UNIVERSITY OF JOHANNESBURG

FACULTY OF SCIENCE

DEPARTMENT OF APPLIED CHEMISTRY
NATIONAL DIPLOMA: ENGINEERING METALLURGY
NATIONAL DIPLOMA: EXTRACTION METALLURGY

MODULE CET1AM2
METALLURGICAL CHEMISTRY 2

CAMPUS **DFC**

DECEMBER EXAMINATION

DATE: /12/2014 **SESSION: 08:30 – 11:30**

ASSESSOR **DR J RAMONTJA**

INTERNAL MODERATOR **MR PP MONAMA**

DURATION 3 HOURS **MARKS 140**

NUMBER OF PAGES: 15 PAGES, INCLUDING 2 ANNEXURES

INSTRUCTIONS: **ANSWER SECTION A (THE MULTIPLE CHOICE QUESTIONS) AND SECTION B (LONG QUESTIONS) IN SEPARATE ANSWER SCRIPTS.**

FOR SECTION A, CLEARLY SHADE THE LETTER CORRESPONDING TO THE ANSWER OF CHOICE.

CONSULT THE DATA SHEET AND THE PERIODIC TABLE FOR ALL SUPPLEMENTARY INFORMATION.

NON-PROGRAMMABLE CALCULATORS ARE PERMITTED (ONLY ONE PER STUDENT).
GIVE ALL NUMERICAL ANSWERS TO THE CORRECT NUMBER OF SIGNIFICANT FIGURES AND WITH APPROPRIATE UNITS.

REQUIREMENTS: **2 ANSWER SCRIPT (INCLUDING MULTIPLE CHOICE).**

SECTION A

1. When the concentrations of reactant molecules are increased, the rate of reaction increases. The best explanation for this phenomenon is that as the reactant concentration increases

A. the average kinetic energy of molecules increases.

B. the frequency of molecular collisions increases.

C. the rate constant increases.

D. the activation energy increases.

E. the order of reaction increases.

2. For the reaction represented below, the experimental rate law is given by

$(CH_3)_3CCl(aq) + OH^- \rightarrow (CH_3)_3COH(aq) + Cl^-$, rate = k $[(CH_3)_3CCl]$

If some solid sodium hydroxide were added to a solution in which $[(CH_3)_3CCl]$ = 0.01 M and [NaOH] = 0.10 M, which of the following would be *true*? (Assume the temperature and volume remains constant.)

A. Both the reaction rate and k would increase.

B. Both the reaction rate and k would decrease.

C. Both the reaction rate and k would remain the same.

D. The reaction rate would increase but k would remain the same.

E. The reaction rate would decrease but k would remain the same.

3. For the overall chemical reaction shown below, which one of the following statements can be rightly assumed?

$2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(l)$

A. The reaction is third-order overall.

B. The reaction is second-order overall.

C. The rate law is, rate = $k[H_2S]_2[O_2]$.

D. The rate law is, rate = $k[H_2S][O_2]$.

E. The rate law cannot be determined from the information given.

4. For the reaction $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$ at a particular time, $-\Delta[BrO_3^-]/\Delta t = 1.5 \times 10^{-2}$ M/s.

What is $-\Delta[Br^-]/\Delta t$ at the same instant?

A. 13 M/s

B. 7.5×10^{-2} M/s

C. 1.5×10^{-2} M/s

D. 3.0×10^{-3} M/s

E. 330 M/s

5. A certain reaction A → *products* is second order in A. If this reaction is 85% complete in 12 minutes, how long would it take for the reaction to be 15% complete?

A. 110 s

B. 27 s

C. 62 s

D. 130 s

E. 22 s

6. It takes 42.0 min for the concentration of a reactant in a first-order reaction to drop from 0.450 M to 0.320 M at 25°C. How long will it take for the reaction to be 90% complete?

