For Examiners' use only:

Question	1 – 3	4 – 5	6 - 8	9	10	Total
Mark	/6	/14	/15	/13	/12	/60

CHEM 111 and 113 TEST

Tuesday 3 May, 2005

Name (Print clearly): ....

Student ID No: ....

Signature: ....

Instructions:

Attempt **all** questions. Enter answers in the spaces provided (continue on the back of the **opposite** sheet if necessary).

Total marks: 60 Time allowed: 60 minutes

Note:

At the end of this paper are:

1. A periodic table
2. A sheet containing physical chemistry formulae

[Please check that both of these pages are attached before starting to answer the test paper!]

1. (3 marks)

Rubidium is an alkali metal that is easily ionized to Rb^+. If the atomic mass of the most common isotope of rubidium is 84.91, calculate the following quantities for the rubidium ion, $_{37}Rb^+$, which is formed from this isotope:

(a) the number of protons

(b) the number of neutrons

(c) the number of electrons

2. (1 mark)

Write the electron configuration for the element Ni. Use Ne $(1s)^2$ $(2s)^2$ $(2p)^6$ as a model for your answer.

3. (2 marks)

How many p orbitals and d orbitals are there in the n = 3 shell?

Number of p orbitals =

Number of d orbitals =

4. (8 marks)

Write balanced equations for each of the following two ion-electron half reactions occurring in aqueous ***acidic*** solution.

$NO_3^-(aq) \rightarrow NO(g)$ (1)

$Cu(s) \rightarrow Cu^{2+}(aq)$ (2)

For each half equation, designate which element is being oxidized or reduced (as appropriate) and give the oxidation numbers.

Half Reaction	Oxidation or Reduction?	Element Oxidised or Reduced	Initial Oxidation Number	Final Oxidation Number
1				
2				

Write a balanced equation for the overall redox reaction that results when these two half reactions are combined.

5. (6 marks)

A 2.5-L flask at 15 °C contains a mixture of three gases: N_2 at a partial pressure of 0.32 atm, Ar at a partial pressure of 0.15 atm and He at a partial pressure of 0.50 atm.

(a) What is the total pressure in the flask in atm?

(b) What is the mole fraction of N_2, X_{N_2}, in the flask?

(c) What is the partial pressure of N_2 in the flask in units of Pa?

(d) Calculate the number of moles of N_2 in the flask.

(1 atm = 1.013×10^5 Pa; $R = 8.314$ J mol^{-1} K^{-1})

6. (4 marks)

Data:

$Be(g) \rightarrow Be^{2+}(g) + 2e^{-}(g)$ $\Delta H_1 = 2660 \text{ kJ mol}^{-1}$

$Be(g) \rightarrow Be^{+}(g) + e^{-}(g)$ $\Delta H_2 = 900 \text{ kJ mol}^{-1}$

(a) Calculate ΔH_3 for the reaction: $Be^{+}(g) \rightarrow Be^{2+}(g) + e^{-}(g)$.

(b) ΔH_2 and ΔH_3, respectively, represent the first and second ionisation energies for Be. Comment on the relative values of these enthalpy changes in terms of the electrostatic properties of the species Be and Be^{+}.

7. (6 marks)

Data:

$Na(g) \rightarrow Na^+(g) + e^-(g)$ $\Delta U = 494 \text{ kJ mol}^{-1}$ at **0 K**

(a) Given that $C_V = 12.47 \text{ J mol}^{-1} \text{ K}^{-1}$ for $e^-(g)$, calculate ΔU at 298 K for the above process. [You may assume that Na(g) and $Na^+(g)$ have equal values of C_V.]

(b) Using your answer for part (a), calculate ΔH at 298 K for the above process. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) [If you were unable to obtain an answer for (a) use the **incorrect** value of $\Delta U_{298K} = 500 \text{ kJ mol}^{-1}$ here.]

8. (5 marks)

Methanol (CH_3OH) is an organic liquid that is used as a fuel in some automobile engines. From the following data, calculate the standard molar enthalpy of formation of methanol:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \qquad \Delta H^\circ = -1452.8 \text{ kJ mol}^{-1}$$

Substance	ΔH_f° (kJ mol^{-1})
$CO(g)$	-110.5
$CO_2(g)$	-393.5
$H_2O(g)$	-241.8
$H_2O(l)$	-285.8
$O(g)$	249.4
$O_3(g)$	142.2

9. (13 marks)

$N_2O_4(g)$ is unstable at room temperature and decomposes according to reaction (1):

$$N_2O_4(g) \rightarrow 2NO_2(g) \qquad (1)$$

(a) Assuming first-order kinetics, give a mathematical expression for the ***differential rate law*** for reaction (1).

(b) Define, ***in words***, what is meant by the half-life of a first-order reaction.

