22/03(a) The University of Sydney

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2004 **TIME ALLOWED: THREE HOURS**

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

FAMILY NAME		SID NUMBER	
OTHER NAMES		TABLE NUMBER	

OFFICIAL USE ONLY

Multiple choice section

	Marks	
Pages	Max	Gained
2-10	36	

Short answer section

Page	Marks			Marker
	Max	Gained		
11	8			
12	6			
14	5			
15	7			
17	8			
18	4			
19	6			
20	6			
21	5			
22	5			
23	4			
Total	64			

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 20 pages of examinable material.
- Complete 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 question of the short answer section 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, standard electrode reduction potentials, a Periodic Table and some useful formulas may be found on the separate data sheets.
- Pages 13, 16 and 24 are for rough working only.

Marks

3

- The most common x-ray source for laboratory diffractometers is a copper anode, which emits so-called $K_{\alpha 1}$ x-rays with wavelength $\lambda = 0.154$ nm. If an anode made of 10.0 g of copper wire emits $K_{\alpha 1}$ x-ray energy at a rate of 2.00 kJ s^{-1}, at what rate are the individual copper atoms emitting $K_{\alpha 1}$ photons (*i.e.* photon $atom^{-1}$ s^{-1})?

ANSWER:

5

- Draw Lewis structures for the following molecules or ions, indicate the hybridisation of the central atom (underlined) and sketch the 3-D shape of the molecule or ion.

Species	Lewis structure	Hybridisation	Sketch of 3-D shape of species
<u>S</u>OF$_4$			
N<u>C</u>O$^-$			

Draw all resonance contributors to the NCO^- ion.

Marks
6

- The final step in the industrial production of urea, $CO(NH_2)_2$, is:

$$CO_2(g) + 2NH_3(g) \rightarrow H_2O(g) + CO(NH_2)_2(s) \qquad \Delta H° = -90.1 \text{ kJ mol}^{-1}$$

Using the following data, calculate the standard enthalpy of formation $\Delta H°_f$ of solid urea.

$$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g) \qquad \Delta H° = -1267.2 \text{ kJ mol}^{-1}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H° = -393.5 \text{ kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H° = -483.6 \text{ kJ mol}^{-1}$$

$\Delta H°_f$ =

The formation of urea in this process is only spontaneous above 821 °C. What is the value of the entropy change $\Delta S°$ (in J K^{-1} mol^{-1}) for the reaction?

$\Delta S°$ =

Rationalise the sign of $\Delta S°$ in terms of the physical states of the reactants and products.

Marks
5

- Equal volumes of carbon monoxide and hydrogen gas are introduced into a sealed 4.5 L flask at 1200 K and the following equilibrium is established.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H° = -205.9 \text{ kJ mol}^{-1}$$

At equilibrium, the flask contains 0.22 mol of CH_4 and the total pressure in the flask is 46.4 atm. Calculate the amount of $H_2(g)$ (in mol) that was initially introduced into the flask.

Answer:

In a separate experiment, it is determined that the reaction is in equilibrium when the same 4.5 L flask contains 0.18 mol of CH_4, 0.24 mol of H_2O, 0.82 mol of CO and 0.65 mol of H_2 at 1200 K. Calculate the concentration equilibrium constant, K_c, for this temperature.

K_c =

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks
7

Calculate the partial pressure equilibrium constant, K_p, at 1200 K.

K_p =

What is the standard free energy change $\Delta G°$ for the forward reaction (in kJ mol^{-1}) at 1200 K?

$\Delta G°$=

What will be the effect on the equilibrium if CO(g) is injected into the flask, which maintains a constant volume.

What will be the effect on the equilibrium if the temperature is decreased?

What will be the effect on the equilibrium if the volume of the flask is decreased?

What will be the effect on the equilibrium if the walls of the flask are refrigerated so that liquid water condenses out?

Marks
8

- Sucrose, $C_{12}H_{22}O_{11}$, is dissolved in 100 mL of water at 25 °C. The osmotic pressure is measured as 12.2 atm. What is the mass of sucrose that was originally dissolved?