A. 13.0 min

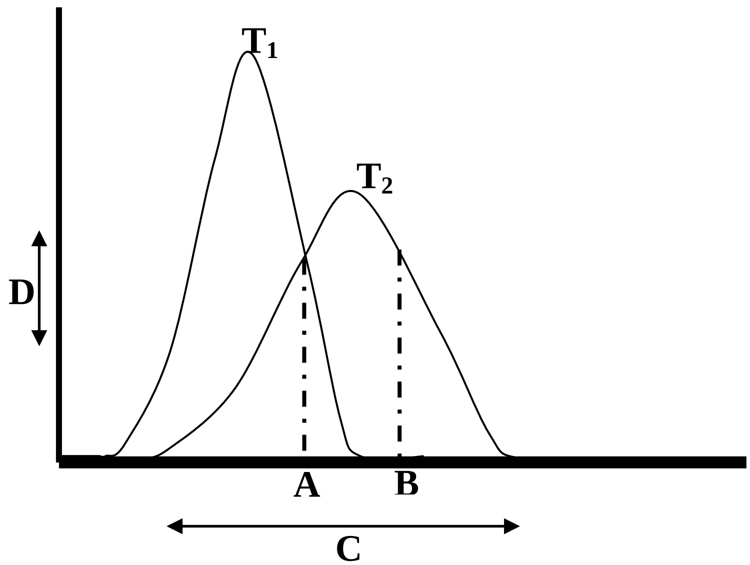
B. 86.0 min

C. 137 min

D. 222 min

E. 284 min

7. Consider the two Boltzmann distributions for an endothermic reaction that was conducted at temperatures T_1 and then T_2 (where $T_1 < T_2$).



Labels A, B, C and D in the diagram above are best described respectively as:

A. activation energy of the forward reaction; activation energy of the reverse reaction; temperature; number of molecules

B. activation energy of the reverse reaction; activation energy of the forward reaction; temperature; number of molecules

C. activation energy of the reverse reaction; activation energy of the forward reaction; number of molecules; kinetic energy

D. activation energy of the forward reaction; activation energy of the reverse reaction; kinetic energy; number of molecules

E. none of the above options

8. For the reaction $COF_2(g) \rightleftharpoons CO(g) + F_2(g)$,

the following mechanism has been proposed:

$2COF_2(g) \rightleftharpoons 2COF(g) + F_2(g)$ ....(1)

$2COF(g) \rightleftharpoons 2CO(g) + F_2(g)$ ....(2) (SLOW)

Based upon this mechanism and the information supplied it can be inferred that:

A. the intermediate in this mechanism is $COF(g)$

B. the rate of formation of $F_2(g)$ in (1) is slower than the rate of formation of $F_2(g)$ in (2)

C. the rate of formation of $COF(g)$ in (1) is slower than the rate of consumption of $COF(g)$ in (2)

D. the rates of consumption and production of $COF(g)$ in (1) are the rate determining steps

E. the overall reaction order is three

9. For the equilibrium: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta H = -12.5$ kJ/mol

When the temperature of the reaction vessel is halved then

A. the quantity of nitrogen monoxide decreases

B. the quantities of nitrogen and oxygen increase

C. the quantity of nitrogen monoxide increases

D. the quantities of nitrogen and oxygen remain the same

E. none of the above options

10. NO(g) and CO_2(g) react according to the following equation:

$$NO(g) + CO_2(g) \rightleftharpoons NO_2(g) + CO(g)$$

In an experiment, 4.00 moles of NO(g) and 0.900 mole of CO_2(g) are placed in a 2.00 dm^3 reaction vessel. At equilibrium, 0.100 mole of CO_2(g) is present. What is the equilibrium constant, Kc, for the reaction?

A. 0.500

B. 1.60

C. 2.00

D. 5.00

E. 5.20

11. Consider the following reaction:

$$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$$

Initially, SO_3(g) is placed in an empty flask. How do the rates of the forward and backward reactions change as the system proceeds to equilibrium?

	Forward reaction rate	Backward reaction rate
A	Increases	increases
B	Increases	decreases
C	Decreases	decreases
D	Decreases	increases

E. None of the above

12. The pH of a solution made by dissolving 522 mg of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water and diluting to a total volume of 250 cm^3 is 4.24. The K_a for the phthalate ion ($HC_8H_4O_4^-$) is:

A. 5.66×10^{-3}

B. 5.75×10^{-5}

C. 1.02×10^{-2}

D. 2.54×10^{-2}

E. 3.26×10^{-7}

13. For which system does the equilibrium constant, Kc, have units?

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

B. $SO_3(g) + NO(g) \rightleftharpoons SO_2(g) + NO_2(g)$

C. $Cu_2^{+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

D. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

E. None of the above.

14. Which of the following buffer compositions of equal volumes can withstand the greatest addition of a 0.050 mol dm^{-3} solution of hydrochloric acid before collapsing?

