CH 231H

Final Exam   Wednesday, December 11, 2013

Name______KEY____

You may use numerical calculators but no other material with chemical information without instructor approval.

Please do not use ipods or other music players.

1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

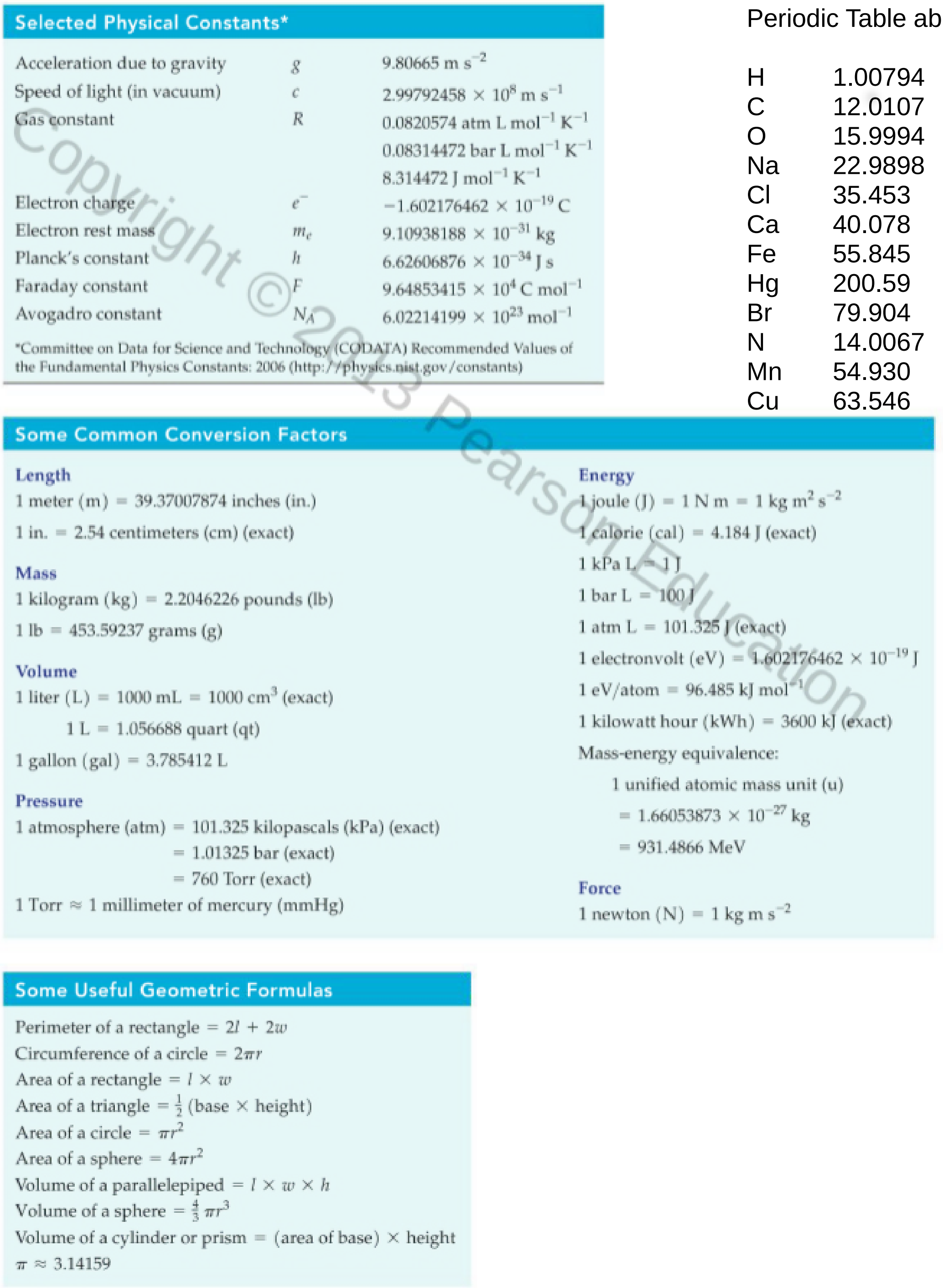
58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Potentially useful information.

