22/03(a)

The University of Sydney

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

SECOND SEMESTER EXAMINATION

CONFIDENTIAL

NOVEMBER 2003

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
2-8	27	

Short answer section

Page	Marks			Marker
	Max	Gained		
9	8			
10	9			
12	9			
13	6			
14	5			
15	9			
16	11			
17	6			
18	7			
19	3			
Total	73			

INSTRUCTIONS TO CANDIDATES

- All questions are to be attempted. There are 17 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.
- Some useful formulas, a Periodic Table and numerical values required for any question may be found on a separate data sheet.
- Pages 11 and 20 are for rough working only.

Marks 8

- The conversion of hydroquinone ($C_6H_6O_2(aq)$) to quinone ($C_6H_4O_2(aq)$) is involved in many important biochemical reactions. The bombardier beetle, for example, uses the explosive reaction between hydroquinone and hydrogen peroxide (as described by the equation below) as a defence mechanism.

$$C_6H_6O_2(aq) + H_2O_2(aq) \rightarrow C_6H_4O_2(aq) + 2H_2O(l)$$

From the following reaction data, calculate ΔH_{rxn} for the reaction between 1.00 mol of hydroquinone and 1.00 mol of hydrogen peroxide.

$C_6H_6O_2(aq) \rightarrow C_6H_4O_2(aq) + H_2(g)$ $\Delta H_{rxn} = +177.4 \text{ kJ mol}^{-1}$

$O_2(g) + 2H_2O(l) \rightarrow 2H_2O_2(aq)$ $\Delta H_{rxn} = +189.1 \text{ kJ mol}^{-1}$

$H_2O(l) \rightarrow H_2(g) + ½O_2(g)$ $\Delta H_{rxn} = +285.8 \text{ kJ mol}^{-1}$

ΔH_{rxn} =

Use the answer you obtained above to calculate the heat liberated (in joules) in the oxidation of 3.86×10^{-4} mol of hydroquinone to quinone.

Answer:

Calculate the temperature rise of 0.250 g of water for this quantity of heat.
(The heat capacity of water, $C_p = 4.184 \text{ J K}^{-1} \text{ g}^{-1}$)

Answer:

Marks
9

- Consider the following equilibrium constants, obtained from experiments conducted at 1000 K.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad K_{p1} = 3.38\ \text{atm}^{-1}$$

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \qquad K_{p2} = 2.75 \times 10^{20}\ \text{atm}^{-1}$$

Calculate the value of K_p at 1000 K for the reaction below.

$$SO_2(g) + CO_2(g) \rightleftharpoons SO_3(g) + CO(g)$$

K_p =

Calculate $\Delta G°$ for this reaction at 1000 K.

$\Delta G°$ =

Does this reaction move toward product formation spontaneously or non-spontaneously at 1000 K?

In which direction will the reaction proceed if the initial reaction conditions are: pSO$_2$(g) = 0.1 atm; pCO$_2$(g) = 0.5 atm; pSO$_3$(g) = 0.01 atm; pCO(g) = 0.01 atm?

Answer:

Marks
9

- In an experiment, NOCl (2.00 mol) was placed in a closed 1.00 L flask. After equilibrium was established at 25 °C, the concentration of NO(g) was 0.66 M. Calculate the value of K_c at 25 °C for the following reaction.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

K_c =

Calculate the value of K_p at 25 °C for the reaction above.

K_p =

Given that $\Delta H_f°$ for NOCl(g) = 51.71 kJ mol^{-1} and $\Delta H_f°$ for NO(g) = 90.29 kJ mol^{-1} at 25 °C, calculate the value of $\Delta H°$ for the reaction above.

$\Delta H°_{rxn}$ =

What is the effect upon the [NOCl] of an equilibrium mixture if the temperature is increased?

In which direction will the equilibrium shift if the volume of the flask is reduced?

Marks

- A newly isolated protein (22.7 mg) was dissolved in 1.45 mL of water at 4 °C and an osmotic pressure of 0.00465 atm was measured. What is the molar mass of the protein? **3**

Answer:

- The boiling point of pure ethanol is 78.50 °C at 1 atm. A known mass (3.05 g) of ethylene glycol ($C_2H_6O_2$) was added to 500 g of ethanol and the boiling point at 1 atm determined to be 78.62 °C. Calculate the value of the Molal Boiling Point Elevation Constant (K_b) for pure ethanol. **3**

Answer:

Marks

- Calculate the mass of chlorine gas generated when a current of 100 A is passed through molten lithium chloride for exactly 1 hour. **2**

Answer:

- Ethylenediamine tetraacetate ($EDTA^{4-}$) is a ligand that forms complexes with many metal ions and consequently may be used to treat heavy metal toxicity in the body. The reaction with lead ions is represented by the following equilibrium: **3**

$$Pb^{2+} + EDTA^{4-} \rightleftharpoons [PbEDTA]^{2-}$$

If a solution had an initial concentration of 1×10^{-4} M Pb^{2+} and 0.05 M EDTA, what will be the concentration of uncomplexed lead ions once equilibrium is established? K_{stab} for $[PbEDTA]^{2-}$ is 1×10^{18} M^{-1}.