A. 0.667 M $Ca(CH_3COO)_2$ and 0.217 M CH_3COOH

B. 0.909 M $Ca(CH_3COO)_2$ and 0.821 M CH_3COOH

C. 0.217 M $Ca(CH_3COO)_2$ and 0.821 M CH_3COOH

D. 0.100 M $Ca(CH_3COO)_2$ and 0.909 M CH_3COOH

E. 0.217 M $Ca(CH_3COO)_2$ and 0.667 M CH_3COOH

15. Consider the following reaction at equilibrium at 450 K:

$C_2A_2(g) \rightleftharpoons C_2(g) + A_2(g)$ …………$K_c = 0.112$

If the same reaction was conducted at 900 K and the new equilibrium constant was found to be twice that of the value of K_c, this would imply that:

A. the forward reaction is exothermic

B. an equilibrium constant is inversely proportional to temperature

C. the pressure of this reaction doubled

D. an equilibrium constant is directly proportional to temperature

E. the forward reaction is endothermic

16. Hydroxide ions ($OH^-(aq)$) are slowly added to a solution that contains 0.0800 M $Ag^+(aq)$ ions and 0.0800 M $Pb^{2+}(aq)$ ions. Given that the K_{sp}(silver hydroxide) = 1.50×10^{-8} and K_{sp}(lead hydroxide) = 1.90×10^{-13}, then the molar concentration of the first cation remaining in solution when the second cation starts to precipitate is:

A. 1.87×10^{-7}

B. 1.95×10^{-2}

C. 9.73×10^{-3}

D. 5.08×10^{-7}

E. none of the above options

17. Consider the reaction below:

$$Cu^{2+}(aq) + 4CN^{-}(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$$

A volume of 100 cm^3 of a 0.0225 mol dm^{-3} solution of cupric nitrate was mixed with 150 cm^3 of a 0.100 mol dm^{-3} solution of potassium cyanide in a single container. The resulting mixture was then allowed to reach equilibrium. If thereafter a volume of 50.00 cm^3 of a 0.0025 mol dm^{-3} solution of nitric acid was added to the equilibrium mixture, then

A. the concentration of $Cu(CN)_4^{2-}(aq)$ increased

B. the concentration of $Cu^{2+}(aq)$ increased

C. the concentration of $Cu(CN)_4^{2-}(aq)$ remained unchanged

D. the concentration of $Cu^{2+}(aq)$ decreased

E. copper (II) nitrate precipitated from the solution

18. The two electrodes $Bi(s)/Bi^{3+}(aq)$ (0.0575 mol dm^{-3}) and $Cr(s)/Cr^{2+}(aq)$ (0.980 mol dm^{-3}) were combined to produce a spontaneous electrochemical reaction. The cell potential for this reaction at 25.00°C is:

A. +1.09 V

B. +1.13 V

C. +1.04 V

D. +1.07 V

E. none of the above options

19. Each of the following transformations takes place at the anode except

A. $Mn^{2+} \rightarrow MnO_2$

B. $Br^{-}(aq) \rightarrow BrO^{-}$

C. $HO_2^{-} \rightarrow O_2(g)$

D. $[Fe(CN)_6]^{3-} \rightarrow [Fe(CN)_6]^{4-}$

E. none of the above options

20. Which one of the following statements is **incorrect**?

A. In any voltaic cell the electrons flow from the anode through the external circuit to the cathode.

B. The more positive the value of E^o red the greater the driving force for reduction.

C. A positive value of the cell potential indicates a nonspontaneous process.

D. The half-reaction with the smallest (least positive) reduction potential is most easily reversed as an oxidation.

E. In any voltaic cell the anions always migrate toward the anode and cations toward the cathode.

[20 x 3 = 60]

SECTION B

QUESTION 1

1.1 Consider the following reaction mechanism:

Step 1 $ClO^- + H_2O \rightarrow HOCl + OH^-$
Step 2 $Br^- + HOCl \rightarrow HOBr + Cl^-$
Step 3 $OH^- + HOBr \rightarrow H_2O + BrO^-$

1.1.1 Identify the intermediates and the catalysts (if any) in the above mechanism. (2)

1.1.2 Write the overall reaction and the rate law of this reaction. (4)

1.2 Consider the reaction: $2B \rightarrow C + 3D$. In one experiment it was found that at 300 K the rate constant is 0.134 L/(mol.s). A second experiment showed that at 450 K, the rate constant was 0.569 L/(mol.s). Determine the activation energy for the reaction. (5)

1.3 Sucrose, $C_{12}H_{22}O_{11}$ reacts slowly with water in the presence of an acid to form two other sugars, (glucose and fructose) which have the same molecular formulas, but different structures.

