

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

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.

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		

- 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?

Marks
3

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.

- 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.

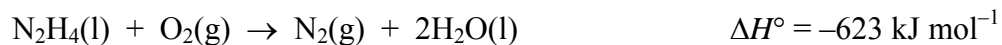
Marks
4

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:



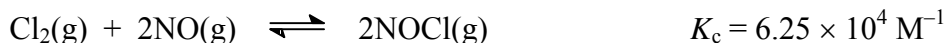
Given that ΔH°_f of $\text{H}_2\text{O}(\text{l})$ is -286 kJ mol^{-1} , find the standard enthalpy of formation of $\text{N}_2\text{H}_4(\text{l})$.

 $\Delta H^\circ_f =$

The combustion of 1.00 mol of $\text{N}_2\text{H}_4(\text{l})$ can also be accomplished using $\text{N}_2\text{O}_4(\text{l})$ as the oxidant, whereupon 629 kJ of energy is released at standard temperature and pressure. What is the standard enthalpy of formation of $\text{N}_2\text{O}_4(\text{l})$?

 $\Delta H^\circ_f =$

- Consider the following equilibrium in the gas-phase at 35 °C.

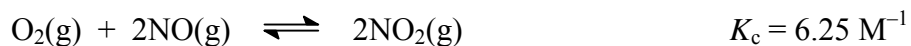


Equimolar amounts of NOCl(g) and Cl₂(g) are introduced into a sealed 1.00 L flask. When the system reaches equilibrium at 35 °C, the concentration of NO(g) in the flask is 4.04×10^{-4} M. What amount of Cl₂(g) (in mol) was initially added to the flask?

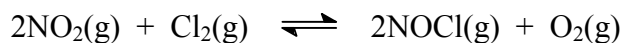
Marks
6

Answer:

At the same temperature (35 °C) O₂(g) reacts with NO(g) according to the equation:



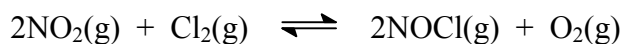
Determine K_c for the following reaction.



$K_c =$

THIS QUESTION CONTINUES ON THE NEXT PAGE

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



Marks
7

$K_p =$

What is the standard free energy change, ΔG° , for the forward reaction (in kJ mol^{-1}) at 35 °C?

$\Delta G^\circ =$

If 0.150 mol of $\text{O}_2(\text{g})$ and 3.00×10^{-4} mol of $\text{NO}_2(\text{g})$ 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.

$\Delta G =$

Will the amount of $\text{NO}_2(\text{g})$ 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 °C in a 'coffee cup' calorimeter. The temperature of the water after dissolution is 27.95 °C. Calculate the standard enthalpy of solution of CaCl_2 (in kJ mol^{-1}). The heat capacity of water is $4.184 \text{ J K}^{-1} \text{ g}^{-1}$. Ignore the heat capacity of the CaCl_2 .

Answer:

What would be the vapour pressure of water above this solution?
($P^0(\text{H}_2\text{O}) = 3.17 \text{ kPa}$)

Answer:

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

Answer:

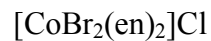
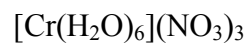
Which would you expect to cause the greater freezing point depression of water, 3.42 g of CaCl_2 or 3.42 g of NaCl ? Explain your answer.

- 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 $\text{Fe}(\text{OH})_3$ is $4 \times 10^{-38} \text{ M}^4$ and that of $\text{Fe}(\text{OH})_2$ is $4 \times 10^{-15} \text{ M}^3$. 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.

Marks
4

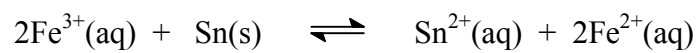
- Name the following complexes.

2



en = ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

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



Marks
2

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

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

Marks
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?

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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

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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

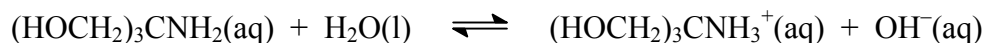
pH =

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.



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
2

- 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?

Answer:

What fraction is left after 30 minutes?

Answer:

2

- 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.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Consider the following reaction.



