Name: KEY

Chemistry 112
Test 4
April 19, 2006

Instructions before starting the test:

1. Your exam booklet should have **eight** pages total, with questions on Pages 2-5, and a periodic table and other reference data on Pages 6-8. Check to see you have eight pages now. If you do not, ask for another copy of the exam.
2. Write your name in the space above and on the backs of Pages 2-5.
3. This exam is closed-everything.
4. You may use programmable calculators, but chemical data should not be stored in them.
5. You have up to **90 minutes** to work on this exam, if you start work at 8:00 a.m.

Possible Points	Your Score
Page 2 (20)	
Page 3 (27)	
Page 4 (26)	
Page 5 (27)	
Total (100)	

Average after Four Tests	
Estimated Grade	

1. (20 points total) A dramatic example of an oxidation-reduction reaction is the very exothermic reaction of potassium chlorate and sugar. The skeleton reaction is as follows:

$$KClO_3(s) + C_6H_{12}O_6(s) \rightarrow K^+(aq) + Cl_2(g) + CO_2(g)$$

(a) (5 points) Assign oxidation numbers to all atoms in the above reaction. You do not need to justify your answers.

+1 +5 −2   0 +1 −2   +1   0   +4 −2

− 1/2 per wrong ON

(b) (15 points) Balance the above skeleton equation, assuming it takes place in acidic aqueous solution. You may use any method you wish, so long as any hydrogen ions present in the overall equation are represented properly as H_3O^+, not H^+.

$12(2\,KClO_3 + 10e^- \rightarrow 2K^+ + Cl_2)$

$5(C_6H_{12}O_6 \rightarrow 6CO_2 + 24e^-)$

$24\,KClO_3(s) + 5\,C_6H_{12}O_6(s) + 24\,H_3O^+(aq) \rightarrow 24K^+(aq) + 12Cl_2(g) + 30CO_2(g) + 66H_2O(l)$

−4 One atom/charge unbalanced

−8 Two atoms/charge "

−11 3 things "

−13 Some work

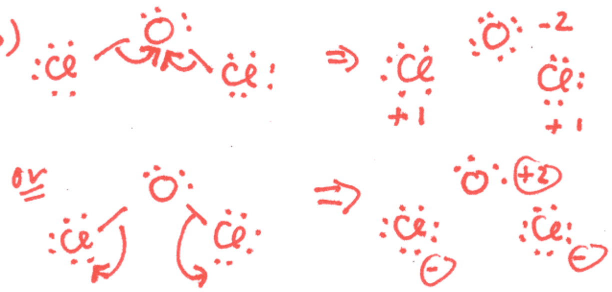
−4 inserted extra species

2. (12 points) Using the arrow-drawing formalism Prof. Fischer taught you, predict and rationalize the (a) formal charges and (b) oxidation numbers for all atoms in the molecule Cl_2O. Your answer must include drawing a valid Lewis structure for Cl_2O—note that the O atom is in the middle of the molecule.

(a)

formal charges - each bond is equally shared - split by single-headed arrows. Ea atom has the same # of valence electrons as it does on the periodic table ⇒ all formal charges = 0

(b)



Oxidation numbers - each bond is donated to either (i) the more electronegative atom or (ii) the central atom. ON = (# of resulting electrons - # of valence e⁻'s)

- 2 wrong ON's
- 2 wrong formal charges
- 4 no arrows for ON's (-3 wrong)
- 4 " " " fc's (-3 wrong)
- 9 no arrows at all

3. (15 points) If we wish to maximize the potential of a voltaic cell, would it be a good idea to use at the anode the half reaction $2\ F^{-}(aq) \rightarrow F_2(g) + 2\ e^{-}$? Explain in detail why or why not, discussing (i) the significance of the charge assigned to the anode, (ii) the half reaction's standard potential, and (iii) the chemical properties of the species in the half reaction.

(-4) no discussion that anode is ⊖ and ∴ repels e⁻'s fr. itself to cathode
(-5) no discussion of ε^0 or incorrect (-4) vague discussion of ε^0
(-4) no discussion of electronegativity or electron affinity
(-3) mis-statement ~~(minor)~~ (minor)
(-5) switched oxidizing and reducing agent in argument at one point (or oxidation and reduction)
(-10) "good idea"

4. (53 points total) Soil in the older neighborhoods of St. Paul and Minneapolis often has high concentrations of lead, due to the historic use of both leaded paint and leaded gasoline. Long-term human exposure to such soil can lead to dangerously high Pb^{2+} levels in the bloodstream. Macalester's newly hired biochemist, Dr. Kathryn Splan, is interested in measuring $[Pb^{2+}]$ electrochemically. She prepares two half cells, one consisting of an Ag electrode immersed in a 1.0 M solution of $AgNO_3$, and the other consisting of a Pb electrode immersed in a $Pb(NO_3)_2$ solution of unknown concentration.

(a) (6 points) Write the balanced chemical equation for the cell reaction using the smallest set of whole number coefficients. <u>The equation you write should be spontaneous in the forward direction</u>.

$2\,(Ag^+(aq) + e^- \rightarrow Ag(s))$ $\mathcal{E}^\circ_{red} = 0.80\,V$

$Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$ $\mathcal{E}^\circ_{ox} = +0.13\,V$

$2\,Ag^+(aq) + Pb(s) \rightarrow 2\,Ag(s) + Pb^{2+}$ $\mathcal{E}^\circ_{cell} = 0.93\,V$

-2 one coefficient off
-5 wrong direction; wrong n

(b) (20 points) At 25°C, the reaction you wrote in part (a) has $\Delta_r S^\circ$ = -106 J mol^{-1} K^{-1}. Compute $\Delta_r H^\circ$ (in kJ mol^{-1}).