$C_{12}H_{22}O_{11}$ (sucrose) + $H_2O \rightarrow C_{12}H_{22}O_{11}$ (glucose) + $C_{12}H_{22}O_{11}$ (fructose)
The reaction is first order and has a rate constant of $6.2 \times 10^{-5}\ s^{-1}$ at 35°C when the H^+ concentration is 0.10M. Suppose that the initial concentration of sucrose in the solution is 0.40 M. How many minutes will it take for the sucrose concentration to drop to 0.30 M? (4)

1.4 For the second order reaction:

$2C_4H_6 \rightarrow 1C_8H_{12}$

If 35 % of the 1.0 M initial concentration has reacted after 2 hours, what is the half-life of the reaction? (5)

[20]

QUESTION 2

Given the following reaction:

$COF_2(g) \rightleftharpoons CO(g) + F_2(g)$

An amount of 7.40 mol of COF_2 is initially placed into a 15.0 dm^3 flexible container at 823 K. At the first equilibrium the pressure in the container was found to be 3.53×10^6 Pa. The pressure was then changed and the reaction was allowed to reach equilibrium for the second time. At the second equilibrium the moles of CO were 25.00% less than those of the first equilibrium.

Calculate the total pressure in the container at the second equilibrium.

[18]

QUESTION 3

A buffer solution with a pH of 4.14 contains 0.166 mol of a weak acid and **Z** mol of a salt of its conjugate base. When 175 cm^3 of a 0.0420 mol dm^{-3} solution of hydrochloric acid was added to this buffer solution the pH changed by 0.360 pH units. Use this information to calculate the value of K_a for the weak acid.

[14]

QUESTION 4

A mixture is first made of 320 cm^3 of a 0.175 mol.dm^{-3} solution of silver nitrate and **x** cm^3 of a 1.54 mol.dm^{-3} solution of sodium cyanide. Thereafter, 260 cm^3 of a 0.112 mol.dm^{-3} solution of sodium iodide is added to this mixture and the resulting solution is diluted to 2.00 dm^3. Calculate the value of **x** that *will just prevent the precipitation* of silver iodide.

[14]

QUESTION 5

The minerals of a 53.3 kg ore sample from a South African mine in Northwest were dissolved by acid leaching to make up a solution whose volume was 25.5 dm^3. When this solution was analysed it was found to contain 0.224 mol.dm^{-3} of $Cd^{2+}(aq)$ ions and 0.148 mol.dm^{-3} of $Ni^{2+}(aq)$ ions. The solution was then subjected to electrolysis at 25.0^{o}C. Calculate the mass percentage **impurity** of the metal that plated last.

[16]

QUESTION 6

The following cell is subjected to electrolysis using a current of 2.00 A for 5.00 hours. Calculate the *thickness* of the Ni plate if the surface area of the cathode is 100 cm^2.

$$\mathrm{Pt} \,\middle|\, \begin{array}{c} CoCl_2(aq) \\ (0.0500\ mol.dm^{-3}) \end{array} \,\middle\|\, \begin{array}{c} NiCl_2(aq) \\ (0.0100\ mol.dm^{-3}) \end{array} \,\middle|\, \mathrm{Ni}$$

The half-cell volumes are 1.00 dm^3 each. The density of nickel is 8.90 $g.cm^{-3}$.

