22/03(a) The University of Sydney

CHEM1909 - CHEMISTRY 1 LIFE SCIENCES B MOLECULAR (ADVANCED)

SECOND SEMESTER EXAMINATION

NOVEMBER 2000

TIME ALLOWED: THREE HOURS

GIVE THE FOLLOWING INFORMATION IN BLOCK LETTERS

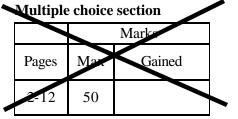
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SURNAME		OTHER NAMES		
SID NUMBER	FACULTY		TABLE NUMBER	

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 begins with a \bullet .
- 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 14 and 20 are for rough working only.

OFFICIAL USE ONLY



Short answer section

	Marks			
Page	Max	Gaineo	1	Marker
13	8			
15	10			
16	8			
17	8			
18	8			
19	8			
Total	50			
Check	Total			

Marks

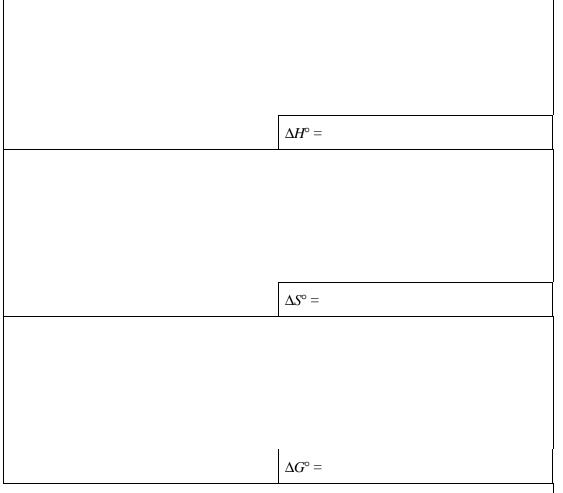
8

• Copper(I) oxide may be reduced by carbon according to the equation:

$$Cu_2O(s) + C(s) \rightarrow 2Cu(s) + CO(g)$$

Given the following data, calculate ΔH° , ΔS° and ΔG° for the reaction at 298 K.

	$\Delta H^{o}_{f}(298 \text{ K}) / \text{kJ mol}^{1}$	<i>S</i> ° (298 K) / J K ⁻¹ mot ¹
$Cu_2O(s)$	-169	93
C(s)	0	6.0
Cu(s)	0	33
CO(g)	-111	198



At what temperature does the reaction become spontaneous?

Answer:

CHEM1909	2000-N-4	November 2000	22/03(a
-	lculate the equilibrium conce	a CO(aq) solution at a concentration of entration of CO(aq) when the partial	Mar 2
	A	nswer:	
Consider the follow	wing equilibria at 300 K.		4
$\frac{1}{2}N_{2}(g)$	$+ \frac{1}{2}O_2(g) \implies NO(g)$	$K_{\rm c} = 4.8 \times 10^{-10}$	
2NO ₂ (g)	\rightarrow 2NO(g) + O ₂ (g)	$K_{\rm c} = 1.1 \times 10^{-5} {\rm M}$	
Determine the valu	e of $K_{\rm c}$ and $K_{\rm p}$ at 300 K for t	the equilibrium.	
	$2NO_2(g) \iff N$		
$\chi_{\rm c} =$	K	, =	
			4
It is a monoprotic a	H(OH)COOH, accumulates i cid with ionisation constant <i>f</i> a 0.050 M lactic acid solution		

2000-N-4

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		pH =	

Marks • The $H_2PO_4^-$ and HPO_4^{2-} ions play a role in maintaining the pH of blood. Write equations to 8 show how a solution containing these ions functions as a buffer. The K_{a2} for phosphoric acid is 6.3×10^{-8} M. At what pH is the H₂PO₄⁻ / HPO₄²⁻ buffer system most effective? pH =Calculate the ratio of $[H_2PO_4^{-}] / [HPO_4^{2-}]$ required to give a buffer with a pH of 7.68.

Answer:

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

4

Marks EDTA is a ligand that forms complexes with many metals and may be used to treat heavy • metal toxicity in the body. The reaction with lead ions is represented by the following equilibrium.

 $K_{\rm stab} = 1 \times 10^{18} \, {\rm M}^{-1}$ $Pb^{2+}(aq) + EDTA^{4-}(aq)$ [PbEDTA]²⁻(aq)

If a solution has an initial concentration of $Pb^{2+}(aq)$ of 0.001 M and $EDTA^{4-}(aq)$ of 0.050 M, what is the concentration of uncomplexed lead ions once equilibrium has been established?

