistent with the result in A5(a) above.

- A6.** The equilibrium for the production methanol from CO and  $\text{H}_2$  is



The value of  $K_p$  at 500 K is  $6.23 \times 10^{-3}$ . Calculate  $\Delta_r G^\circ$ .

- A7.** By how much in degree centigrade will the normal freezing point of benzene ( $T_f^\circ = 5.53 \text{ }^\circ\text{C}$ ,  $K_f = 5.12 \text{ K Kg mol}^{-1}$ ) be reduced by addition of 10 g of hexane ( $M = 84.16 \text{ g/mol}$ ) to 100 g of benzene ( $M = 78.11 \text{ g/mol}$ ).

- A8.** Calculate the activity coefficient of  $\text{H}^+$  and  $\text{CH}_3\text{COO}^-$  in a solution which is 0.0078 M  $\text{CH}_3\text{COOH}$ . The degree of dissociation at this concentration is 4.8 percent.

**SECTION B: Answer any four (4) questions**

- B1. (a)** (i) State the first law of thermodynamics in words.  
 (ii) What equation defines the change in internal energy in terms of heat and work? Define the meaning of the symbols, including the significance of their algebraic signs.
- (b) The decomposition of calcium carbonate in limestone is used to make carbon dioxide



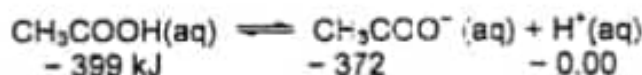
The reaction is endothermic and has  $\Delta H^\circ = +572 \text{ kJ}$ .

- (i) What is the value of  $\Delta E^\circ$  for this reaction?  
 (ii) Determine the percent difference between  $\Delta E^\circ$  and  $\Delta H^\circ$ .  
 (iii) Under what conditions is  $\Delta H^\circ \equiv \Delta E^\circ$ ?
- B2. (a)** A 1.00 mol sample of propane a gas used for cooking in some rural households was placed in a bomb calorimeter with excess oxygen and ignited. The reaction was



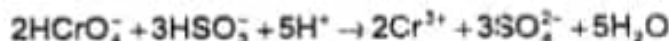
The initial temperature of the calorimeter was 25.000 °C and its total heat capacity was 97.1 kJ °C<sup>-1</sup>. The reaction raised the temperature of the calorimeter to 27.282 °C.

- (i) What is the heat of reaction of propane with oxygen expressed in kJ per mole of C<sub>3</sub>H<sub>8</sub> burned?  
 (ii) What is the internal energy change for the combustion reaction involving propane as described above?
- (b) For ionisation of acetic acid in aqueous solution



The standard free energy of formation  $\Delta G_f^\circ$  at 25 °C are immediately under each species in kJ mol<sup>-1</sup>.

- (i) Calculate the standard free energy change and the equilibrium constant for the reaction.  
 (ii) What additional information is required to determine the equilibrium constant at a different temperature?
- B3. (a)** For the reaction



the rate law is  $= k[\text{HCrO}_4^-][\text{HSO}_3^-]^2[\text{H}^+]$

- (i) What is the order of reaction with respect to each of the reactants?  
 (ii) What is the overall order of reaction?

- (b) The initial stage of decomposition for a new drug just discovered by an UNZA research student according to a consecutive reaction was found to be first order. The initial concentration  $C_0$  of the solution was 0.050 mole/litre and after 10 hrs at 40 °C, the drug concentration  $C$  was 0.015 mole/litre.
- What is the drug concentration after 2 hours?
  - If the  $k$  value for this reaction at 20 °C is  $0.0020 \text{ hr}^{-1}$ , what is the activation energy and the Arrhenius factor  $A$  for the reaction?
- (c) Explain the concept of activation energy within the context of the collision theory.

B4. The following is the schematic for a cell:



The standard electrode potential for the half-cell  $\text{Ag} | \text{Ag}^+$  electrode is 0.7992 V and that for  $\text{Ag} | \text{AgBr} | \text{Br}$  is 0.0732 V.