Answer:

Marks

5

- An important biological redox reaction is the reduction of pyruvate, $CH_3COCO_2^-$, to lactate, $CH_3CHOHCO_2^-$, by reaction with nicotinamide adenine dinucleotide, NADH. Using the standard reduction potentials provided, estimate $\Delta G°'$ for this reaction.

$$\text{Pyruvate} + 2H^+ + 2e^- \rightleftharpoons \text{Lactate} \qquad E°' = -0.0185 \text{ V}$$

$$NAD^+ + 2H^+ + 2e^- \rightleftharpoons NADH + H^+ \qquad E°' = -0.3200 \text{ V}$$

$\Delta G°'$ =

Typical biological concentrations of lactate and pyruvate at equilibrium in goat blood are 1.0×10^{-3} M lactate and 6.0×10^{-5} M pyruvate. What ratio of [NADH] to [NAD^+] would you find in this biological system at 39 °C, the temperature of a healthy goat?

Answer:

4

- Trichloroacetic acid, CCl_3COOH, a corrosive acid used to precipitate proteins, has a K_a of 0.16 M. What is the pH of a 0.050 M solution of trichloroacetic acid?

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

Answer:

Marks

- The $H_2PO_4^-$ and HPO_4^{2-} ions play a major role in maintaining the intracellular pH balance. Write balanced equations to show how a solution containing these ions can act as a buffer. **6**

For phosphoric acid, $K_{a1} = 7.1 \times 10^{-3}$ M, $K_{a2} = 6.3 \times 10^{-8}$ M, $K_{a3} = 4.2 \times 10^{-13}$ M. At what pH would the $H_2PO_4^-$ / HPO_4^{2-} buffer system be most effective? Why?

Calculate the ratio of $H_2PO_4^-$ / HPO_4^{2-} needed to give a solution buffered to a pH of 7.35.

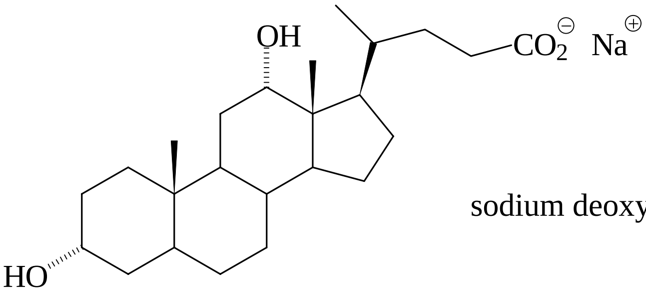
- Briefly outline three kinds of isomerism that can arise in coordination complexes, illustrating each type of isomerism with structural formulas. Give the systematic name for any one of your structures. **5**

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*

- One of the components of bile acid is sodium deoxycholate, whose structure is given below. **3**



sodium deoxycholate

Which one of the following terms: *electrostatic*, *electrosteric* or *steric*, best describes the way sodium deoxycholate functions to solubilise fats. Give a brief explanation.

Marks
7

- In the reaction with the stoichiometry $2H^+ + 2I^- + H_2O_2 \rightarrow 2H_2O + I_2$ the following data were obtained.

initial $[H^+]$ (M)	initial $[H_2O_2]$ (M)	initial $[I^-]$ (M)	$[I_2]$ (M) after 1.0 s
0.10	0.10	0.10	1.2×10^{-3}
0.10	0.10	0.06	0.7×10^{-3}

Determine the rate for both of these conditions.

Determine the order, *n*, of the reaction with respect to $[I^-]$.

In another set of experiments, the reaction was found to be first order with respect to both H^+ and H_2O_2. Deduce the value of the rate coefficient, *k*, for the rate law

$d[I_2]/dt = k[I^-]^n[H_2O_2][H^+]$

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

$H^+ + I^- \rightleftharpoons HI$	(fast)
$HI + H_2O_2 \rightarrow HIO + H_2O$	(slow)
$HIO + HI \rightarrow H_2O + I_2$	(fast)

Marks
3

- A solution of sodium iodide containing the radioisotope ^{131}I has an activity of 20 mCi L^{-1} when freshly prepared. Fifteen days later, a patient is given 0.50 mL of this solution. Calculate the dose of ^{131}I (in microcurie, μCi) received by the patient. The half-life of ^{131}I is 8.04 days.

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}

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

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

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

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

Useful formulas

Acids and Bases

$pK_w = pH + pOH = 14$

$pK_w = pK_a + pK_b = 14$

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

Kinetics

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

$t_{½} = \ln 2/k$

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

Radioactivity

$A = kN$

$\ln(N_0/N_t) = kt$

$t = 8033 \ln(A_0/A_t)$

Electrochemistry

$\Delta G° = -nFE°$

$E = E° - (RT/nF) \ln Q$

$E° = (RT/nF) \ln K$

Moles of e^- $= It/F$

Colligative properties

$\pi = cRT$

$p = kc$

$\Delta T_f = K_f m$

$\Delta T_b = K_b m$

Thermodynamics & Equilibrium

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

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

Quantum Chemistry

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

$\lambda = h/mu$

Gas Laws

$PV = nRT$

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

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

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

November 2003

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]