Answer:

Answer:

• Calculate the mass of copper that deposits when a current of 1.5 A is passed for 10 minutes through a solution containing Cu^{2+} ions.

2

• Briefly describe the structure of a micelle.

2

Marks • One of the key reactions in the formation of acid rain and in the industrial production of nitric 4 acid is the reaction of nitric oxide with oxygen:

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

The following data were obtained at constant temperature.

EXPERIMENT NUMBER	INITIAL CONCENTRATIONS (mol L^{-1}) [O ₂] [NO]		INITIAL REACTION RATE (mol $L^{-1} s^{-1}$)
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}

Deduce the rate equation for this reaction and find the value of the rate constant.

Rate equation	Rate constant
Answer:	Answer:

• The reaction $2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$ is postulated to occur in two steps, the first of which is the rate determining step

$NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$	STEP 1
$NO_2(g) + F(g) \rightarrow NO_2F(g)$	STEP 2

$$NO_2(g) + F(g) \rightarrow NO_2F(g)$$
 ST

Deduce the expected rate expression for this mechanism.

• Sketch an energy diagram to represent a reaction in which $\Delta H = -40$ kJ mol⁻¹ and $E_a = 40 \text{ kJ mol}^{-1}$.

2

2

Marks • Identify the element to which each of the following statements refers. 4 Important metal in Vitamin B₁₂. Dietary deficiency causes goitre. Used in the treatment of manic depression patients. Retained in the body in Menke's syndrome and in Wilson's disease. • Thalassemia, a genetic blood disorder, results in the toxic accumulation of iron in the body. 4 It might be treated by administration of EDTA (ethylenediaminetetraacetic acid) or 3hydroxypyridin-4-one. HO CH₂COOH HOOCCH $-CH_2$ $-CH_2$ HOOCCH CH₂COOH Ĥ **EDTA** 3-hydroxypyridin-4-one Briefly describe the chemical basis for the use of these agents in the treatment of thalassemia.

Giving your reasons, state which of EDTA and 3-hydroxypyridin-4-one would be the agent of choice in this treatment, based on the data in the following table which gives the logarithms of complex formation constants between selected metals and EDTA and 3-hydroxypyridin-4-one.

Ion	EDTA	3-hydroxypyridin-4-one
Fe(III)	25	37
Cu(II)	18	17
Zn(II)	16	12.5

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Faraday constant = F = 96485 coulomb mole⁻¹ Avogadro constant = $N_A = 6.022 \times 10^{23}$ mole⁻¹ Standard atmosphere = 101 325 pascal = 760 mmHg Ideal gas constant = R = 8.314 joule kelvin⁻¹ mole⁻¹ = 0.08206 litre atmosphere kelvin⁻¹ mole⁻¹

Conversion factors

0 degree Celsius = 273 kelvin	$1 \text{ mL} = 1 \text{ millilitre} = 10^{-3} \text{ litre}$
$1 \text{ kJ} = 1 \text{ kilojoule} = 10^3 \text{ joule}$	$1 \text{ mA} = 1 \text{ milliampere} = 10^{-3} \text{ ampere}$
$1 L = 1 \text{ litre} = 10^{-3} \text{ metre}^{3}$	

Standard Reduction Potentials at 298 K

$Cu^{2+}(aq) + 2e^{-}$	~ `	Cu(s)	$E^{\circ} = +0.34$
$Ni^{2+}(aq) + 2e^{-}$		Ni(s)	$E^{\circ} = -0.24$
$2H^{+}(aq) + 2e^{-}$	~``	$H_2(g)$	$E^{\circ} = 0.00$
$^{1}/_{2}O_{2}(g) + 2H^{+}(aq) + 2e^{-}$		H_2O	$E^{\circ} = +1.23$

Useful Formulas

Thermodynamics and Equilibrium $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ $\Delta G^{\circ} = -RT \ln K$ $K_{\rm p} = K_{\rm c} (RT)^{\Delta \rm n}$

Solution properties $\pi = cRT$ p = kc

Acids and Bases

 $pK_{w} = pH + pOH = 14$ $pK_{w} = pK_{a} + pK_{b} = 14$ $pH = pK_{a} + \log\{ \text{ [base] / [acid] } \}$ Kinetics $t_{1/2} = \ln 2/k$ $k = Ae^{-EaRT}$ $\ln[A] = \ln[A]_0 - kt$

Electrochemistry $\Delta G^{\circ} = -nFE^{\circ}$ $E = E^{\circ} - RT/nF \ln Q$ $E^{\circ} = RT/nF \ln K$ Moles of $e^{-} = It/F$

