UNIVERSITY OF JOHANNESBURG

FACULTY OF SCIENCE

DEPARTMENT OF APPLIED CHEMISTRY
NATIONAL DIPLOMA: ANALYTICAL CHEMISTRY

MODULE CET1BP3
PHYSICAL CHEMISTRY 2

CAMPUS **DFC**

NOVEMBER EXAMINATION

DATE: 12/11/2015 **SESSION: 12:30 – 15:30**

ASSESSOR **MR PP MONAMA**

INTERNAL MODERATOR **DR D NKOSI**

DURATION 3 HOURS **MARKS 150**

NUMBER OF PAGES: 9 PAGES, INCLUDING 2 ANNEXURES

INSTRUCTIONS: **ANSWER SECTION A ON THE MULTIPLE CHOICE ANSWER SHEET AND SECTION B IN THE ANSWER SCRIPT PROVIDED.**

FOR SECTION B, GIVE ALL NUMERICAL ANSWERS TO THE CORRECT NUMBER OF SIGNIFICANT FIGURES AND WITH APPROPRIATE UNITS.

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

CALCULATORS ARE PERMITTED (ONLY ONE PER STUDENT).

REQUIREMENTS: **ANSWER SCRIPT**

MULTIPLE CHOICE ANSWER SHEET

SECTION A

1. Which one of the following statements is **correct**?

A. When heat is transferred from the surroundings to the system, q has a negative value.
B. When work is done on the system by the surroundings, *w* has a positive value.
C. During an endothermic process, such as the melting of ice, heat flows out of the system into its surroundings.
D. The temperature change experienced by an object when it absorbs a certain amount of energy is determined by its standard molar entropy. work is done on the system by the surroundings, *w* has a positive value.
E. When heat is lost by the system to the surroundings, q has a positive value.

2. How much heat is needed to raise the temperature of 125 g of ethanol (C_2H_5OH) from 25.2°C to 32.5°C? The specific heat capacity of ethanol is 1.13 $J.g^{-1}.K^{-1}$.

A. 3.56 kJ
B. 4.59 kJ
C. 3.06 kJ
D. 4.08 kJ
E. 1.03 kJ

3. For which of the following reactions would the ΔH^o for the reaction be labelled ΔH_f^o?

A. $PCl_3(g) + \frac{1}{2} O_2(g) \rightarrow POCl_3(g)$
B. $\frac{1}{2} N_2O(g) + \frac{1}{4} O_2(g) \rightarrow NO(g)$
C. $Ca(s) + H_2(g) + O_2(g) \rightarrow Ca(OH)_2(s)$
D. $MgO(s) + SO_2(g) \rightarrow MgSO_3(s)$
E The ΔH^o for all these reactions would be labelled ΔH_f^o.

4. Consider the following reaction:

$$2B(aq) + 3Y(aq) \rightarrow B_2Y_3(aq)$$

At a particular temperature, the molar concentration of substance Y varies with time in the following manner:

Time (min):	[Y] $mol.dm^{-3}$
0.00	0.150
4.00	0.0800

What is the reaction rate (in $mol.dm^{-3}.s^{-1}$) for the **consumption of substance B**?

A. 2.92×10^{-4}
B. 1.75×10^{-2}
C. 1.17×10^{-2}
D. 1.94×10^{-4}
E. 4.38×10^{-4}

5. At a given temperature, a first order reaction has a rate constant of $5.32 \times 10^{-3}\ s^{-1}$. The time required for the reaction to be 78.6 % complete is:

A 45.3 s
B 690 s
C 290 s
D 51.2 s
E 542 s

6. Given the following reaction: $2CB(g) + B_2(g) \rightarrow 2CB_2(g)$

If the mechanism below was proposed, then this implies that:

$CB(g) + CB(g) \rightarrow C_2B_2(g)$…(1)

$C_2B_2(g) \rightarrow CB(g) + CB(g)$…...(2)

$C_2B_2(g) + B_2(g) \rightarrow 2\ CB_2(g)$……(3) (SLOW)

A. the formation of $CB(g)$ is the rate determining step
B. the rate of formation of $CB_2(g)$ is greater than that of $CB(g)$
C. the intermediate is $CB(g)$
D. the overall reaction order is three
E. the rate of formation of $CB_2(g)$ is less than that of $CB(g)$

7. Consider the following reaction at equilibrium at 135°C:

$2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$

If 2.00 mol of $AB_3(g)$ were placed into a 10.0 dm^3 container and the concentration of $B_2(g)$ at equilibrium was 0.0150 $mol.dm^{-3}$, if the gas constant R is 8.20578×10^{-2} $L.atm.K^{-1}.mol^{-1}$, then the value of the equilibrium constant (K_p) is:

A. 4.67×10^{-7}
B. 5.74×10^{-5}
C. 4.17×10^{-10}
D. 5.24×10^{-4}
E. 1.22×10^{-3}

8. For the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$, $K_c = 8000$. What will happen when 0.0100 mol of gaseous hydrogen sulphide ($H_2S(g)$), 0.150 mol of gaseous hydrogen ($H_2(g)$) and 0.150 mol of gaseous sulphur ($S_2(g)$) are added to a 2.00 dm^3 container and allowed to equilibrate?

A. The amount of H_2S will be halved.
B. More H_2S will be formed.
C. More H_2 will be formed than S_2.
D. More S_2 will be formed than H_2.
E. The amount of H_2 formed will be half of the amount of S_2 formed.

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

A. The equilibrium constant of a reaction equation where the coefficients have been multiplied throughout by a number is the equilibrium constant raised to a power equal to that number.
B. Reducing the volume of a gaseous equilbrium mixture causes the system to shift in the direction that increases the number of moles of gas.
C. If a pure solid is involved in a heterogeneous equilibrium, its concentration is not included in the equilibrium-constant expression for the reaction.
D. The reaction quotient (Q) will equal the equilibrium constant (K_C) only if the system is at equilibrium.
E. A catalyst increases the rate at which equilibrium is achieved, but it does not change the composition of the equilibrium mixture.

10. The pH of 0.00520 $mol.dm^{-3}$ BH is 10.8. BH is therefore a

A. weak acid
B. weak base
C. strong base
D. strong acid
E. strong electrolyte

11. A 0.122 $mol.dm^{-3}$ solution of a weak acid HX is dissociated by 7.42%. The pH of the solution and the K_a for the weak acid are:

A. 2.04 and 6.72×10^{-4}
B. 0.914 and 9.05×10^{-3}
C. 2.04 and 7.26×10^{-4}
D. 1.49 and 4.89×10^{-3}
E. 0.914 and 7.28×10^{-4}

12. Consider the reaction: $Cu^{2+}(aq) + 4CN^{-}(aq) \rightleftharpoons Cu(CN)_4^{2-}(aq)$

A volume of 100 cm^3 of a 0.0225 $mol.dm^{-3}$ solution of copper(II) 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 $Cu(CN)_4^{2-}(aq)$ remained unchanged
C. the concentration of $Cu^{2+}(aq)$ decreased
D. copper (II) nitrate precipitated from the solution
E. the concentration of $Cu^{2+}(aq)$ increased

13. 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.

14. According to the following cell diagram, which species undergoes reduction?

$$Sn \mid Sn^{2+} \mid\mid MnO_2 \mid Mn^{2+} \text{ (Pt)}$$

A Sn
B Sn^{2+}
C Pt
D MnO_2
E Mn^{2+}

15. Which transformation **cannot** take place at the cathode of an electrochemical cell?

A. $MnO_4^- \rightarrow MnO_4^{2-}$
B. $Cr_2O_7^{2-} \rightarrow Cr^{3+}$
C. $PbSO_4 \rightarrow Pb$
D. $ClO^- \rightarrow Cl^-$
E. $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-}$

[15 x 3 = 45]

SECTION B

QUESTION 1

1.1 Distinguish between the terms "non-renewable energy" and "renewable energy". (4)

1.2 The combustion of liquid toluene (C_7H_8) produces gaseous carbon dioxide and water liquid. When 1.500 g sample of liquid toluene is combusted with excess oxygen gas in a bomb calorimeter, the temperature of the calorimeter increases from 25.000°C to 26.413°C. In a separate experiment the heat capacity of the calorimeter was measured to be 45.06 kJ.°C^{-1}.

1.2.1 Write the balanced chemical equation for the reaction. (2)
1.2.2 Calculate the heat of reaction for the combustion of a mole of toluene in this calorimeter. (4)

1.3 Use the information supplied in the data sheet to calculate the enthalpy change (in kJ.mol^{-1}) accompanying the formation of 10.0 dm^3 of carbon dioxide gas at 715 torr and 19.0°C in the following reaction:

$$NaHCO_3(s) + H^+(aq) \rightarrow Na^+(aq) + H_2O(l) + CO_2(g)$$ (10)

[20]

