UNIVERSITY OF SIERRA LEONE

FOURAH BAY COLLEGE

FIRST EXAMINATION FOR THE DEGREE OF B. Sc. HONOURS

LEVEL I

SECOND SEMESTER EXAMINATION

WEDNESDAY 12th SEPTEMBER 2018 13.30 – 16.45

CHEM 121 – KINETICS, THERMODYNAMICS AND ELECTROCHEMISTRY

TIME ALLOWED: 3 HOURS PLUS 15 MINUTES READING TIME

INSTRUCTIONS:

- THIS PAPER IS DIVIDED INTO THREE SECTIONS: A, B AND C; ANSWER ALL QUESTIONS IN SECTION A AND ONE QUESTION FROM EACH OF SECTIONS B, C AND D
- A SCIENTIFIC CALCULATOR, PENCIL AND RULER ARE REQUIRED FOR THIS EXAMINATION

SECTION A (ANSWER ALL QUESTIONS)

SECTION B (ANSWER 1 QUESTION)

SECTION C (ANSWER 1 QUESTION)

SECTION D (ANSWER 1 QUESTION)

The value of the molar gas constant R = 8.31 $JK^{-1}mol^{-1}$
The specific heat capacity of water = 4.18 $JK^{-1}mol^{-1}$
Faraday's constant = 96500 $Cmol^{-1}$

The Periodic Table of the Elements

1	2											3	4	5	6	7	0
																	(18)
(1)	(2)			**Key**			1.0 **H** hydrogen 1					(13)	(14)	(15)	(16)	(17)	4.0 **He** helium 2
6.9 **Li** lithium 3	9.0 **Be** beryllium 4			relative atomic mass **symbol** name atomic (proton) number								10.8 **B** boron 5	12.0 **C** carbon 6	14.0 **N** nitrogen 7	16.0 **O** oxygen 8	19.0 **F** fluorine 9	20.2 **Ne** neon 10
23.0 **Na** sodium 11	24.3 **Mg** magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 **Al** aluminium 13	28.1 **Si** silicon 14	31.0 **P** phosphorus 15	32.1 **S** sulfur 16	35.5 **Cl** chlorine 17	39.9 **Ar** argon 18
39.1 **K** potassium 19	40.1 **Ca** calcium 20	45.0 **Sc** scandium 21	47.9 **Ti** titanium 22	50.9 **V** vanadium 23	52.0 **Cr** chromium 24	54.9 **Mn** manganese 25	55.8 **Fe** iron 26	58.9 **Co** cobalt 27	58.7 **Ni** nickel 28	63.5 **Cu** copper 29	65.4 **Zn** zinc 30	69.7 **Ga** gallium 31	72.6 **Ge** germanium 32	74.9 **As** arsenic 33	79.0 **Se** selenium 34	79.9 **Br** bromine 35	83.8 **Kr** krypton 36
85.5 **Rb** rubidium 37	87.6 **Sr** strontium 38	88.9 **Y** yttrium 39	91.2 **Zr** zirconium 40	92.9 **Nb** niobium 41	96.0 **Mo** molybdenum 42	[98] **Tc** technetium 43	101.1 **Ru** ruthenium 44	102.9 **Rh** rhodium 45	106.4 **Pd** palladium 46	107.9 **Ag** silver 47	112.4 **Cd** cadmium 48	114.8 **In** indium 49	118.7 **Sn** tin 50	121.8 **Sb** antimony 51	127.6 **Te** tellurium 52	126.9 **I** iodine 53	131.3 **Xe** xenon 54
132.9 **Cs** caesium 55	137.3 **Ba** barium 56	138.9 **La *** lanthanum 57	178.5 **Hf** hafnium 72	180.9 **Ta** tantalum 73	183.8 **W** tungsten 74	186.2 **Re** rhenium 75	190.2 **Os** osmium 76	192.2 **Ir** iridium 77	195.1 **Pt** platinum 78	197.0 **Au** gold 79	200.6 **Hg** mercury 80	204.4 **Tl** thallium 81	207.2 **Pb** lead 82	209.0 **Bi** bismuth 83	[209] **Po** polonium 84	[210] **At** astatine 85	[222] **Rn** radon 86
[223] **Fr** francium 87	[226] **Ra** radium 88	[227] **Ac †** actinium 89	[267] **Rf** rutherfordium 104	[268] **Db** dubnium 105	[271] **Sg** seaborgium 106	[272] **Bh** bohrium 107	[270] **Hs** hassium 108	[276] **Mt** meitnerium 109	[281] **Ds** darmstadtium 110	[280] **Rg** roentgenium 111	Elements with atomic numbers 112-116 have been reported but not fully authenticated						

