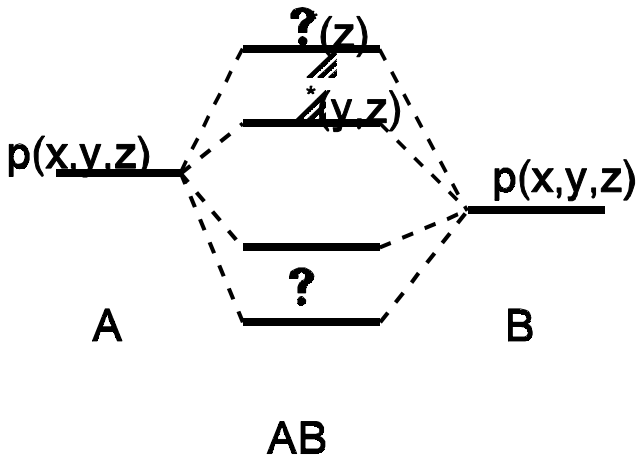
Georgetown University
Department of Chemistry

Chemistry 003
Final Examination Key
16 December 1999

1. (a) Sketch an energy-level diagram showing the relative energies of the molecular orbitals formed by the combination of 2p valence atomic orbitals in a diatomic molecule AB together with the relative energies of the atomic orbitals from which they are generated. Assume that B is slightly more electronegative than A. Label each molecular orbital. [5 points]



(b) Using your diagram from part (A), deduce the electron configurations of NO, NO^+, and NO^-. What is the bond-order in each of these molecules ? Which molecule(s), if any, is/are paramagnetic ? [5 points]

NO:	$\sigma(2p)^2\pi(2p)^4\pi^*$	bond order: 2.5	paramagnetic
NO^+:	$\sigma(2p)^2\pi(2p)^4$	3	(diamagnetic)
NO^-:	$\sigma(2p)2\pi(2p)4\pi^*2$	2	paramagnetic

2. (a) A student heats 15.00 g $KClO_3$ to generate O_2 gas. What is the maximum number of moles of O_2 that she could obtain from this reaction ? [5 points]

$(15.00/122.6 \text{ mol } KClO_3) \times 3/2 \text{ mol } O_2 = 0.1836 \text{ mol } O_2$

(b) In the actual experiment described in part (a) the oxygen was collected over water. Five 600-mL bottles of the gas were collected at 23°C on a day when the atmospheric pressure was 747 torr.
How many moles of oxygen were generated ?

How any grams of KCl were formed as a result ?
[Vapor pressure of water at 23°C = 21 torr] [10 points]

P (O_2) = 747 - 21 = 726 torr = 726/760 = 0.955 atm.

n = RT/PV = 0.08206(296)/0.955(3.00) = 0.118 mol O_2 produced

mol KCl produced = 2/3 x mol O_2 = 0.0783 mol or 5.86 grams

3. State whether or not each of the following equations is an oxidation-reduction reaction. In those cases where redox occurs, (i) specify the changes in oxidation number and (ii) give the correct chemical names for the oxidizing agent and the reducing agent [5 points]

(a) 2 $KHCO_3$ + Δ ===> K_2CO_3 + CO_2 + H_2O

not redox

(b) 6 CuCl + 16 HNO_3 ===> 6 $Cu(NO_3)_2$ + 4 NO + 3 Cl_2 + 8 H_2O

Redox; Cu 1+ to 2+ N 5+ to 2+
oxidizing agent = nitric acid; reducing agent = copper(I) chloride

(c) 2 ClO_2 + 2 NaOH ===> $NaClO_2$ + $NaClO_3$ + H_2O

redox; Cl 4+ to 3+ and 4+ to 5+
oxidizing agent = reducing agent = chlorine dioxide

(d) 12 $MoCl_6$ + H_3PO_4 +36 H_2O ===> $H_3(Mo_{12}PO_{40})$ + 72 HCl

not redox

4. (a) On the phase diagram shown overleaf identify the points labeled A and B. What must be true about the substance at point B ?
A = Triple point B = Critical point
At B densities of liquid and vapor are equal
(b) Point "X" represents a specific temperature and pressure. What phase is stable under these conditions ? Vapor

