CHEMISTRY 209

PRELIM I | October 4, 2007

ANSWER KEY

1. (a) (7 points) Balance the following chemical reaction:

$$\_\_\_\_B_5H_9(g) + \_\_\_\_O_2(g) \longrightarrow \_\_\_\_B_2O_3(s) + \_\_\_\_H_2O(g)$$

First, work on the B; there are 5/formula unit on the left, 2/formula unit on the right; so we need 2 moles on the left and 5 on the right. That gives us 18 H units on the left, that we need to account for on the right; call it 9 H_2O units. In total, that means we have $15 + 9 = 24$ oxygen atoms on the right that we need to account for on the left; or 12 O_2 units. Ending up with:

$$2B_5H_9(g) + 12O_2(g) \longrightarrow 5B_2O_3(s) + 9H_2O(g)$$

(b) (8 points) The hormone adrenaline has the molecular formula $C_9H_{13}O_3N$. Complete combustion of adrenaline yields only CO_2, H_2O and N_2 as products. Balance the chemical equation below representing the combustion of adrenaline by filling in the blanks with appropriate coefficients.

$$\_\_\_\_C_9H_{13}O_3N + \_\_\_\_O_2 \longrightarrow \_\_\_\_CO_2 + \_\_\_\_H_2O + \_\_\_\_N_2$$

Balance the equation by finding the coefficients which belong in the blanks.

Approach as in the previous problem. Each C on the left has to end up in a CO_2 molecule on the right; each 2 H's on the left in an H_2O molecule on the right, and each N atom as a part of N_2 on the right. So let's start by using 2 units of the adrenaline molecule on the left; that gives us 18 CO_2's, and 13 H_2O's on the right. And 1 N_2 product molecule. Without using any of the O_2 species, we have 6 oxygen units on the left, and require $18 \times 2 + 13 \times 1 = 49$ oxygen atoms on the right. So we need $\frac{43}{2}$ units of O_2; multiplying everything by 2 to get to integer coefficients only (which is not strictly required) leads to:

$$4C_9H_{13}O_3N + 43O_2 \longrightarrow 36CO_2 + 26H_2O + 2N_2$$

2. (15 points) Trimethyl aluminum, $Al(CH_3)_3$, must be handled carefully in an air-tight apparatus as it spontaneously bursts into flame upon contact with oxygen. Calculate the mass of trimethyl aluminum which can be prepared from 5.00 g of aluminum metal and 25.0 g of dimethyl mercury via the chemical reaction

$$2Al(s) + 3Hg(CH_3)_2(l) \longrightarrow 2Al(CH_3)_3(l) + 3Hg(l)$$

We need to decide which input is the limiting reagent as a start. That means finding the number of moles of each reactant;

5.00 g of Al metal with a molar mass 26.9815 corresponds to 0.1853 moles of Al;

25.0 g of dimethyl mercury has a molar mass of $(200.59 + 2 \times (12.0112 + 3 \times 1.00797)) = 230.66$ g/mole; corresponding to 0.1084 moles.

Our balanced equation states that we require three moles of the dimethyl mercury reactant for each two moles of Al; thus we have an excess of Al metal, and our limiting reagent is the dimethyl mercury. Each mole yields two-thirds of a mole of our product; therefore our maximum yield (in moles of the trimethyl aluminum compound) is $0.1084 \times 2/3 = 0.07226$ moles of trimethyl aluminum. The molar mass of the trimethyl aluminum is $26.9815 + 3 \times (12.0112 + 3 \times 1.00797)) = 72.08683$; our 0.7226 moles would therefore weigh 0.7226 moles $\times 72.08683$ g/mole $=$ 5.209 g; we only have three significant figures, so call it 5.21 grams of product maximum.

3. (a) (10 points) A compound, cantharene, contains only carbon and hydrogen. The combustion of 0.270 grams of cantharene in excess oxygen yields enough CO_2 to react with just 20.0 mℓ of 2.0 M NaOH solution, according to the chemical equation

$$2\ \mathrm{NaOH} \quad + \quad \mathrm{CO_2} \quad \longrightarrow \quad \mathrm{Na_2CO_3} \quad + \quad \mathrm{H_2O}$$

Given the atomic weights H=1, C=12 and O=16 find the empirical formula for cantharene.

How much CO_2 is formed? That requires that we know how many moles of NaOH are used up in the subsequent reaction; as one mole of CO_2 reacts with 2 moles of the NaOH. How many moles of NaOH are used up?

$$(0.020\ \ell\ \text{solution}) \times (2.0\ \text{moles NaOH}/\ell\ \text{solution}) = 0.040\ \text{moles NaOH}$$

meaning that we generated 0.020 moles of CO_2, meaning our compound contained 0.020 moles of C which weighed 0.020 moles$\times 12$ g/mole $=$ 0.24 grams of C. The remainder must be our H; corresponding to 0.030 grams; at one gram per mole, that corresponds to 0.030 moles of H atoms. So the empirical formula for cantharene is C_2H_3. Note that we didn't really need the mass of the oxygen at all...

