



FACULTY OF SCIENCE

DEPARTMENT OF APPLIED CHEMISTRY NATIONAL DIPLOMA: ANALYTICAL CHEMISTRY

MODULE CET1BP3
 PHYSICAL CHEMISTRY 2

CAMPUS DFC

DECEMBER EXAMINATION

DATE: 01/12/2015

SESSION: 08:30 – 11:30

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**

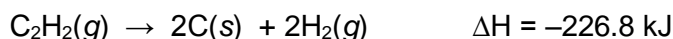
MULTIPLE CHOICE ANSWER SHEET

SECTION A

1. A system suffers a decrease in internal energy of 75 J and at the same time has 45 J of work done on it. What is the heat change of the system?

A. +120 J
B. -30 J
C. +75 J
D. -120 J
E. -45 J

2. Consider the following reaction:



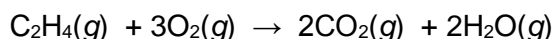
What is the enthalpy change (ΔH) when 996 mg of carbon (C) solid reacts completely with hydrogen (H_2) gas to form ethyne (C_2H_2) gas at constant pressure?

A. -18.8 kJ
B. +227 kJ
C. +9.40 kJ
D. -14.1 kJ
E. +4.39 kJ

3. When 4.45 kJ of heat is added to 62.0 g sample of toluene (C_7H_8) at 25.0°C , the temperature of the sample increases to 88.5°C . The specific heat capacity of toluene is:

A. $0.445 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
B. $1.01 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
C. $1.57 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
D. $2.02 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$
E. $1.13 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$

4. Consider the combustion of ethylene (C_2H_4):



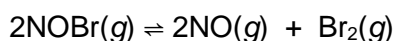
If the rate of appearance of CO_2 at a particular instant in a reaction vessel is $1.25 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$, what is the rate of disappearance of O_2 ?

A. $1.25 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$
B. $3.75 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$
C. $8.33 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$
D. $1.88 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$
E. $2.5 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}$

5. A reaction $2\text{X} + 3\text{Y} \rightarrow \text{X}_2\text{Y}_3$ obeys the following rate law: $\text{Rate} = k[\text{Y}]^2$. If the concentration of X was doubled, the rate would have:

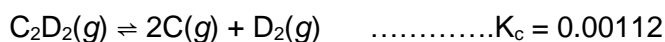
A. increased by a factor of four.
B. stayed the same.
C. increased by a factor of two.
D. decreased by a factor of two.
E. decreased by a factor of four.

6. Which one of the following statements is **correct**?
- A. A catalyst that is present in the same phase as the reacting molecules is a heterogeneous catalyst.
 - B. Absorption refers to the binding of molecules to a surface.
 - C. Because the fast step limits the overall reaction rate, it is called the rate-determining step.
 - D. Elementary steps involving the simultaneous collision of two molecules are bimolecular.
 - E. A balanced chemical equation details the individual steps that occur in the course of a reaction.
7. Nitrosyl bromide $\text{NOBr}(g)$ decomposes according to the following equation:



0.640 mol of $\text{NOBr}(g)$ were placed into a 500 cm^3 flask with 0.160 mol of $\text{NO}(g)$ and the reaction was allowed to equilibrate. At equilibrium it was found that 0.540 mol of $\text{NOBr}(g)$ were present. How many moles of $\text{NO}(g)$ and $\text{Br}_2(g)$ were in the flask at equilibrium?

- A. 0.320 moles NO and 0.160 moles Br_2
 - B. 0.320 moles NO and 0.0800 moles Br_2
 - C. 0.520 moles NO and 0.0500 moles Br_2
 - D. 0.260 moles NO and 0.0500 moles Br_2
 - E. 0.260 moles NO and 0.100 moles Br_2
8. Which one of the following equilibria would **not** be affected by pressure changes at constant temperature?
- A $\text{ZnO}(s) + \text{CO}(g) \rightleftharpoons \text{Zn}(s) + \text{CO}_2(g)$
 - B $\text{MgCO}_3(s) \rightleftharpoons \text{MgO}(s) + \text{CO}_2(g)$
 - C $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$
 - D $2\text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}_2(g)$
 - E $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
9. Consider the following reaction at equilibrium at 339 K:



If the same reaction was conducted at 542 K and the new equilibrium constant was found to be 2.5 times 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 reverse reaction is endothermic
- D. an equilibrium constant is directly proportional to temperature
- E. the forward reaction is endothermic