* **58 – 71** Lanthanides	140.1 **Ce** cerium 58	140.9 **Pr** praseodymium 59	144.2 **Nd** neodymium 60	[145] **Pm** promethium 61	150.4 **Sm** samarium 62	152.0 **Eu** europium 63	157.3 **Gd** gadolinium 64	158.9 **Tb** terbium 65	162.5 **Dy** dysprosium 66	164.9 **Ho** holmium 67	167.3 **Er** erbium 68	168.9 **Tm** thulium 69	173.1 **Yb** ytterbium 70	175.0 **Lu** lutetium 71
† **90 – 103** Actinides	232.0 **Th** thorium 90	231.0 **Pa** protactinium 91	238.0 **U** uranium 92	[237] **Np** neptunium 93	[244] **Pu** plutonium 94	[243] **Am** americium 95	[247] **Cm** curium 96	[247] **Bk** berkelium 97	[251] **Cf** californium 98	[252] **Es** einsteinium 99	[257] **Fm** fermium 100	[258] **Md** mendelevium 101	[259] **No** nobelium 102	[262] **Lr** lawrencium 103

Section A

Answer all questions from this section.

A1. A student carried out an experiment to determine the enthalpy change when a sample of methanol (CH_4O) was burned. The student found that the temperature of 140 g of water increased from 21.0 °C to 28.5 °C when 0.352 g of methanol was burned in air and the heat produced was used to warm the water.

(a) Calculate the molar enthalpy of combustion of methanol.

(b) Hence calculate the energy released when 100 g of methanol is burned

[5]

A2. Gaseous ethanol burns according to the following equation:

$CH_3CH_2OH(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(g)$

(a) Consider these bond enthalpy data:

	C–H	C–C	C–O	O=O	C=O	O–H
Bond enthalpy / kJ mol^{-1}	412	348	360	496	805	463

Use these data to estimate the enthalpy of combustion of gaseous ethanol.

(b) Explain why your answer is only an estimation of the enthalpy of combustion of gaseous ethanol.

[5]

A3. (a) Use the standard enthalpy of formation data from the table and the equation for the combustion of butan-1-ol to calculate a value for the standard enthalpy of combustion of butan-1-ol.

	$CH_3CH_2CH_2CH_2OH(l)$	$O_2(g)$	$CO_2(g)$	$H_2O(l)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–327	0	–394	–286

$CH_3CH_2CH_2CH_2OH(l) + 6O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$

(b) How much energy would be released when enough butan-1-ol was burned to produce 100 g of CO_2?

[5]

A4. (a) Draw a Born-Haber cycle to show the formation of barium chloride ($BaCl_2$) from its elements.

(b) Use your Born–Haber cycle and the standard enthalpy data given below to calculate a value for the electron affinity of chlorine.

Enthalpy of atomisation of barium	+180 kJ mol^{-1}
Enthalpy of atomisation of chlorine	+122 kJ mol^{-1}
Enthalpy of formation of barium chloride	–859 kJ mol^{-1}
First ionisation enthalpy of barium	+503 kJ mol^{-1}
Second ionisation enthalpy of barium	+965 kJ mol^{-1}
Lattice formation enthalpy of barium chloride	–2056 kJ mol^{-1}

[5]

A5. (a) Explain why reactions are generally faster at higher temperatures.

