22/08(a) # The University of Sydney

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2001 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		**SID NUMBER**	
OTHER NAMES		**TABLE NUMBER**	

INSTRUCTIONS TO CANDIDATES

All questions are to be attempted. There are 15 pages of examinable material.

Complete the written section of the examination paper in **INK**.

Read each question carefully. Report the appropriate answer and show all relevant working in the space provided.

The total score for this paper is 100. The possible score per page is shown in the adjacent tables.

Each new short answer question begins with a •

Electronic calculators, including programmable calculators, may be used. Students are warned, however, that credit may not be given, even for a correct answer, where there is insufficient evidence of the working required to obtain the solution.

Numerical values required for any question and a Periodic Table may be found on a separate data sheet.

Pages 6, 11, 15 & 20 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	50	

Short answer section

Page	Marks: Max	Gained		Marker
12	5			
13	10			
14	10			
16	5			
17	7			
18	7			
19	6			
Total	50			
Check Total				

Marks

- Use the information below to calculate the heat of formation of $SO_3(g)$. **2**

$$Pb(s) + PbO_2(s) + 2SO_3(g) \rightarrow 2PbSO_4(s) \qquad \Delta H^\circ_{reaction} = -768 \text{ kJ mol}^{-1}$$

ΔH°_f of $PbO_2(s) = -276.6$ kJ mol^{-1}

ΔH°_f of $PbSO_4(s) = -918.4$ kJ mol^{-1}

ANSWER:

- A neon atom is subjected to UV radiation with a wavelength of 320 nm resulting in the excitation of an electron from a 2p orbital to the 3s orbital. **3**

What is the difference in energy between the 3s and 2p orbitals in Ne?

ANSWER:

How does the radius of the Ne atom change as a result of this excitation? Do you expect this change in radius to be large or small, relative to the size of the original atom? Explain your reasoning.

The first ionisation energies of Ne, Na and Mg are, in order of increasing magnitude, Na < Mg < Ne. Where in this sequence would you expect the ionisation energy of the excited neon atom to come? Explain your answer.

Marks

- Complete the following table 3

Species	$\underline{N}O_2^-$	$\underline{S}O_2$	$\underline{S}O_3$
Number of valence electron pairs about the underlined atom not involved in π bonding			
Shape of species			

- Provide a brief explanation of the physical origin of dispersion forces between non-polar molecules. 2

- Arrange the following molecules in order of increasing molecular dipole moment. 1

CO, CO_2, HF, HCl

smallest molecular dipole moment					largest molecular dipole moment

- Giving a full description and ionic equations for all steps, show how to convert 1 mol of copper(II) sulfate-5-water into copper(II) nitrate-6-water. 4

Marks

- The solvation of sulfuric acid is an exothermic process with a heat of solvation, $\Delta H°$, given by **6**

$$H_2SO_4(l) \xrightarrow{H_2O} 2H^+(aq) + SO_4^{2-}(aq) \qquad \Delta H° = -93.5 \text{ kJ mol}^{-1}$$

Provide an explanation for why this process is exothermic.

Suppose you carry out the dilution of 1.00 mol of H_2SO_4 to produce a 1.00 L solution in a calorimeter. The initial temperature is 25.0 °C, the density of the final solution is 1.060 g mL^{-1}, and its specific heat capacity is 3.50 J g^{-1} K^{-1}. If the total heat capacity of the calorimeter is 90 J K^{-1}, what is the final temperature? *Show all working*.