1 Å = 10^{-10} m = 10^{-8} cm

Selected atomic weights from the Periodic Table above:

H	1.00794
C	12.0107
O	15.9994
Na	22.9898
Cl	35.453
Ca	40.078
Fe	55.845
Hg	200.59
Br	79.904
N	14.0067
Mn	54.930
Cu	63.546



Selected Physical Constants*

Acceleration due to gravity	g	$9.80665\ \mathrm{m\ s^{-2}}$
Speed of light (in vacuum)	c	$2.99792458 \times 10^{8}\ \mathrm{m\ s^{-1}}$
Gas constant	R	$0.0820574\ \mathrm{atm\ L\ mol^{-1}\ K^{-1}}$
		$0.08314472\ \mathrm{bar\ L\ mol^{-1}\ K^{-1}}$
		$8.314472\ \mathrm{J\ mol^{-1}\ K^{-1}}$
Electron charge	e^-	$-1.602176462 \times 10^{-19}\ \mathrm{C}$
Electron rest mass	m_e	$9.10938188 \times 10^{-31}\ \mathrm{kg}$
Planck's constant	h	$6.62606876 \times 10^{-34}\ \mathrm{J\ s}$
Faraday constant	F	$9.64853415 \times 10^{4}\ \mathrm{C\ mol^{-1}}$
Avogadro constant	N_A	$6.02214199 \times 10^{23}\ \mathrm{mol^{-1}}$

*Committee on Data for Science and Technology (CODATA) Recommended Values of the Fundamental Physics Constants: 2006 (http://physics.nist.gov/constants)

Some Common Conversion Factors

Length

1 meter (m) = 39.37007874 inches (in.)

1 in. = 2.54 centimeters (cm) (exact)

Mass

1 kilogram (kg) = 2.2046226 pounds (lb)

1 lb = 453.59237 grams (g)

Volume

1 liter (L) = 1000 mL = 1000 $\mathrm{cm^3}$ (exact)

1 L = 1.056688 quart (qt)

1 gallon (gal) = 3.785412 L

Pressure

1 atmosphere (atm) = 101.325 kilopascals (kPa) (exact)
= 1.01325 bar (exact)
= 760 Torr (exact)

1 Torr ≈ 1 millimeter of mercury (mmHg)

Energy

1 joule (J) = 1 N m = 1 kg $\mathrm{m^2\ s^{-2}}$

1 calorie (cal) = 4.184 J (exact)

1 kPa L = 1 J

1 bar L = 100 J

1 atm L = 101.325 J (exact)

1 electronvolt (eV) = $1.602176462 \times 10^{-19}$ J

1 eV/atom = 96.485 kJ $\mathrm{mol^{-1}}$

1 kilowatt hour (kWh) = 3600 kJ (exact)

Mass-energy equivalence:

1 unified atomic mass unit (u)
= $1.66053873 \times 10^{-27}$ kg
= 931.4866 MeV

Force

1 newton (N) = 1 kg m $\mathrm{s^{-2}}$

Some Useful Geometric Formulas

Perimeter of a rectangle = $2l + 2w$
Circumference of a circle = $2\pi r$
Area of a rectangle = $l \times w$
Area of a triangle = $\frac{1}{2}$ (base × height)
Area of a circle = πr^2
Area of a sphere = $4\pi r^2$
Volume of a parallelepiped = $l \times w \times h$
Volume of a sphere = $\frac{4}{3}\pi r^3$
Volume of a cylinder or prism = (area of base) × height
$\pi \approx 3.14159$

1. (20 points) Cu has two major isotopes. The more abundant ^{63}Cu, has an atomic mass of 62.9298, and has a natural abundance of 69.0900%. The atomic weight of Cu is 63.5460.

A. What is the name of the element Cu?

Copper

B. What is the atomic mass (to 6 significant figures) of the other major isotope, ^{65}Cu? Show how this can be calculated.

(0.690900)(62.9298) + (0.309100)(x) = 63.5460

x = 64.9233

C. What is the electron configuration of Cu?

$[Ar]3d^{10}4s^1$ or $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
(Note that this is one of our exceptions—the s electron jumps to the 3d shell to fill it)

D. Explain how the Pauli exclusion principle and Hund's rule apply in arriving at your predicted electron configuration.

The Pauli exclusion principle means that no two electrons can have all four quantum numbers identical. Therefore, accounting for spin, we can have up to 2 electrons (opposite spins) in any s orbital, 6 in the collection of 3 p orbitals, and 10 electrons in the collection of 5 d orbitals in any shell.

Hund's rule says they will fill the lowest energy orbitals one at a time. Our one issue is which of the 4s or 3d energies is lower. Normally the 4s orbital is lower in energy, but filling the 3d orbitals (and by extension, the entire n=3 shell) makes this more stable than the $[Ar]3d^9 4s^2$ alternative.

2. (20 points) Stearic acid, $C_{18}H_{36}O_2$, is chemically similar to acetic acid (CH_3CO_2H) and has the overall structure $CH_3(CH_2)_{16}CO_2H$. A salt of stearic acid used as a wood sealer/preservative has the following elemental composition:

Cu: 10.08%
O: 10.15%
C: 68.58%
H: 11.19%

A. Calculate a molecular formula for this compound.

$Cu_{10.08/63.5460}C_{68.58/12.01}H_{11.19/1.008}O_{10.15/16.00}$ gives $Cu_{0.1586}C_{5.710}H_{11.10}O_{0.6344}$

Normalizing to 1 copper atom (dividing each coefficient by 0.1586) gives

$CuC_{36}H_{70}O_4$; another way to express this in terms of stearate anions is

$Cu(C_{18}H_{35}O_2)_2$

B. What is the oxidation state of the metal in this salt?

There are 2 anions per Cu, so this is Cu(II).