(b) Explain why gas-phase reactions are generally faster at higher pressures.

[5]

A6. For the reaction $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$, the following rate data were collected:

Initial [NO]/M	Initial [H_2]/M	Initial rate/Ms^{-1}
0.60	0.37	3.0×10^{-3}
1.20	0.37	1.2×10^{-2}
1.20	0.74	1.2×10^{-2}

(a) Deduce the orders of reaction with respect to NO and H_2 and hence deduce the rate equation for the reaction.

(b) Calculate a value for the rate constant for the reaction and state its units.

[5]

A7. The Arrhenius equation shows how the rate constant of a reaction is related to its activation energy and the temperature: $k = Ae^{-\frac{E_a}{RT}}$.

A reaction has an activation energy of 50 $kJmol^{-1}$. How many times faster will this reaction be at 308 K than at 298 K?

[5]

A8. Consider the following electrochemical data:

$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$; $E^o = -0.76$ V

$V^{3+}(aq) + e \rightarrow V^{2+}(aq)$; $E^o = -0.26$ V

(a) Write the conventional representation of an electrochemical cell in which the two electrode half-reactions correspond to the half-equations above.

(b) Write an equation for the reaction taking place in the cell and deduce the emf of the cell.

[5]

A9. The following electrochemical cell was set up: Pt | $H_2SO_3(aq)$, $SO_4^{2-}(aq)$, || $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ |Pt

The emf of the cell was measured and found to be +0.60 V.

The standard electrode potential of the Fe^{3+}, Fe^{2+} electrode is +0.77 V

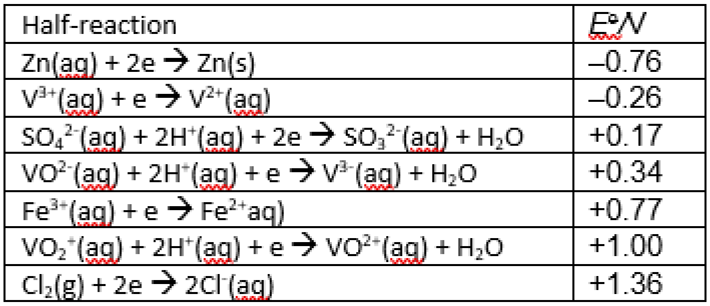
(a) Deduce the standard electrode potential of the H_2SO_3, SO_4^{2-} electrode

(b) Write the half-equation for the oxidation process taking place in this cell.

(c) Deduce the equation for the overall cell reaction.

[5]

A10. Consider the following electrochemical data:



Half-reaction	E^o/V
$Zn(aq) + 2e \rightarrow Zn(s)$	–0.76
$V^{3+}(aq) + e \rightarrow V^{2+}(aq)$	–0.26
$SO_4^{2-}(aq) + 2H^+(aq) + 2e \rightarrow SO_3^{2-}(aq) + H_2O$	+0.17
$VO^{2-}(aq) + 2H^+(aq) + e \rightarrow V^{3-}(aq) + H_2O$	+0.34
$Fe^{3+}(aq) + e \rightarrow Fe^{2+}aq)$	+0.77
$VO_2^+(aq) + 2H^+(aq) + e \rightarrow VO^{2+}(aq) + H_2O$	+1.00
$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$	+1.36

(a) From the table above, identify the species which is the most powerful reducing agent.

(b) identify a species which will oxidise VO^{2+} to VO_2^+ in acidic solution.

(c) Identify a species which will oxidise V^{3+} to VO^{2+} but will not oxidise VO^{2+} to VO_2^+ in acidic solution

(d) Write an equation for the reaction taking place in (b).

[5]

Section B

Answer one question from this section.

B1. This question is about enthalpy, entropy and free energy changes.

