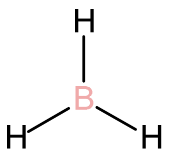
Escuela Politécnica Superior
Universidad Carlos III de Madrid

Chemistry
Mid Term Exam. Topics 1-5

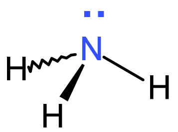
1.- *(1.5 point)* a) *(0.8 point)* Determine de Lewis structure, lone pairs, molecular geometry and hybridization in the following two molecules BH_3 and NH_3. b) *(0.7 point)* Discuss the polarity of both molecules and their acid-base properties.

Solution:
a) BH_3



No lone pairs
Trigonal Planar geometry
sp^2 hybrids

NH_3



One lone pair
Trigonal pyramidal
sp^3

b) BH_3 : Apolar because the dipolar moment sum is zero. Boron atom has empty p atomic orbitals so the molecule has acid properties
NH_3 : Polar because the dipolar moment sum is non zero. Since it has a lone pair, the molecula has base properties.

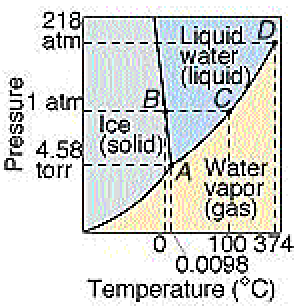
2.- *(1.5 point)* Consider the following statements about electromagnetic radiation and decide whether they are true or false. If they are false correct them
a) *(0.3 point)* Photons of ultraviolet radiation have less energy than photons of infrared radiation.
b) *(0.3 point)* The kinetic energy of an electron ejected from a metal surface when the metal is irradiated with ultraviolet radiation is independent of the frequency of the radiation.
c) *(0.3 point)* The energy of a photon is inversely proportional to the wavelength of the radiation.
d) *(0.6 point)* A lamp rated at 40 W ($1W = 1J{\cdot}s^{-1}$) emits blue light of wavelength 470 nm. How many moles of photons of blue light can the lamp generate in 2 seconds?
DATA: $h = 6.626{\cdot}10^{-34}$ J·s; $c = 2.997{\cdot}10^{8}$ m·s^{-1}; $N_A = 6.022{\cdot}10^{23}$.

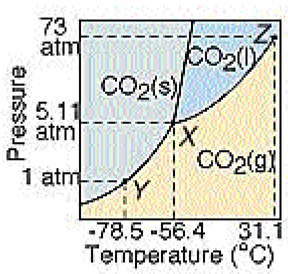
a) False. IR photons have less energy that UV

b) False, kinetic energy of the ejected electron is the difference between the energy of the UV photon and the threshold energy of the metal

c) Correct
d) $E=h\cdot\nu = h\cdot c/\lambda=6.626\cdot10^{-34} \cdot 2.997\cdot10^{8}/ 470\cdot10^{-9} =4.225\cdot10^{-19}$ J. In 2 sec, lamp emits $2\cdot40 = 80$ J. So $80 = N_{photons}\cdot4.225\cdot10^{-19}$; $N_{photons} =1.893\cdot10^{+20}$ photons; number of moles will be $3.144\cdot10^{-4}$.

3.- *(1.5 point)* Consider the equilibrium phase diagrams of water and carbon dioxide and answer the following questions





http://www.science.uwaterloo.ca/~cchieh/cact/c123/phasesdgm.html

a) *(0.3 point)* Which are the coordinates of critical points, triple points and normal boiling points?
b) *(0.9 point)* The slopes for the solid-liquid equilibrium curves have different sign for both substances. Explain why.
c) *(0.3 point)* Describe all the changes that will take place if the pressure of a sample of water at 0ºC is decreased from 218 atm to 0.1 torr.

Solution:
a) H_2O. Critical point 218 atm, 374 ºC; triple point 4.58 torr, 0.0098 ºC; normal boiling temperature 100 ºC
CO_2. Critical point 73 atm, 31 ºC; triple point 5.11 atm, -56.4 ºC; it has no normal boiling temperature because at 1 atm it is a gas.
b) According to the Clausius equation the slope for the coexistence equilibrium line is given by

$$\frac{dp}{dT}=\frac{\Delta H}{T\Delta V_{S-L}}=\frac{\Delta H_V}{T(V_L-V_S)}=\frac{\Delta H_V}{T(\frac{m}{\rho_L}-\frac{m}{\rho_S})}$$

For water, the density of the solid is smaller than for the liquid so the slope is negative. But this is not the case for carbon dioxide which has a positive slope.
c) From 218 to 1 atm, water exists as a liquid. At 1 atm, it transforms in solid and remains as a solid until pressure reaches a value around 4 torr. Then water sublimates and transforms into gas remaining as a gas until P = 0.1 torr.