- Write the cell reaction.
  - Calculate  $E^\circ_{\text{cell}}$ .
  - Calculate the equilibrium constant for the reaction
  - What is the solubility product  $K_{\text{sp}}$  of AgBr?
- B5. The reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  takes place at 298 K and 1 bar and  $K_p = 0.141$ . The extent of reaction of the above reaction is

$$\xi = \frac{1}{\left[1 + \left(\frac{4}{K_p}\right)\left(\frac{P}{P^\circ}\right)\right]^{1/2}}$$

- Calculate  $\xi$  at 1 bar and mole fractions of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ .
- Calculate  $\xi$  at 10 bars and mole fractions of  $\text{N}_2\text{O}_4(\text{g})$  and  $\text{NO}_2(\text{g})$ .
- In what direction is the equilibrium shift when the total pressure of the gases is increased from 1 bar to 10 bars?
- Calculate  $K_p$  using the mole fractions calculated in (b) using the relationship.

$$K_p = K_y \left(\frac{P}{P^\circ}\right)^{\nu}$$

END OF EXAMINATION

### Question 1

- (a) Determine the pressure in atm exerted by 1 mole of methane placed into a bulb with a volume of 244.6 cm<sup>3</sup> at 25 °C. Carry out two calculations:
- (i) In the first calculation, assume that methane behaves as an ideal gas. **[4 marks]**
  - (ii) In the second calculation, assume that methane behaves as a real gas and obeys the van der Waals equation. The values of the constants *a* and *b* for methane are: *a* = 2.303 L<sup>2</sup> atm mol<sup>-2</sup> and *b* = 0.0431 L mol<sup>-1</sup>. **[4 marks]**
  - (iii) Is the gas in the repulsive or attractive region of the molecule-molecule potential **[2 marks]**
- (b) Three moles of an ideal gas expand isothermally from 50 to 300 L at 500 K. If the expansion is carried out reversibly, calculate:  $\Delta U$ , *w*, *q*, and  $\Delta S$ . **[10 marks]**

### Question 2

- (a) The molar heat capacity of solid gold is given by the relation

$$C_{p,m} = 25.69 - 7.32 \times 10^{-4} T + 4.58 \times 10^{-6} T^2,$$

in units of J mol<sup>-1</sup> K<sup>-1</sup>. Calculate the entropy change for heating 2.50 moles of gold from 22 °C to 1000 °C at constant pressure. **[8 marks]**

- (b) Consider that the following enthalpy changes are known for the stated reactions below.



- (i) What is the enthalpy change for the reaction shown known below? **[5 marks]**



- (ii) Draw a fully labeled enthalpy diagram for the reaction depicted in (i) above. **[4 marks]**

- (c) Calculate the quantity of heat required to heat a 1 kg block of aluminum from 30 °C to 60 °C. Assume that the specific heat of aluminum is 1 cal g<sup>-1</sup> °C<sup>-1</sup>. [3 marks]

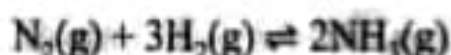
### Question 3

- (a) Consider the dissociation of an initial amount,  $n_0 = 1$  mole, of N<sub>2</sub>O<sub>5</sub> to NO<sub>2</sub> according to the reaction:



At 55 °C and 1 bar the average molar mass of partially dissociated N<sub>2</sub>O<sub>4</sub> is 61.2 g mol<sup>-1</sup>.

- (i) Write an expression for  $K_p$  in terms of the extent of the reaction. [8 marks]  
(ii) Determine the value of the extent of the reaction,  $\xi$ . [3 marks]  
(iii) Hence calculate  $K_p$ . [2 marks]
- (b) The value of  $\Delta_r H^\ominus$  is -12.93 kJ mol<sup>-1</sup> at 800 K for



Assuming the  $\Delta_r H^\ominus$  is independent of temperature, calculate  $K_p$  at 700 K given that  $K_p = 29.1$  at 1000 K [4 marks]

- (c) What is the value of the standard Gibbs energy for reaction in part (b) at 1000 K. [3 marks]