(c) Give a mathematical expression for the ***integrated rate law*** for reaction (1) and use it to show that the half life ($t_{1/2}$) of a first-order reaction can be mathematically defined by equation (2):

$$t_{1/2} = \log_e(2)/k \qquad (2)$$

Question 9 continued on the next page

(d) At a temperature of 273 K, reaction (1) has a rate constant of 4.5×10^3 s^{-1}.

Calculate the half life for the decomposition of N_2O_4(g) at this temperature.

(e) In a particular experiment, N_2O_4(g) at 273 K has an initial partial pressure of 0.5 atm. Calculate the partial pressure of N_2O_4(g) after 100 μs (1×10^{-4} s)?

(f) The rate constant for reaction (1) is 1.00×10^4 s^{-1} at 283 K. Calculate the activation energy? (R = 8.314 J mol^{-1} K^{-1})

10. (12 marks)

Consider the equilibrium between molecular oxygen (O_2) and ozone (O_3) as represented by equation (1):

$$3O_2(g) \rightleftharpoons 2O_3(g) \qquad (1)$$

For this reaction at 25°C, $\Delta H° = +284$ kJ mol^{-1} and $K = 5.545 \times 10^{-58}$.

(a) Calculate $\Delta H°$ for the reaction: $^{2}/_{3}O_3(g) \rightleftharpoons O_2(g)$ at 25°C.

(b) Calculate K for the reaction: $^{2}/_{3}O_3(g) \rightleftharpoons O_2(g)$ at 25°C.

(c) Calculate the partial pressure of ozone that will be present at equilibrium with a partial pressure of 0.20 atm of oxygen at 25°C.

Question 10 continued on the next page

Question 10 continued

(d) What would be the effect on the equilibrium given in equation (1) of increasing the volume of the system?

(e) What would be the effect on the equilibrium given in equation (1) of decreasing the temperature?

END OF PAPER

Physical Chemistry Formulae

$PV = nRT$

$P_A = x_A P_{total}$ where $P_{total} = P_A + P_B$ and $x_i = \frac{n_i}{\sum_i n_i}$

$P_A = X_A P_A^\circ$

$P_B = (k_H)_B X_B$

$\Delta U = q + w$

$w_P = -P\Delta V$

$H = U + PV$

$\Delta H = \Delta U + RT\Delta n_{gas}$ when $\Delta T = 0$ $\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1)$

$C_P = dH/dT$ (when $\Delta P = 0$) $C_V = dU/dT$ (when $\Delta V = 0$)

$\Delta H_{reaction} = \sum_{prods} \nu_{prod}\Delta H_f(prod) - \sum_{reacts} \nu_{react}\Delta H_f(react)$

For $aA + bB \rightarrow cC + dD$, $\text{Rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

For $\text{Rate} = \frac{-d[A]}{dt} = k$, $[A] = [A]_0 - kt$

For $\text{Rate} = \frac{-d[A]}{dt} = k[A]$, $[A] = [A]_0 e^{-kt}$ and $t_{1/2} = (1/k)\log_e(2)$

$k = Ae^{-E_a/RT}$ $\log_e(k_2/k_1) = E_a/R(1/T_1 - 1/T_2)$

$K_a = \frac{[H^+][A^-]}{[HA]}$ $K_b = \frac{[BH^+][OH^-]}{[B]}$

$pH = -\log_{10}[H^+]$

$pH = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) = pK_a + \log_{10}(n(A^-)/n(HA))$

$\Delta S = \sum_{prods} \nu_{prod} S(prod) - \sum_{reacts} \nu_{react} S(react)$

$\Delta S_{phase\ change} = \frac{\Delta H_{phase\ change}}{T_{critical}}$ $\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \sum_{prods} \nu_{prod}\Delta G_f(prod) - \sum_{reacts} \nu_{react}\Delta G_f(react)$

$\Delta G = \Delta G^\circ + RT\log_e Q$ $\Delta G^\circ = -RT\log_e K$

$\log_e K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ $\log_e\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$E_{cell} = E_{RHS} - E_{LHS} = E_{cathode} - E_{anode}$

$w_{elect} = \Delta G = -nFE$

$\Delta G^\circ = -RT\log_e K = -nFE^\circ$

$E^\circ = \frac{RT}{nF}\log_e K = \frac{2.303RT}{nF}\log_{10}K$ At 25˚C: $E^\circ = \frac{0.0591\text{ V}}{n}\log_{10}K$

$E = E^\circ - \frac{RT}{nF}\log_e Q = E^\circ - \frac{2.303RT}{nF}\log_{10}Q$ At 25˚C: $E = E^\circ - \frac{0.0591\text{ V}}{n}\log_{10}Q$

R Gas constant (8.314 J mol^{-1} K^{-1} or 0.082 L atm mol^{-1} K^{-1})

F Faraday Constant (96489 C mol^{-1})

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	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	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	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 (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	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

89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)