Answer:

Calculate the vapour pressure of water above this solution, given that at 25 °C, the density of water is 0.997 g mL^{-1} and the vapour pressure of water is 23.8 mmHg.

Answer:

If this solution is heated at 1.00 atm, at what temperature will the water boil?
The molal boiling point elevation constant (K_b) for pure water is 0.512 °C kg mol^{-1}.

Answer:

Marks

- Calculate the molar solubility of $Fe(OH)_3$ in a pH = 5.0 buffer solution. The solubility product constant of $Fe(OH)_3$ is 4×10^{-38} M^4. **2**

Answer:

- Coordination complexes can display a number of types of isomerism. Draw a simple diagram showing a pair of geometric isomers. Label your diagram with the systematic name of each isomer. **2**

Marks

- A voltaic cell is constructed with a $Cr_2O_7^{2-}/Cr^{3+}$ (in acidic solution) half cell and a Sn/Sn^{2+} half cell. Measurement shows that the Sn electrode is negative. Write the balanced half equations and the overall spontaneous reaction. **3**

reduction half equation	
oxidation half equation	
overall reaction	

- How many hours will it take to produce 1.00 kg of aluminium metal from a molten Al^{3+} salt, using a current of 100 A? **3**

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

- Find the concentration of H_3O^+ in a 0.60 M aqueous solution of nitrous acid. The acid dissociation constant of HNO_2 is $K_a = 7.1 \times 10^{-4}$ M. **2**

Answer:

- An aqueous solution of a weak acid has $[H_3O^+] = 2.54 \times 10^{-4}$ M. Find the pH and pOH of the solution. **1**

pH =	pOH =

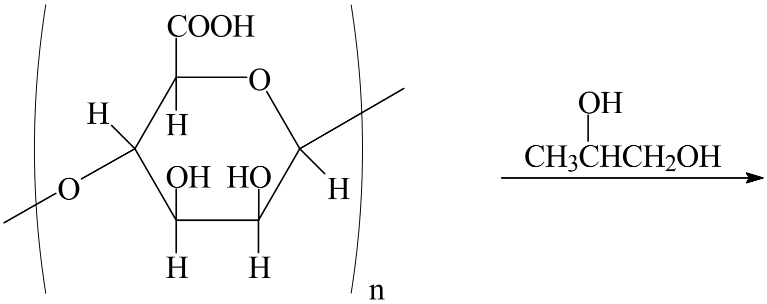
- Ammonia, NH_3, is a Brønsted-Lowry base and a Lewis base, but not an Arrhenius base. Why? **3**

Marks

- Give three examples of colloids in biological systems, and complete the following table. Paint is given as an example of a synthetic (non-biological) system. **3**

Name of colloid	Discrete phase	Continuous phase
paint	*synthetic polymer*	*water*

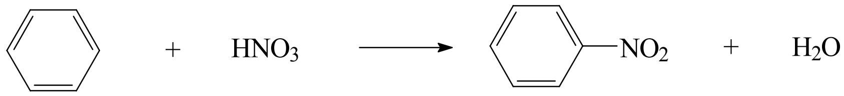
- Alginates are high molecular weight polysaccharides extracted from seaweed. The surface active agent with the common name "propylene glycol alginate" is used as a thickener in foodstuffs. It is made by esterifying approximately 80% of the carboxyl units of the polysaccharide with 1,2-propanediol depicted, in part, below. **2**



Explain in terms of its two components (the polysaccharide and 1,2-propanediol) why the ester functions as (a) a surfactant and (b) a thickener.

Marks
5

- The nitration of benzene to form nitrobenzene may be written with the following stoichiometry.



The reaction was performed in the presence of excess concentrated sulfuric acid and the following data were obtained.

Experiment number	initial [benzene] (M)	initial [nitric acid] (M)	[nitrobenzene] (M) after 100 s
1	0.010	1.0	1.2×10^{-4}
2	0.020	1.0	2.4×10^{-4}
3	0.020	0.50	1.2×10^{-4}

Determine the rate of the reaction for Experiment 1.

Answer:

What is the rate equation for this reaction?

