

For Examiners' use only:

Question	1 – 3	4 – 5	6	7	8	Total
Mark	/9	/11	/16	/10	/14	/60

CHEM 113 TEST

Tuesday 1 May, 2007

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 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)

- (a) How many electrons are there in the **p orbitals** of the $n = 3$ shell when all the orbitals are filled? (Clearly circle around the correct answer)

0	1	3	4	6	9	10	12
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- (b) How many electrons are there in the **d orbitals** of the $n = 3$ shell when all the orbitals are filled? (Clearly circle around the correct answer)

0	1	3	4	6	9	10	12
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- (c) Name **TWO** elements that have completely filled d subshells in their lowest energy states and also have atomic numbers less than 36

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2. (3 marks)

Chlorine is an element that has two stable isotopes in reasonable abundance. For the isotopic anion $^{37}\text{Cl}^-$, which has an atomic mass of 36.966, give the following:

- (a) the number of protons per ion;

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- (b) the number of electrons per ion;

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- (c) the number of neutrons per ion.

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3. (2 marks)

Draw the Lewis dot structure for the chlorate anion ClO_3^- , then select from the possibilities below for the number of **single bonds**, **double bonds** and **lone pairs**.

(Clearly circle around the correct answer)

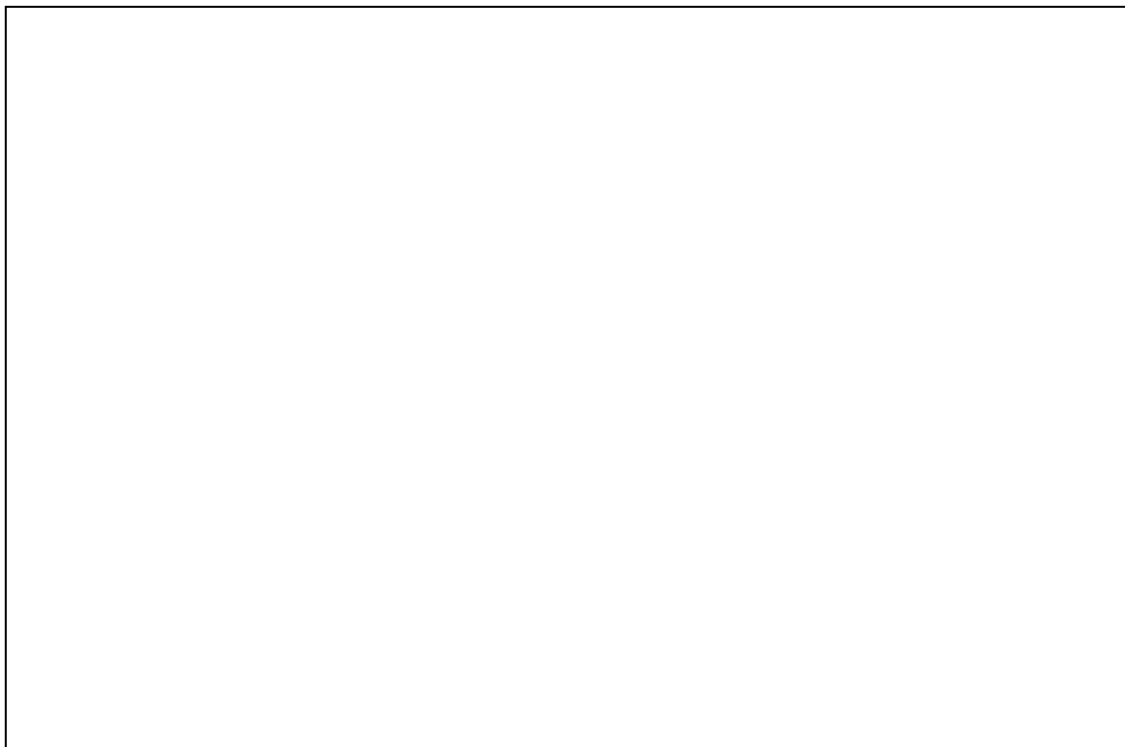
(a) 2,1,0

(b) 3,0,9

(c) 2,1,8

(d) 3,0,10

(e) 3,0,0



4. (6 marks)

An impure sample of calcium carbonate (CaCO_3) of mass 0.384 g was reacted with excess HCl and the CO_2 evolved was collected in a gas burette over water at 20°C on a day when the barometric pressure was 749.70 Torr. The measured volume of gas was found to be 73.4 mL.

Data: At 20°C , the vapour pressure of water is $P_{\text{H}_2\text{O}} = 17.53$ Torr; $1 \text{ atm} = 760 \text{ Torr} = 1.013 \times 10^5 \text{ Pa}$; $20^\circ\text{C} = 293 \text{ K}$; $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; $M(\text{CaCO}_3) = 100.9 \text{ g mol}^{-1}$. (1 Torr \equiv 1 mm of mercury).

(a) Write a balanced equation for the reaction of CaCO_3 and HCl.

(b) Calculate the partial pressure of CO_2 in Pa.

(c) Calculate the number of moles of CO_2 produced.

(d) Calculate the mass of CaCO_3 present in the sample.