### Question 4

- (a) At 1000 °C, cyclobutane (C<sub>4</sub>H<sub>8</sub>) decomposes in a first order reaction, with a very high rate constant of 87 s<sup>-1</sup> to two molecules of ethylene (C<sub>2</sub>H<sub>4</sub>).
- (i) If the initial C<sub>4</sub>H<sub>8</sub> concentration is 2.00 M, what is the concentration after 0.010 s? [3 marks]  
(ii) What fraction of C<sub>4</sub>H<sub>8</sub> has decomposed in this time? [2 marks]
- (b) What is the half-life of a radioisotope that has a rate constant of 0.225 d<sup>-1</sup>? [5 marks]
- (c) The nitrogen dioxide (NO<sub>2</sub>) produced during driving is a health hazard. Chemists attempting to remove it have investigated the effect of heating it to high temperatures. At 300 °C the concentration of NO<sub>2</sub> drops with time as in the table below.

Time (minutes)	[NO <sub>2</sub> ] (M)
0	2.40
5	2.60 × 10 <sup>-1</sup>
10	1.28 × 10 <sup>-1</sup>
20	7.58 × 10 <sup>-2</sup>
30	5.38 × 10 <sup>-2</sup>
40	4.17 × 10 <sup>-2</sup>
50	3.40 × 10 <sup>-2</sup>
60	2.87 × 10 <sup>-2</sup>

- (i) This reaction is thought to be either 1<sup>st</sup> order or second order. Plot the appropriate graphs and find the order of reaction. **[7 marks]**
- (ii) Calculate the rate constant. **[3 marks]**

### Question 5

- (a) A saturated solution of Ag<sub>2</sub>CO<sub>3</sub> had an electrical resistance of 3529.6 Ω when measured in a conductance cell with a cell constant of 38.54 m<sup>-1</sup> at 25 °C. The specific conductance of water was 0.00760 Ω<sup>-1</sup> m<sup>-1</sup>. The limiting molar conductance, Λ<sub>m</sub><sup>0</sup>, of Ag<sub>2</sub>CO<sub>3</sub> is 0.02624 Ω<sup>-1</sup> m<sup>2</sup> mol<sup>-1</sup> at a temperature of 25 °C.
- (i) Calculate the specific conductance of Ag<sub>2</sub>CO<sub>3</sub> corrected for the specific conductance of water. **[5 marks]**
- (ii) Determine the solubility of Ag<sub>2</sub>CO<sub>3</sub>. **[5 marks]**
- (b) The limiting molar conductance, Λ<sub>m</sub><sup>0</sup>, of NaI, NaCH<sub>3</sub>CH<sub>2</sub>, MgCH<sub>3</sub>CH<sub>2</sub>, are 12.69 × 10<sup>-3</sup> S m<sup>2</sup> mol<sup>-1</sup>, 9.10 × 10<sup>-3</sup> S m<sup>2</sup> mol<sup>-1</sup>, and 18.78 × 10<sup>-3</sup> S m<sup>2</sup> mol<sup>-1</sup> respectively, all at 25 °C. Use Kohlraush's law of the independence of migration of ions to calculate the limiting molar conductance of MgI. **[5 marks]**
- (c) The mobility of the acetate ion, CH<sub>3</sub>COO in aqueous solution at 25 °C is 4.24 × 10<sup>-8</sup> m<sup>2</sup> s<sup>-1</sup> V<sup>-1</sup>. Calculate the molar ionic conductance of the ions. **[5 marks]**

### Question 6

- (a) Consider a cell, below at a temperature of 25 °C,



The standard half-cell reduction potentials are:



The cell reaction is



- (i) Use the Debye-Hückel limiting law to calculate the mean ionic activity coefficient of HCl. **[4 marks]**
- (ii) Apply the Nernst equation determine the emf of the cell. **[7 marks]**

(b) An electrochemical cell:



has an emf of 0.5357 V and  $\partial E / \partial T = 1.45 \times 10^{-4} \text{ V K}^{-1}$  at 25 °C.

- (i) Calculate  $\Delta G$  of the cell reaction. **[3 mark]**
- (ii) Determine the entropy change,  $\Delta S$  of cell reaction. **[3 mark]**
- (iii) What is  $\Delta H$  of the cell reaction? **[3 mark]**