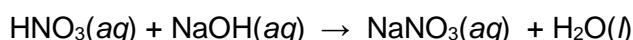
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10. Which of the following solutions has the lowest pH value?
- A. $0.0112 \text{ mol.dm}^{-3} \text{ HF}$
B. $0.0112 \text{ mol.dm}^{-3} \text{ Ca(OH)}_2$
C. $0.0112 \text{ mol.dm}^{-3} \text{ HBr}$
D. $0.0112 \text{ mol.dm}^{-3} \text{ NH}_3$
E. $0.0112 \text{ mol.dm}^{-3} \text{ CH}_3\text{COOH}$
11. Which of the following buffer compositions of equal volumes can withstand the greatest addition of a $0.0685 \text{ mol.dm}^{-3}$ solution of hydrochloric acid before collapsing?
- A. $0.909 \text{ M H}_2\text{CO}_3$ and 0.821 M NaHCO_3
B. $0.821 \text{ M H}_2\text{CO}_3$ and 0.909 M NaHCO_3
C. $0.667 \text{ M H}_2\text{CO}_3$ and 0.821 M NaHCO_3
D. $0.217 \text{ M H}_2\text{CO}_3$ and 0.821 M NaHCO_3
E. $0.821 \text{ M H}_2\text{CO}_3$ and 0.217 M NaHCO_3
12. 1.25 g of a sparingly soluble salt ($\text{X}_4\text{B(s)}$) with a solubility product constant of 9.23×10^{-7} is placed into 100 cm^3 of water. If the salt produces $\text{X}^+(\text{aq})$ ions and $\text{B}^{4-}(\text{aq})$ ions and the volume change is negligible, then its molar solubility is
- A. $6.20 \times 10^{-2} \text{ mol.dm}^{-3}$
B. $1.85 \times 10^{-7} \text{ mol.dm}^{-3}$
C. $7.75 \times 10^{-3} \text{ mol.dm}^{-3}$
D. $4.80 \times 10^{-4} \text{ mol.dm}^{-3}$
E. $2.05 \times 10^{-2} \text{ mol.dm}^{-3}$
13. The oxidation state of arsenic (As) in the arsenate ion (AsO_4^{3-}) is:
- A. +4
B. +5
C. -3
D. +8
E. -4
14. In the voltaic cell $\text{Zn}|\text{Zn}^{2+}||\text{Cu}^{2+}|\text{Cu}$ the electron flow will be from:
- A. Cu to Zn^{2+}
B. Cu^{2+} to Zn
C. Zn to Cu
D. Zn to Cu^{2+}
E. Cu to Zn
15. A current of 10 A is passed through molten magnesium chloride (MgCl_2) for 3.0 hours . The number of moles of magnesium metal (Mg) that will be produced is:
- A. 2.2
B. 1.1
C. 0.56
D. 0.37
E. 0.22

[15 x 3 = 45]

SECTION B**QUESTION 1**

1.1 What is a state function? Give one example of a state function. (4)

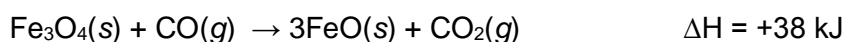
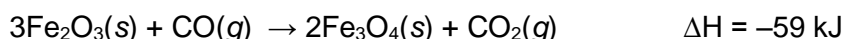
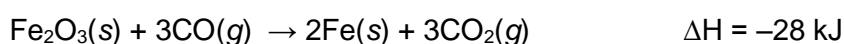
1.2 When 55.0 cm³ of 1.35 mol.dm⁻³ nitric acid and 55.0 cm³ of 1.35 mol.dm⁻³ sodium hydroxide solution are mixed in a constant-pressure calorimeter, the temperature of the mixture rises from 23.5°C to 32.3°C. The temperature increase is caused by the following reaction:



Calculate the enthalpy change (in kJ.mol⁻¹) for the reaction, assuming that the mixture has a density of 1.02 g.cm⁻³ and a specific heat capacity of 4.18 J.g⁻¹.K⁻¹. (5)

1.3 A sample of copper was heated to 120°C and then plunged into 200 g of water at 25.0°C. The temperature of the mixture became 26.5°C, calculate the mass of copper sample. The specific heat capacities of copper and water are 0.387 J.g⁻¹.K⁻¹ and 4.18 J.g⁻¹.K⁻¹. (5)

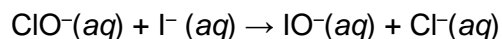
1.4 In the recovery of iron from iron ore, the reduction of the ore is actually accomplished by reactions involving carbon monoxide. Given the following thermochemical equations:



Calculate ΔH for the reaction (**show all steps**)

