22/08(a) **The University of Sydney**

CHEMISTRY 1A (ADVANCED) - CHEM1901

CHEMISTRY 1A (SPECIAL STUDIES PROGRAM) - CHEM1903

FIRST SEMESTER EXAMINATION

CONFIDENTIAL

JUNE 2002

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 16 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 10, 15 & 20 are for rough working only.

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-9	50	

Short answer section

Page	Marks: Max	Gained		Marker
11	6			
12	4			
13	7			
14	6			
16	6			
17	8			
18	7			
19	6			
Total	50			

Check Total		

	Marks
• Copper(I) is oxidised to copper(II) in the following reaction. $Cu_2O(s) + \frac{1}{2}O_2(g) \rightarrow 2CuO(s)$ $\Delta H^\circ = -146$ kJ mol^{-1} Given that ΔH_f° of $Cu_2O(s)$ is –198.8 kJ mol^{-1}, calculate ΔH_f° of CuO(s).	2
ANSWER:	
• Atmospheric greenhouse gases are typically transparent to visible light (i.e. do not absorb in this frequency range) and opaque (i.e. absorb) at infrared frequencies. Briefly explain how these two features result in warming at the Earth's surface.	2
• Explain why electrons in atoms are not simply pulled continuously in towards the positive nucleus.	2

	Marks
• Explain, in terms of the quantum theory of atomic structure, why the Group 2 metals have significantly larger electron affinities than do the Group 1 metals.	2
• Order the following molecules in terms of increasing molecular dipole moment.	1

$CFCl_2H$, CCl_4, CF_3H, CCl_3H

smallest dipole					largest dipole

	Marks
• Write a balanced nuclear equation for the formation of $^{48}_{22}Ti$ through positron emission.	1

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- Complete the following table. **3**

Species	$\underline{S}Cl_2$	$H_3\underline{O}^+$	$\underline{S}OF_4$
Number of valence electron pairs about the underlined atom not involved in π bonding			
Shape of species			

- In a calorimetry experiment similar to E10, 50.0 mL of 1.00 M HNO_3 was combined with 50.0 mL of 0.540 M NaOH in a calorimeter. The heat capacity of the calorimeter is 80.0 J K^{-1} and the heat capacity of the final solution is 426 J K^{-1}. The temperature was found to increase by 2.98 °C. Determine the molar heat of reaction for the process $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$. **4**

ANSWER:

The average bond enthalpy of the O–H bond is 463 kJ mol^{-1}. Explain briefly why the heat of neutralisation calculated in the first part of this question differs significantly from this value.

Marks

- A rock sample is found to contain 2.100×10^{-15} mol of ^{232}Th, a nuclide with a half life of 1.4×10^{10} years. Analysis of the sample reveals that 9.5×10^{6} ^{232}Th nuclei have undergone decay. Using this information, estimate the age of the rock. **2**

ANSWER:

- ClO_3 is a highly reactive molecule. With reference to the Lewis structure of the molecule, explain why this is so. **2**

- Explain briefly how electron pairing arises in the quantum theory of atomic structure. **2**

Marks

- In the equation, $(P + n^2a/V^2)(V - nb) = nRT$, the parameters "*a*" and "*b*" are used to correct the Ideal Gas Equation, $PV = nRT$, for non-ideal behaviour. Briefly explain what aspect of non-ideal behaviour each of these parameters corrects. 2

- One way of separating oxygen isotopes is by gaseous effusion of carbon monoxide. Calculate the relative rates of effusion of $^{12}C^{16}O$ and $^{12}C^{18}O$. 4

How many effusion processes would be needed to give a 23% increase in the $^{12}C^{16}O$ / $^{12}C^{18}O$ ratio?

Marks
8

- The decomposition of ozone to oxygen gas, $2O_3(g) \rightarrow 3O_2(g)$, is found to have the following rate law:

$$\text{Rate} = k[O_3]$$

Provide a mechanism for this reaction that is consistent with this rate law.

At 25 °C and an initial ozone concentration of 0.0100 M, the rate of formation of O_2 is 5.94×10^{-6} mol L^{-1} s^{-1}. How long would it take for the $[O_3]$ to drop to one tenth of its initial value at this temperature?

One important mechanism for the destruction of ozone in the upper atmosphere is

$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$
$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$$

Overall $O_3(g) + O(g) \rightarrow 2O_2(g)$

Name the species that are the catalyst and the intermediate in this two-step reaction.

E_a for the catalysed reaction is 11.9 kJ mol^{-1} whereas E_a for the uncatalysed reaction is 14.0 kJ mol^{-1}. At – 45 ºC, the temperature of the ozone layer, what is the ratio of the rate constant for the catalysed reaction to that of the uncatalysed reaction? Assume that the frequency factor, *A*, is the same for each reaction.

	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 =

• Oxalic acid is a diprotic acid: **2**

$$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^- \qquad K_{a1} = 5.6 \times 10^{-2}\ M$$

$$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{2-} \qquad K_{a2} = 5.4 \times 10^{-5}\ M$$

Calculate the pH of a buffer solution made by adding 3.0 mol of $H_2C_2O_4$ and 1.0 mol of $Na_2C_2O_4$.

pH =

• Calculate the pH of 1.0×10^{-7} M hydrochloric acid. **2**

pH =

	Marks
• Consider the following reaction.	6

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \qquad \Delta H^\circ = -103.8 \text{ kJ mol}^{-1}$$

In a particular experiment, equimolar amounts of $H_2(g)$ and $Br_2(g)$ were mixed in a 1.00 L flask at 25 ºC to give a total pressure of 1.00 atm. After the system had reached equilibrium, 1.10×10^{13} H_2 molecules remained in the flask. Calculate the values of K, ΔG° and ΔS° for this reaction at 25 ºC.

