CH 233H

First Midterm Exam Friday, April 22, 2016

Name____

Please show your work for partial credit. If you need more spacefor an answer, use the back of the page and indicate where we should look.

You may not use notes or other materials with chemical information without the instructor's approval; necessary information is provided on pages at the back of the exam. Please do not use ipods or other music players.

hydrogen 1 H 1.0079																		helium 2 He 4.0026
lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [268]	ununnilium 110 Uun [271]	unununium 111 Uuu [272]	ununbium 112 Uub [277]		ununquadium 114 Uuq [289]				

*Lanthanide series	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
* *Actinide series	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

1. (15 points) Provide a concise definition in terms of energy for each of the three laws of thermodynamics.

First Law:
Energy is neither created nor destroyed.

Second Law:
In any spontaneous physical or chemical process, the entropy of the universe increases.

Third Law:
The entropy of a (pure) perfect crystal at 0K is 0.

2. (20 points) A reaction you saw briefly was the formation of benzene (C_6H_6) from acetylene (C_2H_2):

$$3\ C_2H_2(g) \longrightarrow C_6H_6(g)$$

A. What is $\Delta H_r°$?

$\Delta H_r° = \Delta H_f°$(products) - $\Delta H_f°$(reactants) = 82.6 kJ/mol – 3(226.7 kJ/mol)
= -597.5 kJ/mol

B. What is $\Delta S_r°$?

$\Delta S_r°$ = S°(products) - S°(reactants) = 269.3 J/(mol-K) – 3(200.9 J/mol-K)
= -333.4 J/(mol-K)

2. (continued) C. At what temperature does a total pressure of 1.000 atm show an equilibrium partial pressure of 0.3167 atm benzene?

$$K_{eq} = \frac{P_{benzene}}{P_{acetylene}^3} = \frac{0.3167}{(0.6833)^3} = 0.9927$$

$\Delta G_r° = -RTlnK_{eq} = \Delta H_r° - T\Delta S_r°$; we know K_{eq}, $\Delta H_r°$ and $\Delta S_r°$, so we can solve for T.

-8.314 J/(mol-K) T ln (0.9927) = -597.5 kJ/mol – T(-333.4 J/(mol-K))

0.0610 T (J/mol-K) - 333.4 T (J/mol-K) = -597,500 J/mol

$$T = \frac{-597500 \text{ J/mol}}{333.3 \text{ J/(mol-K)}} = 1792 \text{ K}$$

D. Because of the thermodynamics of this reaction, acetylene is never handled as a compressed gas but rather as a moderately (1.5 atm) pressurized solution (from which it easily vaporizes). Explain why you think this is more because of enthalpy or because of entropy.

Enthalpy is going to be dominant at the "normal" temperatures under which we might want to work (298K or room temperature; certainly never >350 K or 75°C. We have to get to extremely high temperatures for K_{eq} to approach unity.

3. (24 points) Many watch batteries or other “button” type batteries use the following reaction for the electrochemical cell:

$$Zn\ (s) + Ag_2O\ (s) \longrightarrow ZnO\ (s) + 2\ Ag\ (s)$$

A. Write the two half-cell reactions responsible for generating electrons in this battery.

$Zn\ (s) \rightarrow Zn^{+2}\ (aq) + 2\ e^-$ E° = +0.763 V

$Ag^+\ (aq) + e^- \rightarrow Ag\ (s)$ E° = + 0.800 V

B. Specify which metal will represent the anode, and which the cathode. Explain your reasoning.

Oxidation occurs at the anode, so Zn will be the anode.

Reduction occurs at the cathode, so Ag will be the cathode.

C. What is the maximum voltage this cell can produce?

The cell voltage is the sum of the half cells; +1.563 V.

4. (21 points) We saw a demonstration where we bubbled CO_2 through a saturated solution of $Ca(OH)_2$.

A. Write a balanced chemical equation for the reaction that occurred, and point out how the product that forms leads to a visible change in appearance.

Ca^{+2} (aq) + 2 OH^- (aq) + CO_2 (g) → $CaCO_3$ (s) + H_2O (l)

The clear solution of $Ca(OH)_2$ generates solid $CaCO_3$, which precipitates to form a milky white suspension.

B. If enough CO_2 is bubbled through the solution, it becomes clear again. Use the following equilibria to explain what happens.

$$CaCO_3\ (s) \rightleftharpoons Ca^{+2}\ (aq) + CO_3^{-2}\ (aq) \quad K_{sp} = 2.8 \times 10^{-9}$$

$$CO_2\ (g) + 2H_2O\ (l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \quad K_{eq} = 4.4 \times 10^{-7}$$

$$HCO_3^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CO_3^{-2}\ (aq) \quad K_{eq} = 4.7 \times 10^{-11}$$

Calcium carbonate can be transformed into soluble calcium bicarbonate—$Ca(HCO_3)_2$ —by the action of (acidic) H_2CO_3. The net reaction is

$CaCO_3$ (s) + H_2O (l) + CO_2(g) ⇌ Ca_{+2} (aq) + 2 HCO_3^- (aq)

This is eq. 1 + eq. 2 – eq. 3, so $K_{eq} = K_{eq}(1) \times K_{eq}(2) / K_{eq}(3) = 2.62 \times 10^{-5}$

C. Many of the world's historic artwork, monuments and architecture are made of marble, which is mostly crystalline $CaCO_3$. Based on the chemistry you describe in (B), explain whether you think it appropriate to keep a historically significant sculpture in an outdoor setting.