(a) Use the data in the table below to answer the questions which follow:

Substance	$Fe_2O_3(s)$	$Fe(s)$	$C(s)$	$CO(g)$	$CO_2(g)$
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	–824.2	0	0	–110.5	–393.5
$S^{\ominus}$ / J K^{-1} mol^{-1}	87.4	27.3	5.7	197.6	213.6

(i) Calculate the standard enthalpy change and the standard entropy change for the reaction: $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

(ii) Explain why this reaction is feasible at all temperatures.

(iii) Calculate the standard enthalpy change and the standard entropy change for the reaction: $Fe_2O_3(s) + 3C(s) \rightarrow 2Fe(s) + 3CO(g)$

(iv) Calculate the range of temperatures for which the reaction is feasible.

(15)

(b) Water can be converted to steam according to the following equation: $H_2O(l) \rightarrow H_2O(g)$
This process is endothermic and has an enthalpy change of +44 kJmol^{-1}.
The standard entropy of water is 69.9 Jmol^{-1}K^{-1}.
The standard entropy of steam is 188.7 Jmol^{-1}K^{-1}.

(i) Explain why the conversion of water to steam is endothermic.

(ii) Explain why steam has a higher entropy than water.

(iii) Calculate the entropy change for the conversion of water into steam.

(iv) Hence calculate the minimum temperature required for water to spontaneously change into steam and comment on your answer.

(10)

Total 25 marks

B2. This question is about the changes which take place when calcium hydroxide, $Ca(OH)_2$, is dissolved in water.
You will need the following data:
Lattice formation enthalpy of calcium hydroxide: -2637 $kJmol^{-1}$
Hydration enthalpy of hydroxide ion: -460 $kJmol^{-1}$
Hydration enthalpy of calcium ion: -1576 $kJmol^{-1}$
Entropy change of solution of calcium hydroxide: +374 $Jmol^{-1}K^{-1}$

(a) Draw an energy cycle to show the enthalpy changes taking place when calcium hydroxide dissolves in water. Include all state symbols. Use your cycle to calculate the enthalpy of solution of calcium hydroxide.

(6)

(b) Explain why the entropy increases when calcium hydroxide is dissolved in water.

(2)

(c) Use your answer to (a) and the entropy change of solution of calcium hydroxide given above to calculate the free energy change when calcium hydroxide dissolves in water at 298 K.

(2)

(d) What does your answer to (c) suggest about the solubility of calcium hydroxide in water?

(3)

(e) Explain how an increase in temperature is likely to affect the solubility of calcium hydroxide in water.

(3)

(f) The free energy change for a solution process is related to the solubility product by the following expression: $\Delta G = -RT\ln K_{sp}$.
Use this expression to calculate the solubility product for calcium hydroxide at 298 K.

(3)

(g) Hence calculate the solubility of calcium hydroxide in water at 298 K.

(3)

(h) Discuss the relative merits of ΔG, ΔH, ΔS and equilibrium constants in predicting the tendency of reactions to take place.

(3)

Total 25 marks

Section C

Answer one question from this section.

C1. This question is about orders of reaction.

(a) The decomposition of nitrogen dioxide $2NO_2(g) \rightarrow 2NO + O_2(g)$ was monitored using a continuous monitoring method and the following data was collected:

Time, s	$[NO_2]$, moldm^{-3}
0	0.0100
50	0.00787
100	0.00649
200	0.00481
300	0.00380
400	0.00318
500	0.00275
600	0.00234

Plot a graph to show how the concentration of NO_2 varies with time.

(6)

(b) Use your graph to deduce the first half-life of the reaction and the second half-life of your reaction.

(4)

(c) Hence show that the reaction is second order and write a rate equation for the reaction.

(2)

(d) Use your graph to determine the initial rate of the reaction. Hence calculate the rate constant for the reaction and give its units.

(4)

(e) Use your rate equation to suggest a possible rate-determining step for this reaction. Justify your choice.

