For Examiners' use only:

Question	1 – 3	4 – 7	8	9	Total
Mark	/9	/19	/17	/15	/60

CHEM 113 TEST

Monday, 28 April, 2008

Name (Print clearly): ....

Student ID No: ....ANSWERS....

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 is:

1. a periodic table, and
2. a sheet containing physical chemistry formulae.

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

1. (4 marks)

For the elements below, give the full electron configurations. (Use Ne ($Z = 10$) $(1s)^2$ $(2s)^2$ $(2p)^6$ as a model.)

Ca ($Z = 20$)

Ca $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^2$

Cu ($Z = 29$)

Cu $(1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6 (4s)^1 (3d)^{10}$

2. (3 marks)

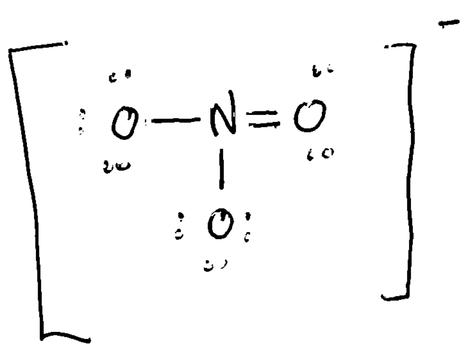
Bromine is an element that has two stable isotopes in roughly equal abundance. For the isotopic cation $^{79}Br^{+}$, give the following:

(a)	The number of protons per ion	35
(b)	The number of electrons per ion	34
(c)	The number of neutrons per ion	44

3. (2 marks)

Draw the Lewis dot structure for the nitrate anion, NO_3^-, and select from the possibilities below the number of single bonds, double bonds and lone pairs.

(a) 2,1,10 (b) 3,1,9 (c) 3,0,10 (d) 1, 2, 7 (e) 2,1,8



4. (4 marks)

Write a balanced half equation for the following (incomplete) ion-electron reaction occurring in **basic** solution

$MnO_4^- \longrightarrow MnO_2$

Acid $MnO_4^- + 4H^+ + 3e \longrightarrow MnO_2 + 2H_2O$ Add $4OH^-$ to both sides

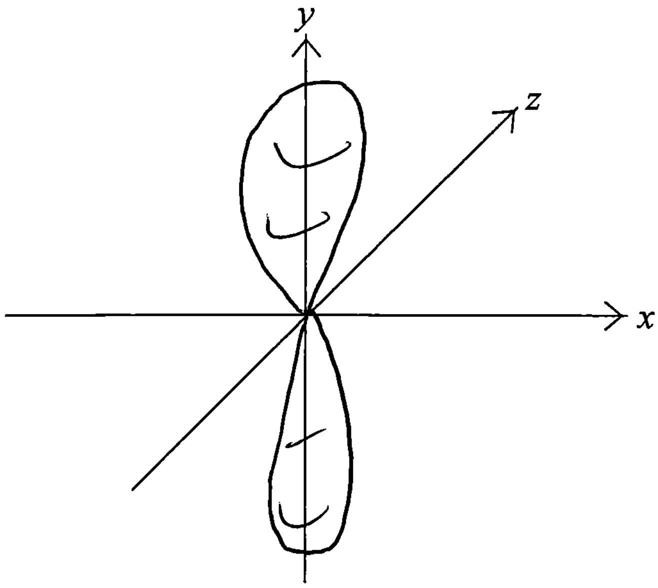
$MnO_4^- + 2H_2O + 3e \longrightarrow MnO_2 + 4OH^-$

What are the two oxidation states of Mn in the reaction? +7, +4

What colour change would you see? Purple → dark brown

5. (2 marks)

Sketch a probability distribution for a $2p_y$ atomic orbital.



6. (7 marks)

A 3.2 L flask at 20 ˚C contains a mixture of two gases and a small quantity (< 1 mL) of liquid water at equilibrium. The gases are N_2 at a partial pressure of 0.79 atm and O_2 at a partial pressure of 0.20 atm.

At 20 ˚C, the vapour pressure of water is 17.5 mm of Hg; 1 atm = 760 mm of Hg = 1.013 × 10^5 Pa; R = 8.314 J mol^{-1} K^{-1}.

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

$P_{total} = P = P_{N_2} + P_{O_2} + P_{H_2O}$ Daltons Law

$= 0.79 + 0.20 + \frac{17.5}{760} = 1.013$ atm $= 1.01$ atm (2 sf)

(b) Of the gas, what is the mole fraction of O_2, X_{O_2} in the flask?

$X_{O_2} = \frac{P_{O_2}}{P} = \frac{0.20}{1.013} = 0.197 = 0.20$ (2sf)

(c) What is the partial pressure of O_2 in the flask in units of Pa?

$P_{O_2} = 0.20$ atm

$= 0.20$ atm $\times 1.013 \times 10^5$ Pa $atm^{-1} = 2.026 \times 10^4$ Pa

$= 2.0 \times 10^4$ Pa (2sf)

(d) Calculate the number of moles of O_2 in the flask. (For the purposes of this calculation ignore the small volume occupied by the liquid water).