Since CO_2 is always part of the atmosphere, rain water will always contain some carbonic acid. This will,over time, dissolve the calcium carbonate in marble. However, due to the low net K_{eq} we see above, this will never happen all at once. But over time, this will erode the stone. It is fortunate that much historical stonework (particularly sculpture and statuary) are housed indoors and not exposed to the elements. (This is also the process that leads to natural formations in the Oregon Caves and other subterranean cave systems.)

The phenomenon has been exacerbated by industrial pollution; nitrogen and sulfur oxides make rain much more acidic and accelerate the process. This has been seen as a particular problem in Greece, where many of the works on the Parthenon are eroding, and in Rome, where a lot of historical stonework shows extreme damage.

5. (20 points) Write the expected products for each of the following (possible) reactions. If you do not expect any reaction, write "NR."

A. $Cu_2O\ (s) + C\ (s) \xrightarrow{\text{Heat}} 2Cu\ (s) + CO_2\ (g)$

B. $Li_2O(s) + C\ (s) \xrightarrow{\text{Heat}}$ No reaction (Li is a better reductant than C)

C. $AgCl\ (s) + 2NH_3\ (aq) \longrightarrow Ag(NH_3)_2^+\ (aq) + Cl\text{-}\ (aq)$

D. $FeCl_3\ (aq) + 6\ KCN\ (aq) \longrightarrow Fe(CN)_6^{-3}\ (aq) + 6\ K^+\ (aq) + 3\ Cl^-\ (aq)$

E. $CoCl_2\ (aq) + 4\ NH_3\ (aq) \longrightarrow Co(NH_3)_4(OH_2)^{+2}\ (aq) + 2\ Cl^-\ (aq)$

Selected data that may be of use:

Physical constants:

$g = 9.8$ m/s^2	Gravitational Constant
$\varepsilon_0 = 8.85419 \times 10^{-12}$ C^2/(Nm^2)	Electric susceptibility of a vacuum
$c = 2.99792458 \times 10^{10}$ cm/s	Speed of light
R = 0.08206 L-atm/(mol-K) = 8.314 J/(mol-K)	Gas constant
$N = 6.022 \times 10^{23}$	Avogadro's Number
$k = 1.381 \times 10^{-23}$ m^{2}kg/(K-s^2)	Boltzmann constant
$h = 6.626 \times 10^{-34}$ m^{2}kg/s	Planck's constant
F = 96485 C/mol	Faraday's constant
$\pi = 3.14159$	
e = 2.71828	

Properties of State

Species	ΔH°_f	S°
N_2 (g)	0 kJ/mol	191.6 J/(mol-K)
O_2 (g)	0 kJ/mol	205.1 J/(mol-K)
NO (g)	90.25 kJ/mol	210.8 J/(mol-K)
C (s) (graphite)	0 kJ/mol	5.74 J/(mol-K)
C_2H_2 (g)	226.7 kJ/mol	200.9 J/(mol-K)
C_6H_6 (g)	82.6 kJ/mol	269.3 J/(mol-K)
CO_2 (g)	-393.5 kJ/mol	213.7 J/(mol-K)
Ag (s)	0 kJ/mol	42.55 J/(mol-K)
Ag^+ (aq)	105.6 kJ/mol	72.68 J/(mol-K)
K^+(aq)	-254.4 kJ/mol	102.5 J/(mol-K)
Zn (s)	0 kJ/mol	41.63 J/(mol-K)
Zn^{+2} (aq)	-153.9 kJ/mol	112.1 J/(mol-K)
Li (s)	0 kJ/mol	29.12 J/(mol-K)
Li_2O (s)	-595.8 kJ/mol	37.89 J/(mol-K)
Cu (s)	0 kJ/mol	33.15 J/(mol-K)
Cu_2O (s)	-170 kJ/mol	93 J/(mol-K)

Electromotive series:

TABLE 20.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C

Reduction Half-Reaction	$E°$, V
Acidic solution	
$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+2.866
$O_3(g) + 2H^+(aq) + 2e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075
$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$	+2.01
$H_2O_2(aq) + 2H^+(aq) + 2e^- \longrightarrow 2H_2O(l)$	+1.763
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Pb^{2+}(aq) + 2H_2O(l)$	+1.455
$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+1.358
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \longrightarrow Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$	+1.229
$2IO_3^-(aq) + 12H^+(aq) + 10e^- \longrightarrow I_2(s) + 6H_2O(l)$	+1.20
$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$	+1.065
$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O(l)$	+0.956
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.800
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$	+0.695
$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+0.340
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow 2H_2O(l) + SO_2(g)$	+0.17
$Sn^{4+}(aq) + 2e^- \longrightarrow Sn^{2+}(aq)$	+0.154
$S(s) + 2H^+(aq) + 2e^- \longrightarrow H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	−0.125
$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	−0.137
$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	−0.440
$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	−0.763
$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	−1.676
$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	−2.356
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.713
$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	−2.84
$K^+(aq) + e^- \longrightarrow K(s)$	−2.924
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.040
Basic solution	
$O_3(g) + H_2O(l) + 2e^- \longrightarrow O_2(g) + 2OH^-(aq)$	+1.246
$OCl^-(aq) + H_2O(l) + 2e^- \longrightarrow Cl^-(aq) + 2OH^-(aq)$	+0.890
$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$	+0.401
$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$	−0.828