4.- *(1.5 point)* Vapor pressure of benzene and ethanol at 50ºC are: 271 and 220 Torr respectively. a) *(0.5 point)* Calculate the vapor pressure of a mixture containing the same weights of both substances at 50ºC as well as, b) *(0.5 point)* the molar fraction of ethanol in the vapor phase assuming ideal behavior. c) *(0.5 point)* Vapor pressure of the mixture at 50 ºC was measured in an experiment and it was obtained a value of 300 torr. Compare with your result and and extract the sign of the enthalpy of mixing both substances. Will the mixture present an azeotropic composition?
DATA: M(ethanol)=46 g/mol, M(benzene)=78g/mol.

Solution

$$X_{ethanol} = \frac{xg * \frac{1mol}{46g}}{xg * \frac{1mol}{46g} + xg * \frac{1mol}{78g}} = 0.629 \qquad X_{benzene} = 1 - 0.629 = 0.371$$

Raoult's law: $p_i = X_i p_i^0$

$$p_{ethanol} = 0.629 * 220Torr = 138.38Torr$$

$$p_{benzeno} = 0.371 * 271Torr = 100.54Torr$$

Dalton's law: $p = \sum_i p_i$

$$p = 138.38 + 100.54 = 238.92Torr$$

b) Dalton's law: $p_i = Y_i * p$

$$Y_{ethanol} = \frac{p_{ethanol}}{p} = \frac{138.38Torr}{238.92Torr} = 0.579$$

c) The mixture has a higher vapor pressure than ideal behavior so the mixing enthalpy will be positive and the mixture will present an azeotrope with minimum boiling temperature

5.- *(2 points)* Citric acid (AH_3) is an organic triprotic acid. The pair $[AH^{2-}]/[A^{3-}]$ is commonly used as a buffer in biochemistry. An enzymatic reaction takes place in 10 mL of a buffered solution with total buffer concentration of 0.12 M and initial pH of 7; during the reaction $2{\cdot}10^{-4}$ mol of an acid are generated. Determine: (a) *(0.8 points)* the initial concentration of the two citrate species forming the buffer, (b) *(0.8 points)* the pH at the end of the enzymatic reaction, and (c) *(0.4 points)* the pH at the end of the enzymatic reaction without using a buffer solution.
DATA: pK (AH^{2-}) = 6.4

Solution:
(a) $AH^{2-} + H_2O \leftrightarrow A^{3-} + H_3O^+$
$Ka=[A^{3-}][H_3O^+]/[AH^{2-}]$; $[H_3O^+]=Ka[AH^{2-}]/[A^{3-}]$; $pH=pKa-\log([AH^{2-}]/[A^{3-}])$
$\log([AH^{2-}]/[A^{3-}]=6.4-7=-0.6$; $[AH^{2-}]/[A^{3-}] = 0.2511$
$0.12=[AH^{2-}] + [A^{3-}]$ and $[AH^{2-}]/[A^{3-}] = 0.2511$ We have a pair of equations that can be solved
$[A^{3-}] = 9.59{\cdot}10^{-2}$ M and $[AH^{2-}] = 2.41{\cdot}10^{-2}$.

b) $pH=pKa-\log([AH^{2-}]/[A^{3-}])= pKa-\log([AH^{2-}]+(2{\cdot}10^{-4}/10^{-2}))/([A^{3-}]-(2{\cdot}10^{-4}/10^{-2})))=6.4-\log(4.41/7.59) = 6.63$.

c)$[H_3O^+] = 2{\cdot}10^{-4}/10^{-2} = 0.02M$ pH = 1.698

6.- (*2 point*) The molar enthalpy of fusion of benzene is 0.9 kJ/mol. Benzene normal melting point is 5.5 ºC. C_P (in J/mol·K) values of benzene in the solid and liquid states are 118.4 and 134.8 respectively. Calculate: (a) (*1.5 point*) the benzene entropy and enthalpy changes when 1 mol of benzene is heated from -20ºC to 50ºC; (b) (0.*5 point*) the free energy change for the solid→liquid process at -20ºC, 5.5 ºC and 50 ºC and discuss the physical meaning of the obtained values.

Solution:
a) $B(s, -20ºC) \xrightarrow{1} B(s, 5.5ºC) \xrightarrow{2} B(l, 5.5ºC) \xrightarrow{3} B(l, 50ºC)$

DS1=Cpln(Tm/T1)=118.4ln((273.15+5.5)/(273.15-20)=11.363 J/K
DH1=Cp(Tm-T1)=118.4(25.5)=3019.2 J

DS2º=DH2º/Tm=3.23J/K
DH2º=900 J

DS3=Cpln(T2/Tm)=134.5ln(273.15+50)/(273.15+5.5)= 19.93 J/K
DS4=Cp(T2-Tm)=134.5(44.5)=5998.6 J

DS= 34.522 J/K
DH= 9917.8 J
b) DG(-20ºC)=DH2º-TDS2º=900-(273.15-20)3.23 =82.58 J
DG(5.5ºC)=DH2º-TDS2º=900-(273.15+5.5)3.23 = 0 J
DG(50ºC)=DH2º-TDS2º=900-(273.15+50)3.23 = -143.8 J