**[20]****QUESTION 2**

2.1 Consider the following reaction of the hypochlorite ion (ClO⁻) with iodide ion (I⁻) in aqueous solution:



At a particular temperature, the rate of this reaction varies with reactant concentrations in the following manner:

Experiment	Initial concentration (M)		Initial rate (M.s ⁻¹)
	ClO ⁻	I ⁻	
1	1.70 x 10 ⁻³	1.70 x 10 ⁻³	1.75 x 10 ⁻⁴
2	3.40 x 10 ⁻³	1.70 x 10 ⁻³	3.50 x 10 ⁻⁴
3	1.70 x 10 ⁻³	3.40 x 10 ⁻³	3.50 x 10 ⁻⁴

2.1.1 Determine the rate law for the reaction. Show all your calculations. (5)

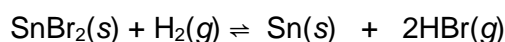
2.1.2 Determine the rate constant for the reaction. (2)

QUESTION 2 (Continued)

- 2.2 The conversion of cyclopropane to propylene has a rate constant $k = 1.30 \times 10^{-6} \text{ s}^{-1}$ at 400°C and $k = 1.10 \times 10^{-5} \text{ s}^{-1}$ at 430°C . Calculate the activation energy for the reaction in $\text{kJ} \cdot \text{mol}^{-1}$. (6)
- 2.3 The oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) is catalysed by nitrogen dioxide (NO_2). The reaction proceeds as follows:
- Step 1: $\text{NO}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{SO}_3(\text{g})$
- Step 2: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
- 2.3.1 Show how the two steps can be added to give the overall equation. (3)
- 2.3.2 Why is NO_2 considered as a catalyst and not an intermediate? (2)
- 2.3.3 Identify any intermediate/s in the mechanism. (1)
- 2.3.4 Is this an example of heterogeneous or homogenous catalysis? (1)

[20]**QUESTION 3**

Consider the following equilibrium for which $\Delta H = +19.23 \text{ kJ/mol}$:



When 6.75 moles of each SnBr_2 and H_2 were placed into an evacuated 25.0 dm^3 container at 758 K and the reaction reached equilibrium the pressure in the container was $2.50 \times 10^6 \text{ Pa}$. A certain amount of moles of H_2 was then carefully added to the mixture in the container and the reaction was allowed to reach equilibrium for the second time. The pressure in the container is found to be $2.95 \times 10^6 \text{ Pa}$ at the second equilibrium.

- 3.1 Calculate the **additional number of moles** of H_2 that was introduced into the container at 758 K . (16)
- 3.2 Use the data provided in this question to predict what would happen to the value of K_c if the **volume** of the container were **fixed** and the **temperature doubled**. Give all details, *but do not perform any calculations in this question*. (4)

[20]**QUESTION 4**

A buffer solution with a pH of 4.24 contains 0.155 mol of a weak acid and $P \text{ mol}$ of a salt of its conjugate base. When 150 cm^3 of a $0.0460 \text{ mol dm}^{-3}$ solution of hydrochloric acid was added to this buffer solution the pH changed by 0.320 pH units . Use this information to calculate the value of K_a for the weak acid.

[14]

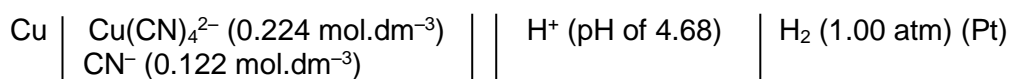
QUESTION 5

The minerals of a 1.05×10^3 kg ore sample from a South African mine in Mpumalanga were extracted by acid leaching to make up a solution whose volume was 45.8 dm^3 . When this solution was analysed it was found to contain $0.00112 \text{ mol.dm}^{-3}$ of $\text{Fe}^{2+}(\text{aq})$ ions and $0.0142 \text{ mol.dm}^{-3}$ of $\text{Mn}^{2+}(\text{aq})$ ions. The solution was slowly made alkaline in order to selectively precipitate the first metal ion (as a metal hydroxide) from the second. The first precipitate was then filtered off from the remaining solution, dried and reduced to its pure metal form. The pH of the remaining solution was then carefully adjusted for the second time until the entire concentration of the second metal ion, together with a trace concentration of the first metal ion, were co-precipitated as metal hydroxides. This co-precipitate was also filtered off, dried and reduced to the metal form.