(2)

(f) Another reaction, between three reactants A, B and C, was monitored using an initial rates method. The following rate data were collected:

Experiment	Initial concentration of **A** / mol dm^{-3}	Initial concentration of **B** / mol dm^{-3}	Initial concentration of **C** / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.10	0.40	0.80×10^{-3}
2	0.20	0.40	0.40	3.20×10^{-3}
3	0.10	0.80	0.40	1.60×10^{-3}
4	0.10	0.30	0.20	0.60×10^{-3}

Deduce the orders of reaction with respect to A, B and C. Hence write the rate equation for the reaction and calculate the value of the rate constant.

(7)

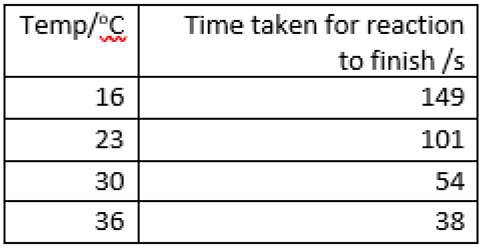
Total 25 marks

C2. This question is about different factors which affect the rate of a chemical reaction.

(a) Sketch a Maxwell-Boltzmann distribution of molecular energies at a particular temperature T_1. Label your graph T_1.
On the same axis, draw a distribution of molecular energies for the same gas at a higher temperature T_2. Label your verve T_2.

(5)

(b) A student carried out an experiment to determine how the rate of a chemical reaction varies with temperature. She obtained the following data:

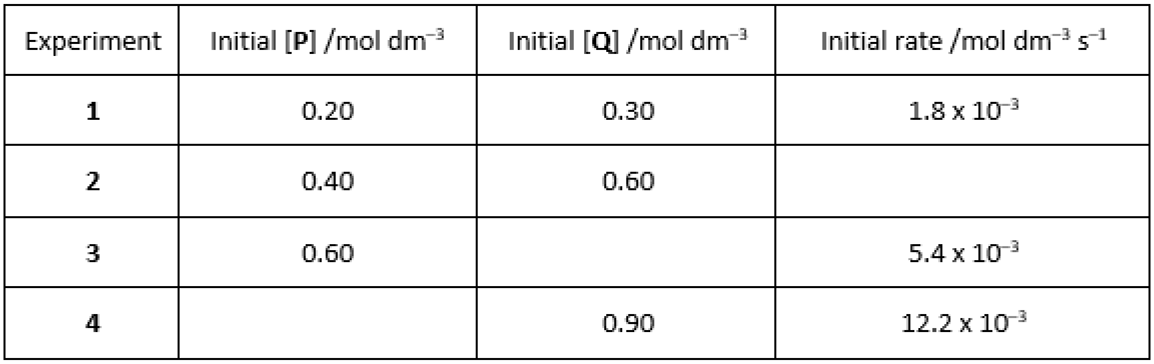


Temp/°C	Time taken for reaction to finish /s
16	149
23	101
30	54
36	38

(i) Use the Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$ to show that a graph of ln(k) against 1/T (in K^{-}) should give a straight line with gradient -Ea/R.
(ii) Explain why 1/time taken is proportional to k.
(iii) Plot a graph of ln(1/time taken) against 1/T (in K^{-1}).
(iv) Hence deduce the activation energy for the reaction.

(12)

(c) The rate equation for the reaction between two gases **P** and **Q** is rate = $k[\mathbf{P}]^2[\mathbf{Q}]$.
The initial rate of this reaction was measured in a series of experiments at a constant temperature.
The following data was obtained:



Experiment	Initial [**P**] /mol dm^{-3}	Initial [**Q**] /mol dm^{-3}	Initial rate /mol dm^{-3} s^{-1}
1	0.20	0.30	1.8 x 10^{-3}
2	0.40	0.60	
3	0.60		5.4 x 10^{-3}
4		0.90	12.2 x 10^{-3}

(i) Deduce the value of the rate constant for the reaction and give its units.
(ii) Calculate the initial rate of reaction in Experiment 2.
(iii) Calculate the initial [Q] in Experiment 3.
(iv) Calculate the initial [P] in Experiment 4.