5. (5 marks)

The concentration of a hydrogen peroxide solution can be determined by titration against an acidified standard potassium permanganate solution.

(a) Use the ion-electron method to write balanced half equations for this redox reaction:



(b) Write a balanced equation for the full redox reaction.

6. (16 marks)


Most packaged foodstuffs list 'nutritional information' about the food they contain. One such piece of information is the 'energy'. This is determined by combusting a sample of the food in a constant-volume (bomb) calorimeter.

- (a) In a constant-volume calorimetry experiment, is the calorimeter taken to approximate an open, closed or isolated system? Explain your answer.

- (b) Briefly explain how the first law of thermodynamics applies when a combustion process is carried out in a constant-volume calorimeter.

- (c) Does a constant-volume calorimeter measure the enthalpy change (ΔH) or the internal energy change (ΔU) for a process? Explain your answer.

- (d) A quantity of 2.86 g of wholemeal bread was burned in a constant-volume calorimeter. The temperature of the calorimeter rose from 19.28 °C to 22.45 °C. Given that the calorimeter and its contents had a heat capacity of 10.17 kJ K⁻¹, calculate the heat change for the combustion of the bread, expressing your answer in terms of kJ g⁻¹.



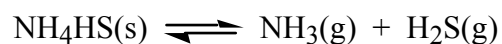
- (e) The human body is not a constant-volume calorimeter. Rather, it burns food by metabolism carried out under approximately constant-pressure conditions. Explain how the heat change measured in a constant-volume calorimeter can be used to calculate the heat change for the same process carried out at constant pressure.



- (f) Explain how a constant-volume calorimeter could be used to determine $\Delta H_f(\text{CO}_2(\text{g}))$, the enthalpy of formation of $\text{CO}_2(\text{g})$. (Your answer should include a chemical equation.)

7. (10 marks)

For the reaction given below, the thermodynamic equilibrium constant at 25 °C is $K = 0.49$.



- (a) Write an expression for the thermodynamic equilibrium constant in terms of the **activities** of the reaction components.

- (b) Indicate the working rules you would use for estimating the activities of **each** of the components in the reaction.

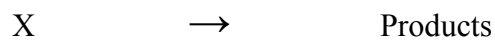
- (c) 10.0 mol of $\text{NH}_4\text{HS}(\text{s})$ are introduced into a closed, evacuated container of volume 2.0 L at 25 °C, and the system allowed to come to equilibrium at this temperature. What is the partial pressure of $\text{H}_2\text{S}(\text{g})$? (You may assumed that all gases are ideal.)

- (d) If the volume of the system in (c) was doubled to 4.0 L, what would be the partial pressure of $\text{H}_2\text{S}(\text{g})$ after re-establishment of equilibrium? **Explain.**

- (e) If 5.0 mol of $\text{NH}_4\text{HS}(\text{s})$ were removed from the system in (c), what would be the partial pressure of $\text{H}_2\text{S}(\text{g})$ after re-establishment of equilibrium? **Explain.**

8. (14 marks)

The decomposition of an organic nitrile (substance X) in aqueous solution is described by the equation:



The following results were obtained in an experiment carried out at 45°C (318 K):

time/s	0	4000	8000	12000	∞
[X]/mol L ⁻¹	1.10	0.67	0.41	0.25	0

(a) Prove that the decomposition is a **first-order** process.

(b) What is the **rate constant**, k , for the decomposition?

(c) What are the **units** for k ?

(d) If the temperature is raised from 45° to 55°C (328 K), the value of k is found to **increase** by a factor of **2.2**. **Explain** how you would determine the activation energy (E_a) for the decomposition reaction.

[No calculation is required in this part.]

END OF PAPER

Physical Chemistry Formulae

$$PV = nRT$$

$$P_A = x_A P_{\text{total}}$$

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

$$P_A = X_A P_A^\circ$$

$$P_B = (k_H)_B X_B$$

$$\Delta U = q + w$$

$$w_P = -P\Delta V$$

$$H = U + PV$$

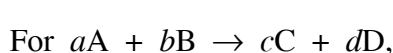
$$\Delta H = \Delta U + RT\Delta n_{\text{gas}} \quad \text{when } \Delta T = 0$$

$$\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1)$$

$$C_P = dH/dT \quad (\text{when } \Delta P = 0)$$

$$C_V = dU/dT \quad (\text{when } \Delta V = 0)$$

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



$$\text{Rate} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

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

$$[A] = [A]_0 - kt$$

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

$$[A] = [A]_0 e^{-kt} \quad \text{and} \quad t_{1/2} = (1/k) \log_e(2)$$

$$k = Ae^{-E_a/RT}$$

$$\log_e \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

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

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

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

$$\Delta S_{\text{phase change}} = \frac{\Delta H_{\text{phase change}}}{T_{\text{critical}}}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

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

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

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

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

$$\log_e K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

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

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

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

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

$$E^\circ = \frac{RT}{nF} \log_e K = \frac{2.303RT}{nF} \log_{10} K$$

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

$$E = E^\circ - \frac{RT}{nF} \log_e Q = E^\circ - \frac{2.303RT}{nF} \log_{10} Q$$

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

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
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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)
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