(b) (10 points) A metallic element (call it M) combines with a halogen (call it X) to form a compound MX_2. At high temperature this compound undergoes quantitative decomposition via the reaction

$$2MX_2(s) \longrightarrow 2MX(s) + X_2(g)$$

From 1.12 g of MX_2 one obtains 0.72 g of the solid MX, and sufficient gaseous X_2 to react completely with 0.061 g of magnesium metal (Mg, with atomic weight 24.3). Find the atomic weights of the halogen X and the metal M (to two significant digits).

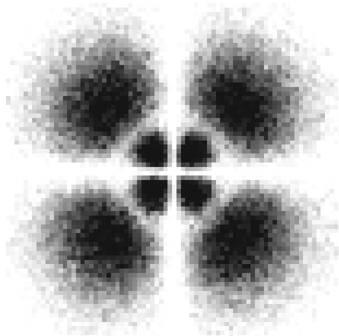
What do we know? We know that 0.40 g of the gas X_2 reacts with 0.061 of magnesium metal; magnesium is a metal that gets assigned a charge state in its ionic form of $+2$, so it should combine with two atoms of X (as halogens are typically assigned an oxidation state of -1). So our compound formed is MgX_2; it contains 0.061 g of Mg and 0.40 g of X_2, corresponding to

$$0.061 \text{ g} \times 1 \text{ mole Mg}/24.3 \text{ g Mg} = 0.00251 \text{ moles Mg}$$

therefore 0.40 g represents 0.00251 moles of X_2, or 0.00502 moles of X, and the molar atomic weight of X is therefore 0.40 g/0.00502 moles $=$ 79.7 g/mole; to 2 significant digits, call it 80. Which is the atomic weight of Br, luckily enough–though the question doesn't ask that we determine that.

Now we need to identify the metal, M; we know that there are as many atoms of X left behind as there are released from the heating of the original compound. So our 0.72 g of the solid MX represents 0.00502 moles of MX; the formula weight of the compound MX is therefore 0.72 g/0.00502 moles $=$ 144 g/mole; and the mass of the metal M is therefore $144 - 80 = 64$. Meaning that we have Cu as our "unknown" metal.

4. (a) (5 points) Below is shown a picture of the population probability density for a H-atom orbital. Which values of n and ℓ does this orbital represent?



Most likely correct answer is a $4d$ orbital; one radial node, two planar nodes in the angular direction. It could, from some perspectives, be confused with a $5f$, or $6g$, or $7h$, etc. orbital. Such answers should get full credit, if they exist. That would correspond to $n = 4, \ell = 2$, or any combination $n = j, \ell = j - 2$ for $j \geq 4$.

(b) (5 points) Which of the following represents an allowed set of quantum numbers n, ℓ, m_ℓ and m_s for an electron in an atomic orbital? Mark clearly in either the "allowed" or "forbidden" columns to indicate whether you believe each row corresponding to a set of quantum numbers is acceptable.

allowed	forbidden	n	ℓ	m_ℓ	m_s
⊗	___	2	0	0	$\frac{1}{2}$
⊗	___	8	4	−3	$-\frac{1}{2}$
___	⊗	3	3	2	$\frac{1}{2}$
___	⊗	2	1	−2	$\frac{1}{2}$
___	⊗	5	3	2	1

(c) (5 points) Which of the following neutral atoms has the largest number of unpaired electrons? Circle your choice.

Na Al Si (P) S

5. The Bohr model for one-electron species with nuclear charge Z states that the energy of any stable electronic orbital is given by

$$E_n = -\frac{2\pi^2 m e^4 Z^2}{h^2}\frac{1}{n^2}$$

and the collection of constants can be gathered into a single constant that we will indicate by $\frac{2\pi^2 m e^4}{h^2} \equiv R_H$ where R_H is the Rydberg constant, and the negative sign exists to clarify that these bound state energies are measured with respect to the state where the electron is free from the influence of the nucleus.

(a) (10 points) The Rydberg formula describing the wavelengths λ for transitions in the emission spectrum of the one-electron species is derived easily from the above, and

$$\frac{1}{\lambda} = R_H Z^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where n_i is the state that the electron is initially found in, and n_f is the state that the electron ends in. Complete ejection of remaining electron in the He^+ species from its lowest energy state requires absorption of light with a wavelength $\lambda \leq 22.8$ nm. Using this information find for the H atom the wavelength of the (Lyman series) emission line arising from a transition from $n_i = 2$ to $n_f = 1$.