$P_{O_2}V = n_{O_2}RT$

$n_{O_2} = \frac{P_{O_2}V}{RT} = \frac{2.026 \times 10^4 \times 3.2 \times 10^{-3}}{8.314 \times 293.15}$

$= 0.0266$ mols $\simeq 0.027$ mols

or//

$n_{O_2} = \frac{0.20 \text{ atm} \times 3.2 \text{L}}{0.082 \text{ L atm mol}^{-1} \text{K}^{-1} \times 293.15 \text{K}}$

$= 0.0266$ mols $= 0.027$ mols.

7. (6 marks)

25.7 mL of a solution of 0.015 mol L^{-1} sodium thiosulfate ($S_2O_3^{2-}$) reacts to completion with 15.5 mL of iodine solution in neutral conditions to give as products tetrathionate ($S_4O_6^{2-}$) and iodide (I^-).

(a) Write a balanced ion-electron half equation for

$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$

$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

(b) Write a balanced ion-electron half equation for

$I_2 \longrightarrow I^-$

$I_2 + 2e^- \rightarrow 2I^-$

(c) Write a balanced equation for the overall redox reaction.

$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

(d) Calculate the concentration of the iodine solution.

$\frac{\text{mols } S_2O_3^{2-}}{\text{mols } I_2} = \frac{2}{1}$

$[S_2O_3^{2-}] \times V_{S_2O_3^{2-}} = 2 \times [I_2] \times V_{I_2}$

$0.015 \text{ mol L}^{-1} \times 25.7 \text{ mL} = 2 \times [I_2] \times 15.5 \text{ mL}$

$[I_2] = 0.012 \text{ M}$

(e) What indicator would you use to enhance the colour change of this reaction?

starch.

8. (17 marks)

$\Delta U° = -5\ 172$ kJ mol^{-1} for the combustion of solid naphthalene, $C_{10}H_8(s)$.

(a) (i) Define the change in internal energy, ΔU, for a reaction.

$\Delta U = U_{products} - U_{reactants}$ (= difference in Energy, U, of products + reactants)

$= q + w$ (Heat absorbed from surroundings + work done on system as the reaction proceeds

(ii) Write the balanced chemical equation for the combustion of 1 mol of naphthalene at 298 K.

$C_{10}H_{8(s)} + 12\ O_{2(g)} \rightarrow 10\ CO_{2\,(g)} + 4H_2O_{(l)}$

(iii) Calculate $\Delta H°$ for the combustion of naphthalene.

[$R = 8.314$ J K^{-1} mol^{-1}] $\Delta n = 10 - 12 = -2$

$\Delta H° = \Delta U° + RT.\Delta n$

$= -5172$ (kJ) $+ [8.314 \times 298 \times (-2)/1000]$

$= -5172 - 4.955$

$= -5177$ kJ mol^{-1}

(iv) Calculate q_P (i.e., q at constant pressure) for combustion of 0.1 mol of naphthalene at 298 K.

$q_P = \Delta H$ For 0.1 mol of Naphth.

$\therefore q_P = 0.1 \times (-5177) = -517.7$ kJ

(v) Calculate w_P (i.e., w at constant pressure) for combustion of 1 mol of naphthalene at 298 K.

