UNIVERSITY OF MINES AND TECHNOLOGY, TARKWA

FIRST SEMESTER EXAMINATIONS, NOV./ DEC. 2018

COURSE NO: ES 279
COURSE NAME: PRINCIPLES OF THERMODYNAMICS
CLASS: ES II **TIME:** 3 HOURS

Name**:** _____Index Number: _____

ANSWER ONLY THREE QUESTIONS (60MARKS)

QUESTION ONE (20 MARKS)

(a) Acid rain is the result of burning fossil fuels. The sulphur contained in the fossil fuels is oxidised to sulphur dioxide, SO_2, during combustion. In the atmosphere, SO_2 dissolves in water droplets where it forms sulphurous acid, H_2SO_3. The sulphurous acid can then be oxidised by other substances in the cloud water (substances such as peroxide, iron, copper) to form sulphuric acid, H_2SO_4. Could the following two reactions, the combustion of FeS_2 (pyrite) in the coal to yield SO_2 and the oxidation of SO_2 by Fe^{3+} in the clouds to yield H_2SO_4 proceed spontaneously at standard conditions? **(6 marks)**

$$2FeS_{2(s)} + 5.5O_{2(g)} \leftrightarrow Fe_2O_{3(s)} + 4SO_{2(g)}$$

$$H_2SO_{3(aq)} + 2Fe^{3+}_{(aq)} + H_2O_{(l)} \leftrightarrow H_2SO_{4(aq)} + 2Fe^{2+}_{(aq)} + 2H^+$$

(b) Determine whether the oxidation of sulphurous acid to sulphuric acid in part (a) could proceed in clouds under the following conditions. Assume that in clouds on an autumn day T = 25ºC, $[H_2SO_3] = 10^{-6}$ M, $[H_2SO_4] = 10^{-3.7}$ M, $[Fe^{3+}] = 10^{-8}$ M, $[Fe^{2+}] = 10^{-10}$ M and $[H^+] = 10^{-4}$ M. **(6 marks)**

(c) Determine the ratio of sulphurous acid to sulphuric acid at equilibrium using the measured concentrations of H^+, Fe^{2+} and Fe^{3+} provided in part (b). State clearly whether this reaction proceeds to the left or to the right under the assumed conditions inside the clouds. **(8 marks)**

NB: The Thermodynamic data below may be useful

Compound	G_f^0 (kJ/mole)
$FeS_{2(s)}$	160
$O_2(g)$	0
$Fe_2O_{3(s)}$	-743
$SO_{2(g)}$	-300
$H_2SO_{3(aq)}$	-534
$Fe^{3+}{}_{(aq)}$	-4.60
$H_2O_{(l)}$	-237
$H_2SO_{4(aq)}$	-745
$Fe^{2+}{}_{(aq)}$	-78.9
$H^{+}{}_{(aq)}$	0

QUESTION TWO (20 MARKS)

(a) The hypothetical reaction below is a second order with respect to A.

$$aA \longrightarrow Products$$

(i) Derive an expression for the integrated rate law for this reaction. **(4 marks)**

(ii) Derive an expression for the *half-life* $t_{1/2}$ of the reaction. **(3 marks)**

(b) A certain first-order reaction has a half-life of 40.0 min.

(i) Calculate the rate constant for this reaction. **(2 marks)**

(ii) Determine the time required for this reaction to be 75% complete. **(3 marks)**

(c) The reaction below was studied at several temperatures and the following values of k were obtained as shown in the table below.

$$2N_2O_{5(g)} \longrightarrow 4NO_{2(g)} + O_{2(g)}$$

T (^oC)	k (s^{-1})
20	2.0×10^{-5}
30	7.3×10^{-5}
40	2.7×10^{-4}
50	9.1×10^{-4}
60	2.9 x 10-3

Determine the value of the activation energy E_a, for this reaction. **(8 marks)**

QUESTION THREE (20 MARKS)

(a) In what order would the divalent cations Mg and Cu, be removed as the pH of a solution is raised assuming the molar concentration of all metals equals 9.6×10^{-6}? The K_{sp} for formation of metals hydroxide precipitates are 6.9×10^{-12} and 7.8×10^{-20}, respectively. Determine the pH at which the precipitate of each metal begins to form. **(9 marks)**

(b) Calculate the percentage of HF molecules ionised in **(i)** a 0.10 *M* HF solution **(ii)** a 0.010 *M* HF solution.

(11 marks)

QUESTION FOUR (20 MARKS)

At a temperature near 800^{o}C, steam is passed over hot coke (a form of carbon obtained from coal) reacts to form CO and H_2:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The mixture of gases that results is an important industrial fuel called water gas.

(a) At 800^{o}C the equilibrium constant for this reaction is K_p = 14.1. What are the equilibrium partial pressures (atm) of H_2O, CO and H_2 in the equilibrium mixture at this temperature if we start with solid carbon and 0.100 mol of H_2O in a 1.00-L vessel? **(11 marks)**

(b) What is the minimum amount of carbon required to achieve equilibrium under these conditions? **(4 marks)**

(c) What is the total pressure in the vessel at equilibrium? **(2 marks)**

(d) At 25^{o}C the value of K_p for this reaction is 1.7×10^{-21}. Is the reaction exothermic or endothermic? Justify your answer. **(1.5 marks)**

(e) To produce the maximum amount of CO and H_2 at equilibrium, should the pressure of the system be increased or decreased? Justify your answer. **(1.5 marks)**

Periodic Table of the Elements

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 *La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 #Ac 227.0															

* Lanthanide Series	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
# Actinide Series	89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

6 <-- Atomic Number
C <-- Symbol
12.00 <-- Atomic Weight (Relative Atomic Mass)

Volumes are given in the units of litres (L), or millilitres (mL)

Temperatures are given in the units of degrees Celsius (°C) or Kelvin (K).

It may be assumed that 0.0°C = 273.1 K

Energy changes are given in the SI unit kilojoule (kJ)

Pressures are given in the SI unit kilopascal (kPa), in atmospheres (atm), or in millimetres of mercury (mmHg)

1.000 atm = 101.3 kPa = 760.0 mmHg

Solution concentrations are given in the unit moles per litre (mol L^{-1})

Relating commonly used symbolism, 1 mol L^{-1} = 1 M

Universal Gas Constant, R = 8.315 J K^{-1} mol^{-1} or 0.08206 L atm K^{-1} mol^{-1}

Avogadro Constant, N = 6.022 x 10^{23} mol^{-1}

Magnitude of the electronic charge, q_e = 1.602 x 10^{-19} coulomb (C)

Magnitude of the charge carried by one mole of electrons = 1 faraday (F) = 9.649 x 10^4 C

Volume of 1.000 mol of an ideal gas at 0.0°C and 101.3 kPa is 22.41 L and at 25.0°C and 101.3 kPa is 24.47 L

S.T.P. is 0.0°C and 101.3 kPa