C. Basic sources of Cu include: $Cu(OH)_2$, CuO, Cu_2O, $CuCO_3$ and Cu_2CO_3. Write a balanced equation for a chemical reaction that can form this salt.

We must use a Cu(II) salt. Options are:

$Cu(OH)_2 + 2\ C_{18}H_{36}O_2 \rightarrow Cu(C_{18}H_{35}O_2)_2 + 2\ H_2O$

$CuO + 2\ C_{18}H_{36}O_2 \rightarrow Cu(C_{18}H_{35}O_2)_2 + H_2O$

$CuCO_3 + 2\ C_{18}H_{36}O_2 \rightarrow Cu(C_{18}H_{35}O_2)_2 + H_2O + CO_2$

3. (15 points) Nitroglycerine is used as both a high explosive and as a vasodilator (blood vessel expander) for cardiac patients. Alfred Nobel made his fortune from his discovery of how to turn the unstable pure compound into the more stable form of dynamite.

The decomposition is represented by the following balanced equation:

$4\ C_3H_5N_3O_9\ (l) \rightarrow\ 12\ CO_2(g) + 10\ H_2O(g) + 6\ N_2(g) + O_2(g)$

A. From the heats of formation given below, calculate the enthalpy of reaction for decomposition.

$C_3H_5N_3O_9\ (l)$	-370 kJ/mol
$CO_2(g)$	-393.5
$H_2O(g)$	-241.8

$\Delta H^o = \sum \Delta H^o_{f(products)} - \sum \Delta H^o_{f(reactants)}$

= (12)(-393.5 kJ/mol) +(10)(-241.8 kJ/mol) + 6(0 kJ/mol) + (0 kJ/mol) – (4)(-370.0 kJ/mol)

= -5660 kJ per 4 moles nitroglycerine, or -1415 kJ/mol nitroglycerine

B. Does the exothermicity of this reaction alone explain the explosive force of nitroglycerine? Explain.

A large portion of the products are in the gas phase, so therefore our usual assumption that $\Delta U \approx \Delta H \approx q$ as in condensed-phase reactions does not hold. There will be substantial work (from $\Delta(PV)$) done as well, and this is a major feature of many explosive reactions.

4. (30 points) 500.0 mL of 0.1233 M $Fe(NO_3)_2$ is added to 150.0 mL of 0.1019 M $Na_2Cr_2O_7$ that has been acidified. The two react to give Fe^{+3} and Cr^{+3}.

A. Write the half-reactions for the reduction and oxidation reactions.

$Fe^{+2} \rightarrow Fe^{+3} + e^-$

$6\ e^- + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{+3} + 7H_2O$

B. Write the balanced redox equation.

$6\ Fe^{+2} + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 6\ Fe^{+3} + 2\ Cr^{+3} + 7H_2O$

C. What is the limiting reagent? Show how you calculate this.

Find the initial number of moles:

Fe^{+2}: 0.5000 L x 0.1233 M = 0.06165 mol
$Cr_2O_7^{2-}$: 0.1500 L x 0.1019 M = 0.01529 mol

We need 6 times as much iron as dichromate (we only have 4 times as much), so this makes Fe^{+2} the limiting reagent.

D. Presuming nothing precipitates, list the final concentrations of the following ions.

$[Fe^{+3}] = \frac{0.06165 \text{ mol}}{0.6500 \text{ L (total volume)}} = 0.09485 \text{ M}$

$[Cr_2O_7^{2-}] = \frac{\{0.01529 \text{ mol} - (0.06165 \text{ mol}/6)\}}{0.6500 \text{ L}} = 0.007715 \text{ M}$

$[Fe^{+2}] = 0 \text{ M}$

$[Cr^{+3}] = [Fe^{+3}]/3 = 0.03162 \text{ M}$

$[NO_3^-] = \frac{2(0.06165) \text{ mol}}{0.6500 \text{ L}} = 0.1897 \text{ M}$

$[Na^+] = \frac{2(0.01529 \text{ mol})}{0.6500 \text{ L}} = 0.04705 \text{ M}$

5. (25 points) The sodium atom has an empirically measured atomic radius of 1.86 Å.

A. Let's treat the outermost electron as a one-dimensional particle in a box with a dimension L matching the circumference of the atom. Calculate the wavelength of the electron if it satisfies the standing wave requirements of the wavefunction

$\psi(x) = \sqrt{2/L}\,\sin(n\pi x/L)$.

(Hint: be sure to consider the relationship between L and λ.)