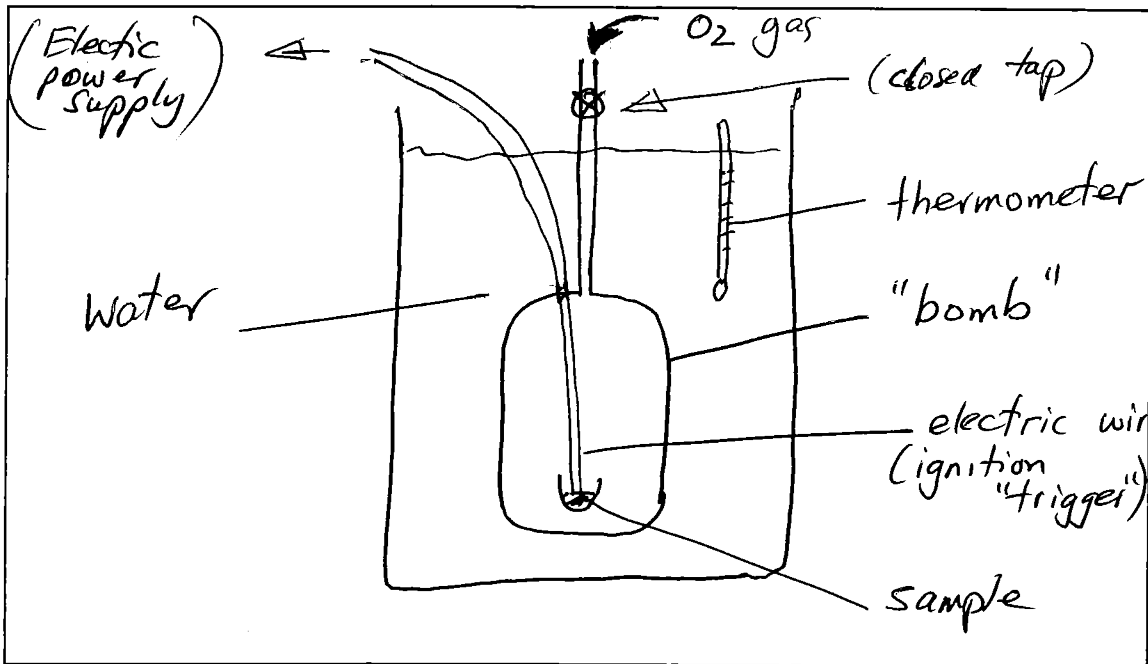
$w_P = -P.\Delta V = -RT.\Delta n$

$= +4.955$ kJ mol^{-1}

(b) A constant-**volume** calorimeter containing 1.000 kg of water is calibrated by combustion of 1.28 g of naphthalene in it at 298 K. A temperature rise of 6.56 °C is observed.

[Useful information: $M(C_{10}H_8) = 128\ \text{g mol}^{-1}$; specific heat of water: $4.184\ \text{J g}^{-1}\ \text{K}^{-1}$; ΔU° for combustion of naphthalene is given at start of question]

(i) Sketch a constant-volume calorimeter, labelling its essential features.



(ii) Calculate the heat capacity of the complete calorimeter, including the water.

$$\Delta U_{total} = C_{V(total)} \cdot \Delta T = -\Delta U_{combustion}$$

$$\Delta U_{combustion} = \frac{1.28}{128} \times \Delta U^{\circ} = 0.01 \times (-5172)\ \text{kJ}$$

$$\therefore C_{V(total)} = \frac{+0.01 \times 5172}{6.56}$$

$$= 7.884\ \text{kJ K}^{-1}$$

$$= 7884\ \text{J K}^{-1}$$

(iii) Calculate the heat capacity of the empty calorimeter, excluding the water.

$$C_V(\text{total}) = C_V(\text{water}) + C_V(\text{calorimeter})$$

$$\therefore 7884 = 1000 \times 4.184 + C_V(\text{calorimeter})$$

$$\therefore C_V(\text{calorimeter}) = 7884 - 4184$$

$$= 3700\ \text{J K}^{-1}$$

9. (15 marks)

Pure NOCl gas was heated to 240 °C in a 1.00 L container. The following equilibrium was established:

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

At equilibrium it was found that the total pressure was 1.00 atm and that the NOCl partial pressure was 0.70 atm.

(a) Explain why the symbol $\rightleftharpoons$ is used to denote chemical equilibrium.

The forward and backward reactions both occur (and at equal rates)

(b) Calculate the partial pressures of NO and Cl_2 in the equilibrium system.

$P_{total} = 1$ atm

$P_{NOCl} = 0.70$ atm.

From Dalton's law $P_{NO} + P_{Cl_2} = P_{total} - P_{NOCl}$

$P_{NO} / P_{Cl_2} = 2/1$ from stoichiometry $= 0.3$ atm

So, $P_{NO} = 0.2$ atm, $P_{Cl_2} = 0.1$ atm

(c) Calculate the value of the thermodynamic equilibrium constant, *K*, for this process at 240 °C.

$$K = \frac{P_{NO}^2 P_{Cl_2}}{P_{NOCl}^2} = \frac{0.2^2 \times 0.1}{0.7^2}$$

$$= 0.00816$$

Pressures in atm, not Pa

(d) Given the standard enthalpies of formation, $\Delta H_f^o(NOCl(g)) = 51.7$ kJ mol^{-1} and $\Delta H_f^o(NO(g)) = 90.4$ kJ mol^{-1}, show that the above process is endothermic.

$\Delta H^o = 2\Delta H_f^o(NO(g)) + \Delta H_f^o(Cl_2(g))$
$- 2\Delta H_f^o(NOCl(g))$
$= 2 \times 90.4 + 0 - 2 \times 51.7$
$= 77.4$ kJ mol^{-1}

(e) Given that the above process is endothermic, use Le Châtelier's principle to predict how the partial pressures will change if the temperature of the system is lowered from 240 °C to 140 °C.

If we write the reaction:
$Q + 2NOCl \rightarrow 2NO + Cl_2$
Q is heat supplied to the system
A drop in T lowers Q
So reactants favoured.
NO, Cl_2 pressures drop
NOCl pressure increase

(f) Explain how the equilibrium will adjust if the volume is increased from 1.00 L to 5.00 L.

If V increased, P_{total} decreased.
System moves to increase P by increasing products (more gas molecules)
NO, Cl_2 pressures increase ~~relative to~~ to NOCl. Equilibrium position moves towards products.