ANSWER:

- Explain briefly why the atomic orbital energy increases with *n*, the principal quantum number. **2**

- Explain briefly why the atomic orbital energy is typically observed to increase with *l*, the angular momentum quantum number. **2**

	Marks
• Explain why it is, that under certain conditions, some gases (such as ammonia) have $\frac{PV}{nRT} < 1$ while other gases (such as helium) have $\frac{PV}{nRT} > 1$.	3
• In an experiment conducted at high temperature, the effusion of gaseous phosphorus and neon was studied. Under identical conditions, the phosphorus took 2.48 times as long to effuse as the neon. How many atoms are there in a molecule of gaseous phosphorus?	2
ANSWER:	

Marks

- For the reaction: $2NO(g) + Br_2(g) \rightarrow 2NOBr(g)$ 3

  a suggested mechanism is: Step 1 $NO(g) + Br_2(g) \rightarrow 2NOBr_2(g)$

  Step 2 $NOBr_2(g) + NO(g) \rightarrow 2NOBr(g)$

  (i) Write the rate law if the first step in this mechanism is slow and the second fast.

  (ii) Write the rate law if the second step is slow, with the first step being a rapidly established equilibrium.

- The isomerisation $CH_3NC(g) \rightarrow CH_3CN(g)$ obeys first order kinetics. It has an activation energy of 160 kJ mol^{-1} and the rate constant measured at 600 K is 0.41 s^{-1}. Calculate the half-life of this reaction at 800 K. Show all working. 4

ANSWER:

	Marks
• A biochemist needs 0.400 L of an acetic acid/sodium acetate buffer with pH = 4.44. Solid sodium acetate, $NaCH_3CO_2$ and glacial acetic acid are available. Glacial acetic acid is 99% CH_3COOH by weight and has a density of 1.05 g mL^{-1}. If the K_a of CH_3COOH is 1.8×10^{-5} and the buffer is to be 0.30 M in CH_3COOH, what mass of $NaCH_3CO_2$ and what volume of glacial acetic acid must be used?	4

mass of $NaCH_3CO_2$ =	volume of glacial acetic acid =

	Marks
• A 0.25 M water solution of trimethylamine, $(CH_3)_3N$, has a pOH of 2.40. Find the K_b for trimethylamine and the pK_a for the trimethylammonium ion, $(CH_3)_3NH^+$.	3

K_b =	pK_a =

Marks

- By determining the Gibbs free energy of reaction, determine whether the reaction **2**

$$2Fe(s) + 3O_2(g) \rightarrow Fe_2O_3(s)$$

is a spontaneous process under standard conditions at 298 K.

Data: $\Delta_f S^\circ\{Fe_2O_3\} = -272$ J K^{-1} mol^{-1} at 298 K;

$\Delta_f H^\circ\{Fe_2O_3\} = -826$ kJ mol^{-1} at 298 K.

- The hemoglobin molecule (Hb) carries O_2 in the blood in the form $Hb{\cdot}O_2$. One reason CO is toxic is that it competes with O_2 for binding to Hb. **4**

$Hb{\cdot}O_2(aq) + CO(g) \rightleftharpoons Hb{\cdot}CO(aq) + O_2(g)$ $\Delta G^\circ = -14$ kJ mol^{-1} at 37 °C.

What is the ratio of $[Hb{\cdot}CO]/[Hb{\cdot}O_2]$ at 37 °C if $[O_2] = [CO]$?

ANSWER:

Use Le Châtelier's principle to suggest how to treat a victim of CO poisoning.

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Numerical Data

Physical constants

Planck constant = h = 6.626×10^{-34} J s

Speed of light in vacuum = c_o = 2.998×10^{8} ms^{-1}

Avogadro constant = N_A = 6.022×10^{23} mol^{-1}

Standard atmosphere = 1.013×10^{5} Pa = 760.0 mmHg

Ideal gas constant = R = 8.314 J K^{-1} mol^{-1}

= 0.08206 L atm K^{-1} mol^{-1}

Conversion factors

1 nm = 10^{-9} m

1 kJ = 10^{3} J

1 kPa = 10^{3} Pa

1 L = 10^{-3} m^{3}

Thermochemical Data at 298 K

	ΔH_f^o / kJ mol^{-1}
NH_3(g)	–46
NO(g)	90
H_2O(l)	–285

A periodic table is printed on the other side of this data sheet.
Atomic weights are included in the periodic table.