The He^+ species is entirely analogous to the H atom except for the fact that $Z = 2$ in He; while in H atoms $Z = 1$. Our expression for the transitions given above tells us that $1/\lambda \propto Z^2$; equivalently, that λZ^2 is a constant for all one-electron species (assuming that n_f and n_i are the same). Thus we require $\lambda Z^2 = 22.8 \times Z^2 = 91.2$ nm for the $n_i = \infty$ to $n_f = 1$ transition in all one-electron species; if $Z = 1$–as it is in H–then ionization of the H atom, corresponding to the transition from the ground state to the $n = \infty$ state would occur at $\lambda = 91.2$nm; in this problem, we are asked to find the $n_i = 2$ to $n_f = 1$ transition, which corresponds to an energy $(\frac{1}{1^2} - \frac{1}{2^2}) = \frac{3}{4}$ as large as the ionization energy. As energy is inversely proportional to the wavelength, the required line would appear at $\frac{4}{3} \times 91.2$ nm $=$ 121.6 nm.

(b) (10 points) The wavelength λ of the Lyman series line described above in the H atom spectrum is also found in the emission spectrum of the He^+ species. Find n_i and n_f for the emission line at this wavelength in the He^+ species.

Look to the Rydberg formula provide above. We have the same λ for two different lines, one originating in the $Z = 1$ species and the second in a $Z = 2$ species. This would tend to increase the value of $1/\lambda$ in the larger Z species, by the factor $2^2 = 4$; if we are told that the same value of $1/\lambda$ is found then we must require that some other part of the equation for $1/\lambda$ be smaller by exactly 4. R_H is a constant, that leaves only n_f and n_i; if we double each of them, and then calculate the difference $(\frac{1}{n_f^2} - \frac{1}{n_i^2})$ we will find that we have exactly compensated for the increased value of Z. So the He^+ species has an emission line at 121.6 nm if we are observing the transition $n_i = 4$ to $n_f = 2$.

6. (a) (5 points) A substance X_2Z has a composition (by mass) of 40.0% X and 60.0% Z. What is the composition (by mass) of the compound XZ_2?

Take one gram of the compound X_2Z; it contains 0.400 g of X and 0.600 g of Z. The compound XZ_2 would contain 4 times as many Z atoms per X atom; or would require that we have 2.400 g of Z for every 0.400 g of X. In that 2.800 g sample, the % by mass of X would be $0.400/2.800 \times 100\% = 14.3\%$ and the remainder would be Z; that is, $2.400/2.800 \times 100\% = 85.7\%$.

(b) (10 points) John Dalton was provided with three compounds, each corresponding to a binary compound of two of the three elements X, Y or Z. Each compound was treated chemically to release quantitatively the elements, and their masses determined as follows:

From the compound formed from X and Y, 400 mg of X and 4200 mg of Y were recovered.

From the compound formed from Y and Z, 1400 mg of Y and 1000 mg of Z were recovered.

From the compound formed from X and Y, 2000 mg of X and 7000 mg of Y were recovered.

Dalton was asked to determine the relative masses of X, Y and Z. Assigning X a mass of exactly 1 Chem209 experimental mass unit (call it the Cemu), find the masses of Y and Z in Cemus. Discuss the assumptions made in the derivation of those masses. Assume each of the masses above are reported to 3 significant digits.

Binary compounds are composed of two elements, with formulae such as A_aB_b for a and b typically small integers. When more than one binary compound is possible, we expect that for fixed mass of A the ratio of the masses of B will be a small integer n so that the compounds represented will look like A_aB_b and A_aB_{nb} (note; it is also possible that n will be the ratio of two small integers). In the experiment above, the X-Y binaries have mass ratios of 1:10:5 and 1:3.5; thus it would appear that they represent compounds of the form X_xY_{3y} and X_xY_y. Without any more information, we cannot uniquely identify x and y; so we'll assume that they are both 1, and would predict that the mass of Y is 3.5 Cemu's. Of course, if we assumed $x = 2$ and $y = 1$, we would get a different answer; then we would find Y to have mass 7 Cemu's. Other choices are possible though less likely; one could perhaps imagine $x = 1$ and $y = 2$, leading to a mass of 1.75 Cemu's, and so on; potentially any set of small integers p and q could be chosen leading to masses that are $3.5p/q$.

Assume that the mass of Y is 3.5 Cemu's. Then Y-Z compound tells us that the mass of Z is $2.5k/j$ Cemu's, depending on what assumptions we make about the formula of the Y-Z binary, Y_kZ_j. If the formula is YZ, then the mass of Z is 2.5; if it were YZ_2, then 1.25 Cemu's, and so on.

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PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES
1 H 1.00797																1 H 1.00797	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	✳57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	‡89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

✳ Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97

‡ Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)