QUESTION 2

2.1 The rate constant for the decomposition of hydrogen iodide (HI) at 700ºC equals 0.00160 $M^{-1}.s^{-1}$:

$2HI(g) \rightarrow H_2(g) + I_2(g)$

2.1.1 Based on the units of the rate constant, is the reaction first order or second order? Explain. (2)

2.1.2 Suppose a reaction is started with 0.0552 mol of HI in a volume of 735 cm^3. How many minutes will the reaction take for the moles of HI to drop by 66.6%? (4)

2.1.3 Calculate the moles of HI that will remain after 15 minute and 25 seconds. (4)

2.1.4 Calculate the half–life (in minutes) for the reaction. (2)

2.2 Suppose a reaction occurs according to the following mechanism:

Step 1: $2A \rightleftharpoons A_2$ (***fast***)

Step 2: $A_2 + E \rightarrow B + C$ (***slow***)

2.2.1 Write the rate Law for the forward reaction in step1. (1)

2.2.2 Write the rate Law for the reverse reaction in step1. (1)

2.2.3 Write the rate Law for the rate determining step. (1)

2.2.4 Write the balanced chemical equation for the overall reaction. (1)

2.2.5 Write the rate Law in terms of the concentrations of the reactants in the overall balanced equation. (3)

2.2.6 Identify any intermediate/s in the mechanism. (1)

[20]

QUESTION 3

Consider the following equilibrium for which ΔH = +23.12 kJ/mol:

$NiBr_2(s) + H_2(g) \rightleftharpoons Ni(s) + 2HBr(g)$

When 2.00 moles of $NiBr_2(s)$ and $H_2(g)$ were each placed into an evacuated 10.0 dm^3 container at 578.25 K and the reaction reached equilibrium the pressure in the container was 9.38 x 10^3 mmHg. The volume of the container was then changed and the reaction was allowed to reach equilibrium for the second time. At the second equilibrium it was found that the concentration of $HBr(g)$ was 0.0855 M. Calculate the **new volume of the container**.

[16]

QUESTION 4

4.1 A 900 cm^3 buffer solution of pH of 4.70 contains **P** mol of a weak acid and **Q** mol of a salt of its conjugate base. When 100 cm^3 of a 0.0100 $mol.dm^{-3}$ solution of sodium hydroxide was added to this buffer solution the pH changes by 0.300 pH units. If the K_a value for the weak acid is 1.38×10^{-5}, calculate the values of **P** and **Q**. (14)

4.2 A mixture is first made of 150 cm^3 of a 0.200 $mol.dm^{-3}$ solution of silver nitrate and **y** cm^3 of a 2.50 $mol.dm^{-3}$ solution of potassium cyanide. Thereafter, 100 cm^3 of a 0.120 $mol.dm^{-3}$ solution of potassium chloride is added to this mixture and the resulting solution is diluted to 2.00 dm^3. Calculate the value of **y** that *will just prevent the precipitation* of silver chloride. (16)

[30]

QUESTION 5

5.1 Balance the following reaction and construct an electrochemical cell that represents this reaction by using the correct cell notation and an appropriate junction:

Oxidation of Pb to PbO_2 with ClO^- to Cl^- (alkali medium) (10)

5.2 The minerals of a 126 kg ore were dissolved by acid leaching to make up a solution whose volume was 50.0 dm^3. When this solution was analysed it was found to contain 0.445 $mol.dm^{-3}$ of Sn^{2+}(*aq*) ions and 0.0355 $mol.dm^{-3}$ of Pb^{2+}(*aq*) ions. The solution was then subjected to electrolysis at 25.0°C. Calculate the mass percentage **purity** of the metal that plated last. (15)

[25]

DATA SHEET

$0^oC = 273.15$ 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 x 10^4 $C.mol^{-1}$

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

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

K_{sp} (Silver chloride, AgCl) = 1.80 x 10^{-10}

K_f ($Ag(CN)_2^-$) = 1.00 x 10^{21}

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

E^o red (Pb^{2+}/ Pb) = –0.126 V

E^o red (Sn^{2+}/ Sn) = –0.136 V

Standard enthalpy of formation (T = 25.0 ^{o}C)

ΔH_f^o, $CO_2(g)$ = –393.5 $kJ.mol^{-1}$

ΔH_f^o, $H_2O(l)$ = –285.83 $kJ.mol^{-1}$

ΔH_f^o, $H^+(aq)$ = 0 $kJ.mol^{-1}$

ΔH_f^o, $Na^+(aq)$ = –240.10 $kJ.mol^{-1}$

ΔH_f^o, $NaHCO_3(s)$ = –947.7 $kJ.mol^{-1}$

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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)*