[8]
Total 25 marks

Section D

Answer one question from this section.

D1. This question is about electrochemical cells.
The standard electrode potential for the half-reaction $Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$ is +0.77 V
The standard electrode potential for the half-reaction $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ is +0.34 V
These half-reactions can be used in a number of electrochemical cells.

(a) The standard electrode potential for $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ was measured directly using a standard hydrogen electrode.

- (i) Draw a fully labelled diagram to show the electrochemical cell you would set up in order to do this.
- (ii) Write half-equations for the reactions taking place at each electrode, and the overall chemical reaction taking place in the cell.
- (iii) Explain how charge moves around the different parts of the circuit.
- (iv) Explain why the emf of cells like this decrease over time.

(12)

(b) The half-reactions $Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$ and $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ can also be used together to make an electrochemical cell.

- (i) Write the conventional representation for this cell.
- (ii) Deduce the emf of the cell if both electrodes are set up under standard conditions.
- (iii) Suggest how the value of the emf of the cell would change if the concentration of Cu^{2+} ions was decreased. Explain your answer.
  Suggest how the value of the emf of the cell would change if the concentration of Fe^{2+} ions was decreased. Explain your answer.

(7)

(c) The quantitative relationship between an electrode potential and the concentration of aqueous species is expressed by the Nernst equation: $E = E^{o} + \frac{RT}{nF}\ln Q$. For $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$, $Q = \frac{[1]}{[Cu^{2+}]}$

- (i) State the meaning of "n" in the Nernst equation.
- (ii) Calculate the electrode potential of the Cu^{2+}/Cu electrode when $[Cu^{2+}] = 0.1\ moldm^{-3}$

(6)

Total 25 marks

D2. This question is about how electrochemical data can be used to predict the feasibility of different reactions.

(a) Use the following data to answer the questions below:

			$E^{\ominus}$/ V
$Ce^{4+}(aq) + e^{-}$	$\rightleftharpoons$	$Ce^{3+}(aq)$	+1.70
$MnO^{-}(aq) + 8H^{+}(aq) + 5e^{-}$	$\rightleftharpoons$	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^{-}$	$\rightleftharpoons$	$2Cl^{-}(aq)$	+1.36
$Fe^{3+}(aq) + e^{-}$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+0.77
$SO_4^{2-}(aq) + 4H^{+}(aq) + 2e^{-}$	$\rightleftharpoons$	$H_2SO_3(aq) + H_2O(l)$	+0.17

(i) State and explain what you would expect to happen when a solution containing Fe^{3+} ions was added to a solution containing Cl^{-} ions under standard conditions.

(ii) State and explain what you would expect to happen when a solution containing Fe^{3+} ions was added to a solution containing H_2SO_3 under standard conditions.

(iii) Identify a species which you could add to Mn^{2+} in order to convert it to MnO_4^{-} and write an equation for the reaction taking place.

(9)

(b) Use the following data to answer the questions below:

$Cu^{2+}(aq) + e \rightarrow Cu^{+}(aq)$, $E^{o} = +0.15$ V

$Cu^{+}(aq) + e \rightarrow Cu(s)$, $E^{o} = +0.52$ V

(i) Write an equation to show the disproportionation of Cu^{+} into Cu and Cu^{2+}.

(ii) Use the data above to deduce whether this reaction should take place under standard conditions.

(iii) Use the relationship $\Delta G = -nFE_{cell}$ to calculate the free energy change for the disproportionation of Cu^{+}.

(6)

(c) Use the following data to answer the questions below:

$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$, $E^{o} = -2.37$ V

$H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}(aq)$, $E^{o} = -0.44$ V

(i) Use the half-equations above to write an equation for the reaction of magnesium with water and show that is should be feasible under standard conditions.

(ii) Suggest why magnesium shows little reaction with water under standard conditions.

(iii) Use you answer to (c) (ii) to explain the difference between kinetic stability and thermodynamic stability.

(10)

Total 25 marks)