22/49(a) **The University of Sydney**

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B (ADVANCED)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2006 **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	35	

Short answer section

Page	Marks			Marker
	Max	Gained		
11	6			
12	5			
13	5			
14	3			
15	4			
16	6			
18	6			
19	6			
20	5			
21	7			
22	7			
23	5			
Total	65			

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 21 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 17 & 24 are for rough working only.

Marks
6

- High-purity benzoic acid, C_6H_5COOH, (ΔH°_{comb} = –3227 kJ mol^{-1}) is used to calibrate a bomb calorimeter that has a 1.000 L capacity. A 1.000 g sample of C_6H_5COOH is placed in the bomb calorimeter, along with 750 mL of pure $H_2O(l)$, and the remaining 250 mL cavity is filled with pure $O_2(g)$ at 10.00 atm. The C_6H_5COOH is ignited and completely burned, causing the temperature of the water and the bomb calorimeter to rise from 27.20 ºC to 33.16 ºC. Write the chemical equation corresponding to the standard enthalpy of combustion (ΔH°_{comb}) of C_6H_5COOH.

Given that $H_2O(l)$ has a heat capacity of 4.184 J K^{-1} g^{-1} and a density of 0.997 g mL^{-1}, calculate the heat capacity of the bomb calorimeter itself (in units of J K^{-1}). Ignore the heat capacity of the gases and of C_6H_5COOH.

Answer:

If 30.0% of the CO_2 produced dissolves in the water, calculate the final total pressure (in atm) inside the 250 mL cavity of the bomb calorimeter. Assume oxygen is insoluble in water and ignore the vapour pressure of water.

Answer:

	Marks
• The specific heat capacity of water is 4.18 J g^{-1} K^{-1} and the specific heat capacity of copper is 0.39 J g^{-1} K^{-1}. If the same amount of energy were applied to a 1.0 mol sample of each substance, both initially at 25 °C, which substance would get hotter? Show all working.	**2**

Answer:

• Explain why the acidity of hydrogen halides *increases* with increasing halogen size (*i.e.*, K_a (HCl) < K_a (HBr) < K_a (HI)), while the acidity of hypohalous acids *decreases* with increasing halogen size (*i.e.*, K_a (HOCl) > K_a (HOBr) > K_a (HOI)).	**3**

Marks
5

- The K_a of benzoic acid is 6.3×10^{-5} M at 25 °C.

  Calculate the pH of a 0.0100 M aqueous solution of sodium benzoate (C_6H_5COONa).

Answer:

A buffer solution is prepared by adding 375 mL of this 0.0100 M aqueous solution of sodium benzoate to 225 mL of 0.0200 M aqueous benzoic acid. Calculate the pH of the buffer solution.

Answer:

Marks
3

- "Water gas" is a mixture of combustible gases produced from steam and coal according to the following reaction:

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad \Delta H° = 131 \text{ kJ mol}^{-1}$$

The equation for the complete combustion of 1 mol of water gas (*i.e.* 0.5 mol CO(g) and 0.5 mol H_2(g)) can be written as:

$$\tfrac{1}{2}CO(g) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow \tfrac{1}{2}CO_2(g) + \tfrac{1}{2}H_2O(g)$$

Calculate the standard enthalpy of combustion of water gas, given the following thermochemical data.

$\Delta H°_{vap}$ (H_2O) = 44 kJ mol^{-1}
$\Delta H°_f$ ($H_2O(l)$) = –286 kJ mol^{-1}
$\Delta H°_f$ ($CO_2(g)$) = –393 kJ mol^{-1}

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
4

The CO(g) in water gas can be reacted further with H_2O(g) in the so-called "water-gas shift" reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

At 900 K, K_c = 1.56 for this reaction. A sample of water gas flowing over coal at 900 K contains a 1:1 mole ratio of CO(g) and H_2(g), as well as 0.250 mol L^{-1} H_2O(g). This sample is placed in a sealed container at 900 K and allowed to come to equilibrium, at which point it contains 0.070 mol L^{-1} CO_2(g). What was the initial concentration of CO(g) and H_2(g) in the sample?

[CO] = [H_2] =

If the walls of the container are chilled to below 100 ºC, what will be the effect on the concentration of CO_2(g)?

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

- The isomerisation of glucose-6-phosphate (G6P) to fructose-6-phosphate (F6P) is a key step in the metabolism of glucose for energy. At 298 K,

$$\text{G6P} \rightleftharpoons \text{F6P} \qquad \Delta G° = 1.67 \text{ kJ mol}^{-1}$$

Calculate the equilibrium constant for this process at 298 K.

Answer:

What is the free energy change (in kJ mol^{-1}) involved in a mixture of 3.00 mol of F6P and 2.00 mol of G6P reaching equilibrium at 298 K?

Answer:

Sketch a graph of G_{sys} *versus* "extent of reaction", with a curve showing how G_{sys} varies as G6P is converted to F6P. Indicate the position on this curve corresponding to 3.00 mol of F6P and 2.00 mol of G6P.

Marks
6

- Assume that NaCl is the only significant solute in seawater. A 1.000 L sample of seawater at 25 ºC and 1 atm has a mass of 1.0275 kg and contains 33.0 g of NaCl. At what temperature would this seawater freeze? The freezing point depression constant of water is 1.86 ºC kg mol^{-1}.

Answer:

The vapour pressure above pure H_2O is 23.76 mmHg at 25 ºC and 1 atm. Calculate the vapour pressure above this seawater under the same conditions.