Rate =

What is the value of the rate constant?

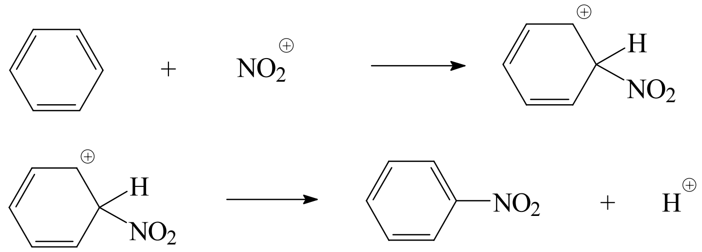
k =

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks

Show that the observed kinetics are consistent with the following mechanism. **2**

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^{+} + HSO_4^{-} + H_2O \qquad \text{(fast)}$$



(slow)

(fast)

- A watch contains a radioactive substance with a decay constant of 1.4×10^{-2} year^{-1}. After 50 years 25 mg of the radioactive material remains. Calculate the amount originally present. **2**

Answer:

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DATA SHEET

Physical constants

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

Faraday constant, $F = 96485$ C mol^{-1}

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

Speed of light in vacuum, $c = 2.998 \times 10^{8}$ m s^{-1}

Rydberg constant, $E_R = 2.18 \times 10^{-18}$ J

Boltzmann constant, $k_B = 1.381 \times 10^{-23}$ J K^{-1}

Gas constant, $R = 8.314$ J K^{-1} mol^{-1}

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

Properties of matter

Volume of 1 mole of ideal gas at 1 atm and 25 °C = 24.5 L

Volume of 1 mole of ideal gas at 1 atm and 0 °C = 22.4 L

Density of water at 298 K = 0.997 g cm^{-3}

Conversion factors

1 atm = 760 mmHg = 101.3 kPa

0 °C = 273 K

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

1 Å = 10^{-10} m

1 eV = 1.602×10^{-19} J

1 Ci = 3.70×10^{10} Bq

1 Hz = 1 s^{-1}

Decimal fractions

Fraction	Prefix	Symbol
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

Decimal multiples

Multiple	Prefix	Symbol
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

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Standard Reduction Potentials, *E* °

Reaction	$E°$ / V
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	+1.82
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+0.92
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
$Cu^+(aq) + e^- \rightarrow Cu(s)$	+0.53
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
$Fe^{3+}(aq) + 3e^- \rightarrow Fe(s)$	–0.04
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	–0.13
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	–0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	–0.24
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	–0.76
$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	–0.89
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	–1.68
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+(aq) + e^- \rightarrow Na(s)$	–2.71

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Useful Formulas

Quantum Chemistry

$E = h\nu = hc/\lambda$

$\lambda = h/mu$

$4.5k_BT = hc/\lambda$

$E = Z^2E_R(1/n^2)$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$K_p = K_c (RT)^{\Delta n}$

Kinetics

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

$t_{½} = \ln 2/k$

$\ln[A] = \ln[A]_o - kt$

Radioactivity

$A = \lambda N$

$\ln(N_0/N_t) = \lambda t$

^{14}C age = 8033 $\ln(A_0/A_t)$

Gas Laws

$PV = nRT$

$(P + n^2a/V^2)(V - nb) = nRT$

Acids and Bases

$pK_w = pH + pOH = 14.00$

$pK_w = pK_a + pK_b = 14.00$

$pH = pK_a + \log\{[A^-] / [HA]\}$

Colligative Properties

$\pi = cRT$

$p = kc$

$P_{solution} = X_{solvent} \times P°_{solvent}$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Electrochemistry

$\Delta G° = -nFE°$

Moles of e^- $= It/F$

$E = E° - (RT/nF) \ln Q$

$\quad = E° - (RT/nF) \times 2.303 \log Q$

$E° = (RT/nF) \ln K$

$\quad = (RT/nF) \times 2.303 \log K$

$E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)

Polymers

$R_g = \sqrt{\frac{nl_0^2}{6}}$

Mathematics

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

$\ln x = 2.303 \log x$

November 2004

CHEM1909

22/03(b)

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]