[10]

DATA

Avogadro's number: $N = 6.02 \times 10^{23}$

$0^oC = 273.15\ K$

Standard pressure = 1 atm = 101.325 kPa = 760 mmHg = 760 torr = 1.01325 bar

$R = 8.31451\ L.kPa\ .K^{-1}.mol^{-1}$
$= 8.31451\ J.K^{-1}.mol^{-1}$
$= 8.31451 \times 10^{-2}\ L.bar\ .K^{-1}.mol^{-1}$
$= 8.20578 \times 10^{-2}\ L.atm\ .K^{-1}.mol^{-1}$
$= 62.364\ L.torr\ .K^{-1}.mol^{-1}$

$F = 9.6485 \times 10^{4}\ C.mol^{-1}$

$V = J.C^{-1}$

Equilibrium constants (T = 25.0^{o}C)

K_{sp} (Silver Iodide, AgI) = 8.3×10^{-17}

K_f ($Ag(CN)_2^-$) = 1.00×10^{21}

Standard reduction potentials (T = 25.0 ^{o}C)

E^o red (Al^{3+}/ Al) = –1.66 V

E^o red (Cd^{2+}/ Cd) = –0.403 V

E^o red (Co^{2+}/ Co) = –0.277 V

E^o red (Ni^{2+}/ Ni) = –0.280 V

E^o red (Bi^{3+}/ Bi) = +0.20 V

E^o red (Cr^{2+}/ Cr) = -0.91 V

/11…

UNIVERSITY OF JOHANNESBURG

Department of Applied Chemistry

Atomic Number	2 **He** *4.0026*	Atomic Weight

1 **H** *1.0079*																	2 **He** *4.0026*
3 **Li** *6.941*	4 **Be** *9.0122*											5 **B** *10.811*	6 **C** *12.011*	7 **N** *14.007*	8 **O** *15.999*	9 **F** *18.998*	10 **Ne** *20.179*
11 **Na** *22.990*	12 **Mg** *24.305*											13 **Al** *26.982*	14 **Si** *28.086*	15 **P** *30.974*	16 **S** *32.064*	17 **Cl** *35.453*	18 **Ar** *39.948*
19 **K** *39.098*	20 **Ca** *40.078*	21 **Sc** *44.956*	22 **Ti** *47.88*	23 **V** *50.942*	24 **Cr** *51.996*	25 **Mn** *54.938*	26 **Fe** *55.847*	27 **Co** *58.933*	28 **Ni** *58.69*	29 **Cu** *63.546*	30 **Zn** *65.39*	31 **Ga** *69.723*	32 **Ge** *72.61*	33 **As** *74.922*	34 **Se** *78.96*	35 **Br** *79.904*	36 **Kr** *83.80*
37 **Rb** *85.47*	38 **Sr** *87.62*	39 **Y** *88.906*	40 **Zr** *91.224*	41 **Nb** *92.906*	42 **Mo** *95.94*	43 **Tc** *(98)*	44 **Ru** *101.07*	45 **Rh** *102.91*	46 **Pd** *106.42*	47 **Ag** *107.87*	48 **Cd** *112.41*	49 **In** *114.82*	50 **Sn** *118.71*	51 **Sb** *121.75*	52 **Te** *127.60*	53 **I** *126.90*	54 **Xe** *131.29*
55 **Cs** *132.91*	56 **Ba** *137.33*	57 **La** *138.91*	72 **Hf** *178.49*	73 **Ta** *180.95*	74 **W** *183.85*	75 **Re** *186.2*	76 **Os** *190.2*	77 **Ir** *192.22*	78 **Pt** *195.08*	79 **Au** *196.97*	80 **Hg** *200.59*	81 **Tl** *204.38*	82 **Pb** *207.2*	83 **Bi** *208.98*	84 **Po** *(209)*	85 **At** *(210)*	86 **Rn** *(222)*
87 **Fr** *(223)*	88 **Ra** *226.03*	89 **Ac** *227.03*															
			58 **Ce** *140.12*	59 **Pr** *140.91*	60 **Nd** *144.24*	61 **Pm** *146.92*	62 **Sm** *150.36*	63 **Eu** *151.97*	64 **Gd** *157.25*	65 **Tb** *158.93*	66 **Dy** *162.50*	67 **Ho** *164.93*	68 **Er** *167.26*	69 **Tm** *168.93*	70 **Yb** *173.04*	71 **Lu** *174.97*	
			90 **Th** *232.04*	91 **Pa** *231.04*	92 **U** *238.03*	93 **Np** *237.05*	94 **Pu** *(244)*	95 **Am** *(234)*	96 **Cm** *(247)*	97 **Bk** *247*	98 **Cf** *(251)*	99 **Es** *(252)*	100 **Fm** *(257)*	101 **Md** *(258)*	102 **No** *(259)*	103 **Lr** *(260)*	