Answer:

The desalination of seawater by reverse osmosis has been suggested as a way of alleviating water shortages in Sydney. What pressure (in Pa) would need to be applied to this seawater in order to force it through a semi-permeable membrane, yielding pure H_2O?

Answer:

Marks

- The molar solubility of lead(II) fluoride, PbF_2, is found to be 2.6×10^{-3} M at 25 °C. Calculate the value of K_{sp} for this compound at this temperature. **2**

K_{sp} =

- Draw all stereoisomers of the complex ion of $[Co(en)_3]Br_3$. (en = ethylenediamine = $NH_2CH_2CH_2NH_2$) **2**

- Name the following complexes. **2**

$[Co(H_2O)_4Br_2]Cl$	
$K[Au(CN)_2]$	

Marks

- Write the chemical equation for the formation of the complex ion $[Cd(NH_3)_4]^{2+}$. **2**

Write the associated stability constant expression (K_{stab}).

- The physiological properties of chromium depend on its oxidation state. Consider the half reaction in which Cr(VI) is reduced to Cr(III). **3**

$$CrO_4^{2-}(aq) + 4H_2O(l) + 3e^- \rightarrow Cr(OH)_3(s) + 5OH^-(aq) \qquad E^o = -0.13 \text{ V}$$

Calculate the potential for this half reaction at 25 ^oC, where pH = 7.40 and $[CrO_4^{2-}(aq)] = 1.0 \times 10^{-6}$ M.

Answer:

Marks

5

- Consider the following reaction at 298 K.

$$Ni^{2+}(aq) + Zn(s) \rightleftharpoons Ni(s) + Zn^{2+}(aq)$$

Calculate ΔG^{o} for the cell. (Relevant electrode potentials can be found on the data page.)

Answer:

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

Answer:

Express the overall reaction in voltaic cell notation.

2

- Using a current of 2.00 A, how long (in minutes) will it take to plate out all of the silver from 0.250 L of a 1.14×10^{-2} M $Ag^{+}(aq)$ solution?

Marks

- If a medical procedure calls for 2.0 mg of ^{48}V, what mass of isotope would be required to be able to use it exactly one week later? The half life of ^{48}V is 1.61 days. **2**

Answer:

- Describe how hydrophilic and hydrophobic colloids are stabilised in water. **3**

- Calculate the standard free-energy change for the following reaction at 298 K. **2**

$$2Au(s) + 3Mg^{2+}(1.0\ M) \rightarrow 2Au^{3+}(1.0\ M) + 3Mg(s)$$

Answer:

Marks
5

- The major pollutants NO(g), CO(g), NO_2(g) and CO_2(g), which are emitted by cars, can react according to the following equation.

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The following rate data were collected at 225 °C.

Experiment	$[NO_2]_0$ (M)	$[CO]_0$ (M)	Initial rate ($d[NO_2]/dt$, M s^{-1})
1	0.263	0.826	1.44×10^{-5}
2	0.263	0.413	1.44×10^{-5}
3	0.526	0.413	5.76×10^{-5}

Determine the rate law for the reaction.

Calculate the value of the rate constant at 225 °C.

Answer:

Calculate the rate of appearance of CO_2 when $[NO_2]$ = [CO] = 0.500 M.

Answer:

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your 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}

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

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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
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Cl_2 + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
$O_2 + 4H^+(aq) + 4e^- \rightarrow 2H_2O$	+1.23
$Br_2 + 2e^- \rightarrow 2Br^-(aq)$	+1.10
$MnO_2(s) + 4H^+(aq) + e^- \rightarrow Mn^{3+} + 2H_2O$	+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
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	–0.28
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	–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

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Useful formulas

Quantum Chemistry $E = h\nu = hc/\lambda$ $\lambda = h/mv$ $4.5k_BT = hc/\lambda$ $E = Z^2E_R(1/n^2)$ $\Delta x \cdot \Delta(mv) \geq h/4\pi$ $q = 4\pi r^2 \times 5.67 \times 10^{-8} \times T^4$	**Electrochemistry** $\Delta G° = -nFE°$ $Moles\ of\ e^- = It/F$ $E = E° - (RT/nF) \times 2.303 \log Q$ $= E° - (RT/nF) \times \ln Q$ $E° = (RT/nF) \times 2.303 \log K$ $= (RT/nF) \times \ln K$ $E = E° - \frac{0.0592}{n} \log Q$ (at 25 °C)
Acids and Bases $pK_w = pH + pOH = 14.00$ $pK_w = pK_a + pK_b = 14.00$ $pH = pK_a + \log\{[A^-] / [HA]\}$	**Gas Laws** $PV = nRT$ $(P + n^2a/V^2)(V - nb) = nRT$
Colligative properties $\pi = cRT$ $P_{solution} = X_{solvent} \times P°_{solvent}$ $p = kc$ $\Delta T_f = K_f m$ $\Delta T_b = K_b m$	**Kinetics** $t_{½} = \ln 2/k$ $k = Ae^{-E_a/RT}$ $\ln[A] = \ln[A]_o - kt$ $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Radioactivity $t_{½} = \ln 2/\lambda$ $A = \lambda N$ $\ln(N_0/N_t) = \lambda t$ ^{14}C age $= 8033 \ln(A_0/A_t)$	**Thermodynamics & Equilibrium** $\Delta G° = \Delta H° - T\Delta S°$ $\Delta G = \Delta G° + RT \ln Q$ $\Delta G° = -RT \ln K$ $K_p = K_c (RT)^{\Delta n}$
Polymers $R_g = \sqrt{\frac{nl_0^2}{6}}$	**Mathematics** If $ax^2 + bx + c = 0$, then $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ $\ln x = 2.303 \log x$

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]