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

Experiment number	initial $[\text{ClO}_2]$ (M)	initial $[\text{OH}^-]$ (M)	initial rate of decrease of $[\text{ClO}_2]$ (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 =

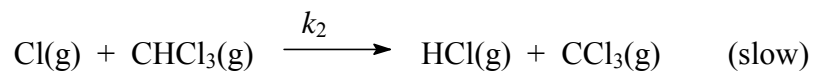
What is the value of the rate constant? Include units in your answer.

$k =$

What is the relationship between the rate of decrease of $[\text{ClO}_2]$ and the rate of increase of $[\text{ClO}_3^-]$?

Marks
5

- It has been proposed that the reaction $\text{Cl}_2(\text{g}) + \text{CHCl}_3(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{CCl}_4(\text{g})$ proceeds by the following mechanism:



Derive the rate expression for this mechanism.

Marks
2

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, $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ Faraday constant, $F = 96485 \text{ C mol}^{-1}$ Planck constant, $h = 6.626 \times 10^{-34} \text{ J s}$ Speed of light in vacuum, $c = 2.998 \times 10^8 \text{ m s}^{-1}$ Rydberg constant, $E_R = 2.18 \times 10^{-18} \text{ J}$ Boltzmann constant, $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ Gas constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$ Charge of electron, $e = 1.602 \times 10^{-19} \text{ C}$ Mass of electron, $m_e = 9.1094 \times 10^{-31} \text{ kg}$ Mass of proton, $m_p = 1.6726 \times 10^{-27} \text{ kg}$ Mass of neutron, $m_n = 1.6749 \times 10^{-27} \text{ kg}$ *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 m³1 Å = 10⁻¹⁰ m1 eV = 1.602 × 10⁻¹⁹ J1 Ci = 3.70 × 10¹⁰ Bq1 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
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightarrow \text{Ce}^{3+}(\text{aq})$	+1.72
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2 + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \text{Mn}^{3+} + 2\text{H}_2\text{O}$	+0.96
$\text{Pd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pd}(\text{s})$	+0.92
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Cu}^+(\text{aq}) + \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.53
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0 (by definition)
$\text{Fe}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.04
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.24
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.89
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.68
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.36
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)*Useful formulas*

<p>Quantum Chemistry</p> $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_B T = hc/\lambda$ $E = Z^2 E_R (1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$	<p>Radioactivity</p> $t_{1/2} = \ln 2 / \lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ $^{14}\text{C age} = 8033 \ln(A_0/A_t)$
<p>Acids and Bases</p> $\text{p}K_w = \text{pH} + \text{pOH} = 14.00$ $\text{p}K_w = \text{p}K_a + \text{p}K_b = 14.00$ $\text{pH} = \text{p}K_a + \log\{[A^-] / [\text{HA}]\}$	<p>Gas Laws</p> $PV = nRT$ $(P + n^2 a/V^2)(V - nb) = nRT$
<p>Colligative properties</p> $\pi = cRT$ $P_{\text{solution}} = X_{\text{solvent}} \times P^{\circ}_{\text{solvent}}$ $p = kc$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	<p>Kinetics</p> $t_{1/2} = \ln 2 / k$ $k = A e^{-E_a/RT}$ $\ln[A] = \ln[A]_0 - kt$ $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$
<p>Electrochemistry</p> $\Delta G^{\circ} = -nFE^{\circ}$ $\text{Moles of } e^- = It/F$ $E = E^{\circ} - (RT/nF) \times 2.303 \log Q$ $= E^{\circ} - (RT/nF) \times \ln Q$ $E^{\circ} = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E^{\circ} - \frac{0.0592}{n} \log Q \text{ (at } 25^{\circ}\text{C)}$	<p>Thermodynamics & Equilibrium</p> $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ $\Delta G = \Delta G^{\circ} + RT \ln Q$ $\Delta G^{\circ} = -RT \ln K$ $K_p = K_c (RT)^{\Delta n}$
<p>Polymers</p> $R_g = \sqrt{\frac{nl_0^2}{6}}$	<p>Mathematics</p> $\text{If } ax^2 + bx + c = 0, \text{ then } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

PERIODIC TABLE OF THE ELEMENTS

November 2005

CHEM1909

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 YTRIUM 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
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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 BERKELIUM 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]
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22/03(b)