K =	ΔG° =	ΔS° =

Using Le Châtelier's principle, predict the direction in which the equilibrium will shift if the temperature is increased. Explain your answer.

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Numerical Data

Physical constants

Planck constant = $h = 6.626 \times 10^{-34}$ J s

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

Avogadro constant = $N_A = 6.022 \times 10^{23}$ mol^{-1}

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}

1 atm = 101.3 kPa

Solution to the quadratic equation

If $ax^2 + bx + c = 0$ then $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

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

... / 2

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 HYDROGEN **H** 1.008																	2 HELIUM **He** 4.003
3 LITHIUM **Li** 6.941	4 BERYLLIUM **Be** 9.012											5 BORON **B** 10.81	6 CARBON **C** 12.01	7 NITROGEN **N** 14.01	8 OXYGEN **O** 16.00	9 FLUORINE **F** 19.00	10 NEON **Ne** 20.18
11 SODIUM **Na** 22.99	12 MAGNESIUM **Mg** 24.31											13 ALUMINIUM **Al** 26.98	14 SILICON **Si** 28.09	15 PHOSPHORUS **P** 30.97	16 SULFUR **S** 32.07	17 CHLORINE **Cl** 35.45	18 ARGON **Ar** 39.95
19 POTASSIUM **K** 39.10	20 CALCIUM **Ca** 40.08	21 SCANDIUM **Sc** 44.96	22 TITANIUM **Ti** 47.88	23 VANADIUM **V** 50.94	24 CHROMIUM **Cr** 52.00	25 MANGANESE **Mn** 54.94	26 IRON **Fe** 55.85	27 COBALT **Co** 58.93	28 NICKEL **Ni** 58.69	29 COPPER **Cu** 63.55	30 ZINC **Zn** 65.39	31 GALLIUM **Ga** 69.72	32 GERMANIUM **Ge** 72.59	33 ARSENIC **As** 74.92	34 SELENIUM **Se** 78.96	35 BROMINE **Br** 79.90	36 KRYPTON **Kr** 83.80
37 RUBIDIUM **Rb** 85.47	38 STRONTIUM **Sr** 87.62	39 YTTRIUM **Y** 88.91	40 ZIRCONIUM **Zr** 91.22	41 NIOBIUM **Nb** 92.91	42 MOLYBDENUM **Mo** 95.94	43 TECHNETIUM **Tc** [98.91]	44 RUTHENIUM **Ru** 101.07	45 RHODIUM **Rh** 102.91	46 PALLADIUM **Pd** 106.4	47 SILVER **Ag** 107.87	48 CADMIUM **Cd** 112.40	49 INDIUM **In** 114.82	50 TIN **Sn** 118.69	51 ANTIMONY **Sb** 121.75	52 TELLURIUM **Te** 127.60	53 IODINE **I** 126.90	54 XENON **Xe** 131.30
55 CAESIUM **Cs** 132.91	56 BARIUM **Ba** 137.34	57-71	72 HAFNIUM **Hf** 178.49	73 TANTALUM **Ta** 180.95	74 TUNGSTEN **W** 183.85	75 RHENIUM **Re** 186.2	76 OSMIUM **Os** 190.2	77 IRIDIUM **Ir** 192.22	78 PLATINUM **Pt** 195.09	79 GOLD **Au** 196.97	80 MERCURY **Hg** 200.59	81 THALLIUM **Tl** 204.37	82 LEAD **Pb** 207.2	83 BISMUTH **Bi** 208.98	84 POLONIUM **Po** [210.0]	85 ASTATINE **At** [210.0]	86 RADON **Rn** [222.0]
87 FRANCIUM **Fr** [223.0]	88 RADIUM **Ra** [226.0]	89-103	104 RUTHERFORDIUM **Rf** [261]	105 DUBNIUM **Db** [262]	106 SEABORGIUM **Sg** [266]	107 BOHRIUM **Bh** [262]	108 HASSIUM **Hs** [265]	109 MEITNERIUM **Mt** [266]									

LANTHANIDES														
57 LANTHANUM **La** 138.91	58 CERIUM **Ce** 140.12	59 PRASEODYMIUM **Pr** 140.91	60 NEODYMIUM **Nd** 144.24	61 PROMETHIUM **Pm** [144.9]	62 SAMARIUM **Sm** 150.4	63 EUROPIUM **Eu** 151.96	64 GADOLINIUM **Gd** 157.25	65 TERBIUM **Tb** 158.93	66 DYSPROSIUM **Dy** 162.50	67 HOLMIUM **Ho** 164.93	68 ERBIUM **Er** 167.26	69 THULIUM **Tm** 168.93	70 YTTERBIUM **Yb** 173.04	71 LUTETIUM **Lu** 174.97

ACTINIDES	89 ACTINIUM **Ac** [227.0]	90 THORIUM **Th** 232.04	91 PROTACTINIUM **Pa** [231.0]	92 URANIUM **U** 238.03	93 NEPTUNIUM **Np** [237.0]	94 PLUTONIUM **Pu** [239.1]	95 AMERICIUM **Am** [243.1]	96 CURIUM **Cm** [247.1]	97 BERKELLIUM **Bk** [247.1]	98 CALIFORNIUM **Cf** [252.1]	99 EINSTEINIUM **Es** [252.1]	100 FERMIUM **Fm** [257.1]	101 MENDELEVIUM **Md** [256.1]	102 NOBELIUM **No** [259.1]	103 LAWRENCIUM **Lr** [260.1]