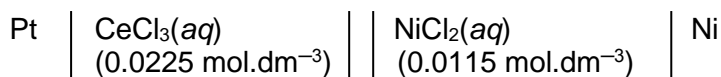
- 5.1 The pH at which maximum separation of the two metal ions was achieved. (6)
 5.2 The percentage mass **impurity** of the metal that was obtained from the last precipitate. (8)

[14]**QUESTION 6**

- 6.1 Calculate the cell potential of the following cell at 25.0°C : (13)



- 6.2 The following cell is subjected to electrolysis using a current of 2.98 A for a total of 15 hours 15 minutes and 15 seconds. Calculate the *thickness* of the cerium plate if the surface area of the cathode is 12.0 mm^2 .



The half-cell volumes are 1.00 dm^3 each. The density of cerium metal is 6.67 g.cm^{-3} . (10)

[23]

DATA SHEET

$$0^{\circ}\text{C} = 273.15 \text{ K}$$

$$\text{Standard pressure} = 1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ mmHg} = 760 \text{ torr} = 1.01325 \text{ bar}$$

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

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

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

Equilibrium constants (T = 25.0°C)

$$K_{\text{sp}} (\text{Iron(II) hydroxide, Fe(OH)}_2) = 7.90 \times 10^{-16}$$

$$K_{\text{sp}} (\text{Manganese(II) hydroxide, Mn(OH)}_2) = 1.60 \times 10^{-13}$$

$$K_{\text{f}} (\text{Cu(CN)}_4^{2-}) = 1.00 \times 10^{25}$$

Standard reduction potentials (T = 25.0 °C)

$$E^{\circ} \text{ red (Cu}^{2+}/\text{Cu)} = +0.337 \text{ V}$$

$$E^{\circ} \text{ red (H}^{+}/\text{H}_2) = 0.000 \text{ V}$$

2
He
4.0026

					2
					He 4.0026
5	6	7	8	9	10
B 10.811	C 12.011	N 14.007	O 15.999	F 18.998	Ne 20.179
13	14	15	16	17	18
Al 26.982	Si 28.086	P 30.974	S 32.064	Cl 35.453	Ar 39.948
31	32	33	34	35	36
Ga 69.723	Ge 72.61	As 74.922	Se 78.96	Br 79.904	Kr 83.80
49	50	51	52	53	54
In 114.82	Sn 118.71	Sb 121.75	Te 127.60	I 126.90	Xe 131.29
81	82	83	84	85	86
Tl 204.38	Pb 207.2	Bi 208.98	Po (209)	At (210)	Rn (222)

1 H 1.0079		
3 Li 6.941	4 Be 9.0122	
11 Na 22.990	12 Mg 24.305	
19 K 39.098	20 Ca 40.078	
37 Rb 85.47	38 Sr 87.62	
55 Cs 132.91	56 Ba 137.33	
87 Fr (223)	88 Ra 226.03	

21	22	23	24	25	26	27	28	29	30
Sc <i>44.956</i>	Ti <i>47.88</i>	V <i>50.942</i>	Cr <i>51.996</i>	Mn <i>54.938</i>	Fe <i>55.847</i>	Co <i>58.933</i>	Ni <i>58.69</i>	Cu <i>63.546</i>	Zn <i>65.39</i>
39	40	41	42	43	44	45	46	47	48
Y <i>88.906</i>	Zr <i>91.224</i>	Nb <i>92.906</i>	Mo <i>95.94</i>	Tc <i>(98)</i>	Ru <i>101.07</i>	Rh <i>102.91</i>	Pd <i>106.42</i>	Ag <i>107.87</i>	Cd <i>112.41</i>
57	72	73	74	75	76	77	78	79	80
La <i>138.91</i>	Hf <i>178.49</i>	Ta <i>180.95</i>	W <i>183.85</i>	Re <i>186.2</i>	Os <i>190.2</i>	Ir <i>192.22</i>	Pt <i>195.08</i>	Au <i>196.97</i>	Hg <i>200.59</i>
89									
Ac <i>227.03</i>									

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce <i>140.12</i>	Pr <i>140.91</i>	Nd <i>144.24</i>	Pm <i>146.92</i>	Sm <i>150.36</i>	Eu <i>151.97</i>	Gd <i>157.25</i>	Tb <i>158.93</i>	Dy <i>162.50</i>	Ho <i>164.93</i>	Er <i>167.26</i>	Tm <i>168.93</i>	Yb <i>173.04</i>	Lu <i>174.97</i>
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th <i>232.04</i>	Pa <i>231.04</i>	U <i>238.03</i>	Np <i>237.05</i>	Pu <i>(244)</i>	Am <i>(234)</i>	Cm <i>(247)</i>	Bk <i>247</i>	Cf <i>(251)</i>	Es <i>(252)</i>	Fm <i>(257)</i>	Md <i>(258)</i>	No <i>(259)</i>	Lr <i>(260)</i>