The circumference is 2πr, so L = 2(3.14)(1.86 Å) = 11.7 Å

$\lambda = 2L = 23.4$ Å

B. Using the deBroglie equation, $\lambda = h/mv$, calculate the velocity of an electron with this wavelength.

$23.4\ \text{Å} \times 1\ \text{m}/10^{10}\ \text{Å} = 6.626 \times 10\text{-}34\ \text{kg m}^2\text{s}^{-1}/\{(9.109 \times 10^{-31}\ \text{kg})(v)\}$

$v = 3.11 \times 10^5$ m/s

C. Calculate the kinetic energy ($E_k = \frac{1}{2}mv^2$) of an electron with this velocity.

$E_k = \frac{1}{2}\ (9.109 \times 10^{-31}\ \text{kg})(3.11 \times 10^5\ \text{m/s})^2 = 4.405 \times 10^{-20}$ J

(on a molar basis this would be 26.5 kJ/mol)

D. The sodium atom exhibits a pair of very strong lines in the emission spectrum; the stronger is at 588.9950 nm. Calculate ΔE for this transition using the Planck equation.

$E = h\nu = hc/\lambda = (6.626069 \times 10^{-34}\ \text{kg m}^2\text{s}^{-1})(2.997925 \times 10^8\ \text{ms}^{-1})/588.9950 \times 10^{-9}$ m

$= 3.372602 \times 10^{-19}$ J (1 J = 1 kg m^2s^{-2}) On a molar basis this is 203.10 kJ/mol.

E. Assuming that this added energy in the excited state purely adds to the kinetic energy of the excited electron (not actually true), what would the velocity of the excited electron be?

The total energy would be 3.8131×10^{-19} J.

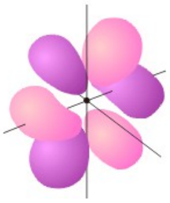
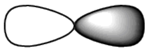
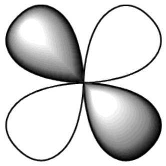
If this is all kinetic energy,

$E_k = 3.8131 \times 10^{-19}\ \text{kg m}^2\text{s}^{-2} = \frac{1}{2}\ (9.109 \times 10^{-31}\ \text{kg})(v^2)$

$$v^2 = \frac{2 \times 3.8131 \times 10^{-19}\ \text{kg m}^2\text{s}^{-2}}{9.109 \times 10^{-31}\ \text{kg}} = 8.37 \times 10^8\ \text{m}^2\text{s}^{-2};\quad v = 9.15000 \times 10^5\ \text{m/s}$$

6. (20 points) You saw in the textbook (and on the Web site) several representations of orbital wavefunctions with different colors or shading representing the mathematical sign of the function.

A. Match representations of atomic orbital wavefunctions (on the right) with the following sets of quantum numbers (on the left).

n = 1, ℓ = 0, m_ℓ = 0	**n=5, ℓ = 3, $m\ell$ = -2**	
n = 2, ℓ = 1, m_ℓ = 0	**n = 2, ℓ = 1, m_ℓ = 0**	
n = 3, ℓ = 2, m_ℓ = -1	**n = 1, ℓ = 0, m_ℓ = 0**	
n = 3, ℓ = 1, m_ℓ = -1	**n = 3, ℓ = 1, m_ℓ = -1**	
n=5, ℓ = 3, $m\ell$ = -2	**n = 3, ℓ = 2, m_ℓ = -1**	

B. Circle the functions that will have one or more additional radial nodes.

n=5, ℓ = 3, $m\ell$ = -2 and n = 3, ℓ = 1, m_ℓ = -1 will have additional radial nodes.

7. (20 points) We saw in a video the reaction of different halogens with aluminum metal.

A. The table below shows the ionization potentials and electron affinities (all in kJ/mol) for the halogens and aluminum.

	I_1	I_2	I_3	I_4	EA_1
F	1681	3374	6050	8408	-328.0
Cl	1251	2298	3822	5159	-349.0
Br	1140	2103	3470	4560	-324.6
I	1008	1845	3180		-295.2
Al	577.6	1817	2745	11580	-42.5

Explain how you can use this information exclusively to predict the product that forms when Al and I_2 react.

Aluminum can relatively easily give up its first three electrons (but no more) and become Al^{+3}. Iodine can very easily gain an electron to become I^-.

B. Write a balanced equation for this reaction, based on your prediction.

$2Al + 3\ I_2 \rightarrow 2\ AlI_3$

C. If we assume the primary contributor to the enthalpy of reaction is the electronic reorganization that occurs (not entirely true), would you predict the reaction between Cl_2 and Al to be more or less exothermic? Explain.

The loss of electrons from aluminum will be energetically identical in both cases. However, the electron affinity of Cl is approximately 54 kJ/mol more exothermic and thus the overall reaction should be about 162 kJ/mol more exothermic.