22/03(a) **The University of Sydney**

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2005 **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	3			
12	4			
13	3			
14	6			
15	7			
16	8			
17	6			
18	2			
19	8			
20	6			
21	4			
22	5			
23	2			
Total	64			

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 22 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.
- Page 24 is for rough working only.

Marks
3

- Neutrons with wavelengths of 0.165 nm are produced in a nuclear reactor and used to study the positions of atoms in a crystal. At what velocity are these neutrons travelling?

ANSWER:

If that velocity can be measured with an uncertainty of 1%, what is the uncertainty in their positions when they reach the crystal?

ANSWER:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

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

Species	Lewis structure (include resonance forms)	Hybridisation	Sketch of 3-D shape of species
<u>C</u>O_3^{2-}			
<u>S</u>F_4			

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
3

- The combustion of hydrazine, N_2H_4, with oxygen is described by the following equation:

  $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$ $\Delta H° = –623$ kJ mol^{-1}

  Given that $\Delta H°_f$ of $H_2O(l)$ is –286 kJ mol^{-1}, find the standard enthalpy of formation of $N_2H_4(l)$.

$\Delta H°_f =$

The combustion of 1.00 mol of $N_2H_4(l)$ can also be accomplished using $N_2O_4(l)$ as the oxidant, whereupon 629 kJ of energy is released at standard temperature and pressure. What is the standard enthalpy of formation of $N_2O_4(l)$?

$\Delta H°_f =$

Marks
6

- Consider the following equilibrium in the gas-phase at 35 ºC.

$$Cl_2(g) + 2NO(g) \rightleftharpoons 2NOCl(g) \qquad K_c = 6.25 \times 10^4 \text{ M}^{-1}$$

Equimolar amounts of NOCl(g) and Cl_2(g) are introduced into a sealed 1.00 L flask. When the system reaches equilibrium at 35 ºC, the concentration of NO(g) in the flask is 4.04×10^{-4} M. What amount of Cl_2(g) (in mol) was initially added to the flask?

Answer:

At the same temperature (35 ºC) O_2(g) reacts with NO(g) according to the equation:

$$O_2(g) + 2NO(g) \rightleftharpoons 2NO_2(g) \qquad K_c = 6.25 \text{ M}^{-1}$$

Determine K_c for the following reaction.

$$2NO_2(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) + O_2(g)$$

K_c =

THIS QUESTION CONTINUES ON THE NEXT PAGE

Marks
7

Calculate the partial pressure equilibrium constant, K_p, at 35 ºC for the reaction:

$$2NO_2(g) + Cl_2(g) \rightleftharpoons 2NOCl(g) + O_2(g)$$

K_p =

What is the standard free energy change, $\Delta G°$, for the forward reaction (in kJ mol^{-1}) at 35 ºC?

$\Delta G°$ =

If 0.150 mol of O_2(g) and 3.00×10^{-4} mol of NO_2(g) are added to the 1.00 L flask, determine the free energy change, ΔG, (in kJ mol^{-1}) as the system moves to its new equilibrium point.

ΔG =

Will the amount of NO_2(g) in the flask increase or decrease as the system moves to its new equilibrium position? Explain.

Marks 8

- Calcium chloride (3.42 g) is completely dissolved in 200 mL of water at 25.00 ºC in a 'coffee cup' calorimeter. The temperature of the water after dissolution is 27.95 ºC. Calculate the standard enthalpy of solution of $CaCl_2$ (in kJ mol^{-1}). The heat capacity of water is 4.184 J K^{-1} g^{-1}. Ignore the heat capacity of the $CaCl_2$.

Answer:

What would be the vapour pressure of water above this solution?
(P^0 (H_2O) = 3.17 kPa)

Answer:

What would be the freezing point of this solution? The molal freezing point depression constant (K_f) for water is 1.86 °C kg mol^{-1}.

Answer:

Which would you expect to cause the greater freezing point depression of water, 3.42 g of $CaCl_2$ or 3.42 g of NaCl? Explain your answer.

Marks

- The presence of iron in inorganic qualitative analysis is detected by the precipitation of the hydroxide using a buffer of pH 8. The solubility product constant of $Fe(OH)_3$ is 4×10^{-38} M^4 and that of $Fe(OH)_2$ is 4×10^{-15} M^3. Is it more sensible to try and detect the presence of Fe^{2+} ions or Fe^{3+} ions? Show all working and then give a reason for your answer. **4**

- Name the following complexes. **2**

$[Cr(H_2O)_6](NO_3)_3$	
$[CoBr_2(en)_2]Cl$	

en = ethylenediamine = $NH_2CH_2CH_2NH_2$

Marks
2

- What is the value of the equilibrium constant for the following reaction at 298 K?

$$2Fe^{3+}(aq) + Sn(s) \rightleftharpoons Sn^{2+}(aq) + 2Fe^{2+}(aq)$$

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- Write the balanced half equations (including states) and the overall spontaneous reaction for a galvanic cell consisting of $Ag^{+}|Ag$ and $Sn^{2+}|Sn$ half cells. **6**

half equation at anode	
half equation at cathode	
overall reaction	

Express the overall reaction in voltaic cell notation.