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

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Z		1															1	
	1 hydrogen																	2 HELIUM
	H																	He
	1.008	4	T										5	6	7	0	9	4.003
	LITHIUM	4 BERYLLIUM											5 boron	6 carbon	/ NITROGEN	8 oxygen	9 FLUORINE	10 NEON
	Li	Be											В	С	Ν	0	F	Ne
	6.941	9.012	_										10.81	12.01	14.01	16.00	19.00	20.18
	11 sodium	12 magnesium											13 ALUMINIUM	14 SILICON	15 phosphorus	16	17 CHLORINE	18 Argon
	Na	MAGNESIUM											ALUMINIUM	Silicon	PHOSPHORUS	SULFUR S	CHLORINE	Argon
	22.99	24.31											26.98	28.09	30.97	32.07	35.45	39.95
CHEM1909	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	POTASSIUM K	CALCIUM CA	SCANDIUM Sc	TITANIUM Ti	VANADIUM V	CHROMIUM	MANGANESE		COBALT	NICKEL	COPPER	ZINC	GALLIUM	GERMANIUM		SELENIUM	BROMINE D	KRYPTON
	K 39.10	Ca 40.08	SC 44.96	11 47.88	v 50.94	Cr 52.00	Mn 54.94	Fe 55.85	Co 58.93	Ni 58.69	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.59	As 74.92	Se 78.96	Br 79.90	Kr 83.80
	39.10	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	RUBIDIUM	STRONTIUM	YTTRIUM	ZIRCONIUM	NIOBIUM	MOLYBDENUM	TECHNETIUM	RUTHENIUM	RHODIUM	PALLADIUM	SILVER	CADMIUM	INDIUM	TIN	ANTIMONY	TELLURIUM	IODINE	XENON
\mathbf{O}	Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Те	Ι	Xe
	85.47	87.62	88.91	91.22	92.91	95.94	[98.91]	101.07	102.91	106.4	107.87	112.40	114.82	118.69	121.75	127.60	126.90	131.30
	55 caesium	56 barium	57-71	72 hafnium	73 tantalum	74 TUNGSTEN	75 RHENIUM	76 05MIUM	77 iridium	78 Platinum	79 ‱	80 mercury	81 THALLIUM	82 LEAD	83 bismuth	84 polonium	85 astatine	86 rado n
	Cs	Ba		Hf	Та	W	Re	Os	Ir	Pt	Au	Hg	П	Pb	Bi	Ро	At	Rn
	132.91	137.34		178.49	180.95	183.85	186.2	190.2	192.22	195.09	196.97	200.59	204.37	207.2	208.98	[210.0]	[210.0]	[222.0]
	87	88	89-103		105	106	107	108	109									
	FRANCIUM Fr	RADIUM Ra		rutherfordium Rf	DUBNIUM Db	seaborgium Sg	BOHRIUM Bh	hassium HS	MEITNERIUM Mt									
	[223.0]	[226.0]		[261]	[262]	[266]	[262]	[265]	[266]									
	[22010]																	
		5	7 4	58	59	60	61	62	63	64	65		56	67	68	69	70	71
	LANTHANIC	DE LANTHA	ANUM CE	RIUM PR/	ASEODYMIUM	NEODYMIUM	PROMETHIUM	SAMARIUM	EUROPIUM	GADOLINIU	M TERBIU	M DYSI	PROSIUM	HOLMIUM	ERBIUM	THULIUM	YTTERBIUM	LUTETIUM
22/03(b) 2000	S	L		e Pr		Nd	Pm	Sm	Eu	Gd	Tb)y	Но	Er	Tm	Yb	Lu
		138.			140.91	144.24	[144.9]	150.4	151.96	157.25				164.93	167.26	168.93	173.04	174.97
	ACTINIDE	s ACTIN		DRIUM PR	91 otactinium	92 uranium	93 NEPTUNIUM	94 PLUTONIUM	95 AMERICIUM	96 curium	97 BERKELL		98 fornium e	99 INSTEINIUM	100 FERMIUM	101 mendelevium	102 NOBELIUM	103 LAWRENCIUM
22/	ACTINIDE	A		ĥ	Pa	U	Np	Pu	Am	Cm	Bk	: (Cf	Es	Fm	Md	No	Lr
$\frac{1}{20}$		[227	.0] 23	2.04 [231.0]	238.03	[237.0]	[239.1]	[243.1]	[247.1]] [247.	1] [2:	52.1] [252.1]	[257.1]	[256.1]	[259.1]	[260.1]

PERIODIC TABLE OF THE ELEMENTS

14 15

16 17