$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ = -nF\mathcal{E}^\circ_{cell}$ $(\Delta_r G^\circ = -1.7_{95} \times 10^5\ J\,mol^{-1})$

$\Delta_r H^\circ = T\Delta_r S^\circ - nF\mathcal{E}^\circ_{cell}$

$= (298._{15}\,K)\left(-\frac{106\,J}{K}\right) - 2\left(\frac{96485\,C}{mol}\right)(0.93\,V)\left(\frac{J\,C^{-1}}{V}\right)$

$= \left(-316_{03}\frac{J}{mol} - 17_{9462}\frac{J}{mol}\right)\left(\frac{kJ}{10^3\,J}\right)$

$\boxed{\Delta_r H^\circ = -21_1\ kJ\,mol^{-1}}$

-1 3 sig figs
-2 more than 3 sig figs
-4 math, sign, unit error (-2 if already -12)
-6 wrong $\mathcal{E}^\circ_{cell}$
-6 wrong n
-15 $\Delta G^\circ = 0$
-15 some work

[Problem 4 continued on the next page.]

(c) (7 points) Is **lead** or **silver** the more active metal? Briefly justify your answer.

Pb is more active, because it's the stronger reducing agent ($Pb^{2+} + 2e^- \rightarrow Pb$ has the lower $\mathcal{E}°$)

−6 silver

−4 false reason for Pb

(d) (20 points) In the voltaic cell Dr. Splan has designed, the highest cell potential she can measure accurately is 2.00 V. What is the lowest Pb^{2+} concentration (in M) that she can measure accurately at 20.0°C? Assume that the standard cell potential at 20.0°C and 25.0°C is the same. (Hint: Your answer will be very tiny! As I mentioned at the end of class last Wednesday, the big challenge in electrochemistry is not sensitivity (the ability to measure very small concentrations), but selectivity (the ability to discriminate between different ions.))

$$\mathcal{E}_{cell} = \mathcal{E}°_{cell} - \frac{RT}{nF} \ln \frac{[Pb^{2+}]}{[Ag^+]^2}$$

As $[Pb^{2+}] \downarrow$, $\mathcal{E}_{cell} \uparrow$. Max $\mathcal{E}_{cell} = 2.00$ V

$$\frac{RT}{nF} \ln \frac{[Pb^{2+}]}{[Ag^+]^2} = \mathcal{E}°_{cell} - \mathcal{E}_{cell} \Rightarrow \frac{[Pb^{2+}]}{[Ag^+]^2} = \exp\left[\frac{nF}{RT}(\mathcal{E}°_{cell} - \mathcal{E}_{cell})\right]$$

$$[Pb^{2+}] = [Ag^+]^2 \exp\left[\frac{nF}{RT}(\mathcal{E}°_{cell} - \mathcal{E}_{cell})\right]$$

$$= (1.0\,M)^2 \exp\left[2\left(\frac{96485\,C}{mol}\right)\left(\frac{mol\,K}{8.315\,J}\right)\left(\frac{1}{293.15\,K}\right)(0.93 - 2.00)\frac{J}{C}\right]$$

$$[Pb^{2+}] = e^{-84.7074} = \boxed{2 \times 10^{-37}\,M}$$ no pts off for sig figs here

If $\mathcal{E}°_{cell} = 0.67$ V, $[Pb^{2+}] = e^{-105.2505} = 2 \times 10^{-46}$ M

(−4) math

(−5) wrong T

−7 (−8) incorrect algebra

(−15) didn't use Nernst

(−17) same thing

Possibly Useful Information

T (K) = T (°C) + 273.15 T (°F) = 1.800T (°C) + 32.00

$$\Delta H = \Delta U + P\Delta V \qquad \Delta S = \Delta S^o - R\ln Q \qquad \Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta G^o + RT\ln Q \qquad \Delta G^o = -RT\ln K \qquad \ln\frac{K_2}{K_1} = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta G = -nFE_{\text{cell}} \qquad \Delta G^o = -nFE^{\text{o}}_{\text{cell}} \qquad E_{\text{cell}} = E^{\text{o}}_{\text{cell}} - \frac{RT}{nF}\ln Q$$

$$E^{\text{o}}_{\text{cell}} = E^{\text{o}}_{\text{cathode}} - E^{\text{o}}_{\text{anode}} = E^{\text{o}}_{\text{red}} + E^{\text{o}}_{\text{ox}}$$

F = 96485 C mol^{-1} R = 8.315 J mol^{-1} K^{-1}

N_A = 6.022 x 10^{23} mol^{-1} 1 kJ = 10^3 J

Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.22
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons SO_2(g) + 2H_2O(l)$	+0.20
$Cu^{2+}(aq) + e^- \rightleftharpoons Cu^+(aq)$	+0.15
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq)$	−0.23
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	−0.31
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	−2.89
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	−2.90
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

PERIODIC TABLE OF THE ELEMENTS

1A	2A	3B	4B	5B	6B	7IB	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	Pt 195.08	Au 196.97	Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 †Ac 227.03															

*58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

HOCl(g) $N_2O(g)$ 220