What is the sign of the cathode?

What voltage would need to be applied to convert this galvanic cell into an electrolytic cell?

Answer:

- Using at least one equation, explain how colloids contribute to the hole in the ozone layer. Include mention of the type of colloid in your answer **2**

Marks

4

- Triethylamine, $N(CH_2CH_3)_3$, is a weak base with $K_b = 5.2 \times 10^{-4}$ M. A 20.00 mL solution of 0.100 M triethylamine was titrated with 0.100 M HCl. Calculate the pH of the titration solution after the addition of:

a) 5.00 mL HCl solution

pH =

b) 20.10 mL HCl solution

pH =

2

- Tris(hydroxymethyl)aminomethane, commonly called TRIS, is a weak base with $K_b = 1.19 \times 10^{-6}$ M. It is often used in buffers for biochemical research. It reacts with water according to the following equation.

$$(HOCH_2)_3CNH_2(aq) + H_2O(l) \rightleftharpoons (HOCH_2)_3CNH_3^+(aq) + OH^-(aq)$$

At what pH does TRIS show its maximum buffering ability?

pH =

What is the TRIS/TRIS-H^+ ratio in a buffer of pH 7.40?

Answer:

Marks

- Technetium-99 is used in imaging internal organs in the body, and is often used to assess heart damage. The rate constant for decay of ${}^{99m}_{43}\text{Tc}$ is 0.116 hour^{-1}. What is the half life of this nuclide? **2**

Answer:

What fraction is left after 30 minutes?

Answer:

- Boron-13 is a synthetic (not naturally occurring) isotope of boron. Using the N/Z ratio, predict a possible mode of decay for the isotope boron-13. Give a reason for your choice and write the nuclear equation for this decay. **2**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- Consider the following reaction.

$$2ClO_2(aq) + 2OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$$

A series of experiments gave the rate data shown in the table below.

Experiment number	initial $[ClO_2]$ (M)	initial $[OH^-]$ (M)	initial rate of decrease of $[ClO_2]$ ($M\ s^{-1}$)
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.050	1.15×10^{-1}

Determine the rate expression for the above reaction.

Rate =

What is the value of the rate constant? Include units in your answer.

k =

What is the relationship between the rate of decrease of $[ClO_2]$ and the rate of increase of $[ClO_3^-]$?

Marks
2

- It has been proposed that the reaction $Cl_2(g) + CHCl_3(g) \rightarrow HCl(g) + CCl_4(g)$ proceeds by the following mechanism:

$$Cl_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl(g) \qquad \text{(fast equilibrium)}$$

$$Cl(g) + CHCl_3(g) \xrightarrow{k_2} HCl(g) + CCl_3(g) \qquad \text{(slow)}$$

$$CCl_3(g) + Cl(g) \xrightarrow{k_3} CCl_4(g) \qquad \text{(fast)}$$

Derive the rate expression for this mechanism.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

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}

Charge of electron, $e = 1.602 \times 10^{-19}$ C

Mass of electron, $m_e = 9.1094 \times 10^{-31}$ kg

Mass of proton, $m_p = 1.6726 \times 10^{-27}$ kg

Mass of neutron, $m_n = 1.6749 \times 10^{-27}$ kg

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

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

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
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+0.96
$Pd^{2+}(aq) + 2e^- \rightarrow Pd(s)$	+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
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	–2.87
$Li^+(aq) + e^- \rightarrow Li(s)$	–3.04

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

Useful formulas

Quantum Chemistry	Radioactivity
$E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$	$t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age = $8033 \ln(A_0/A_t)$
Acids and Bases	**Gas Laws**
$pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	$PV = nRT$ $(P + n^2a/V^2)(V – nb) = nRT$
Colligative properties	**Kinetics**
$\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_fm$ $\Delta T_b = K_bm$	$t_{½} = \ln 2/k$ $k = Ae^{-E_a/RT}$ $\ln[A] = \ln[A]_o – kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Electrochemistry	**Thermodynamics & Equilibrium**
$\Delta G° = –nFE°$ *Moles of* e^- $= It/F$ $E = E° – (RT/nF) \times 2.303 \log Q$ $= E° – (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° – \frac{0.0592}{n} \log Q$ (at 25 °C)	$\Delta G° = \Delta H° – T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = –RT \ln K$ $K_p = K_c (RT)^{\Delta n}$
Polymers	**Mathematics**
$R_g = \sqrt{\frac{nl_0^2}{6}}$	If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

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]