(c) Describe what happens to the substance defined by point X as the temperature is lowered, but the pressure remains constant.
Vapor condenses to liquid, liquid freezes to solid

(d) Show **on the diagram**. where the normal freezing and boiling points appear

[10 points]

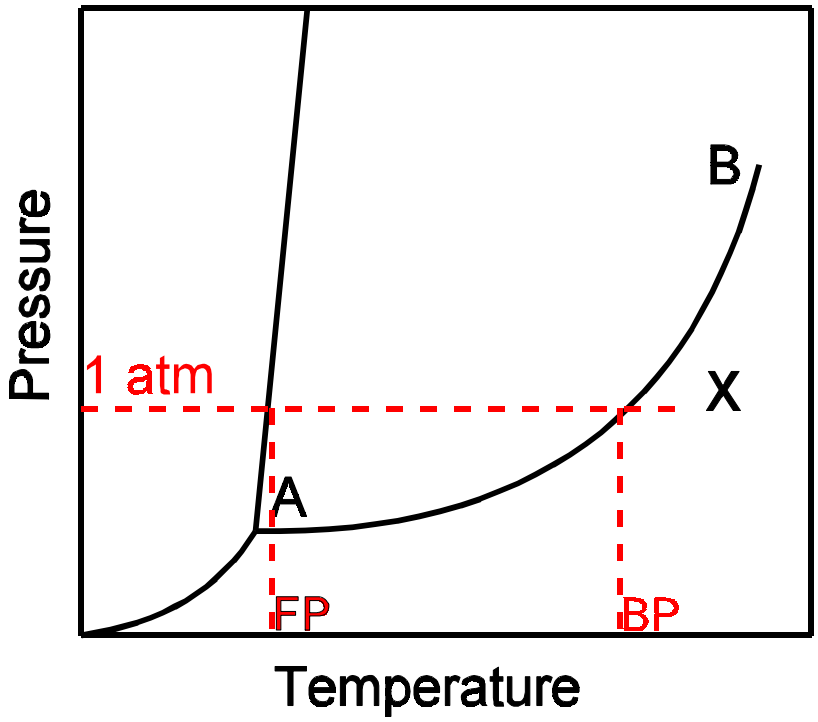


Figure for Question 4

5. (a) Consider the gases H_2, He, O_2, SO_2, and HI all at the same temperature and pressure. On average, which gas molecules are traveling the fastest ?

H_2

(b) Assume each gas in part (a) is confined to a container with a small hole through which the gas can effuse. Select two gases from the list, one of which would effuse about twice as fast as the other.

O_2 and HI

(c) Under what conditions of temperature and pressure do real gases most closely approach ideal behavior ? Why is this so ?

Low pressure and high temperature

Molecules far apart and travelling at high speeds - attractive forces less important, volume of molecules negligible compared with volume of gas.

[5 points]

6. (a) Write balanced chemical equations ***in molecular form*** that illustrate ***real***

examples of each of the following types of reaction [15 points]

(i) direct combination of a metal and non-metal

(ii) neutralization of a WEAK acid

(iii) metathesis involving two salts

(iv) combustion of a covalent compound in oxygen

(v) An activity series displacement that occurs in aqueous solution

(b) Write the following equation ***balanced in net ionic form***

$10\ NH_4Cl + 2\ KMnO_4 + 8\ H_2SO_4 \Longrightarrow 5\ Cl_2 + 5\ (NH_4)_2SO_4 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$

$10\ Cl^- + 2\ MnO_4^- + 16\ H^+ \Longrightarrow 5\ Cl_2 + 2\ Mn^{++} + 8\ H_2O$

7. (a) How many grams of HCl are produced when 1.00 g ammonia reacts with 3.00 L chlorine gas (measured at STP) according to the reaction

$NH_3 + 3Cl_2 \Longrightarrow NCl_3 + 3\ HCl$ [7 points]

$3/22.4 = 0.134$ mol Cl_2 $1/17 = 0.059$ mol NH_3

0.134 mol HCl formed = 4.89 g

(b) What is the limiting reagent in the above reaction ? [3 points]

Chlorine

8. (a) List the kinds of intermolecular forces that contribute to the boiling point (-6°C) of methylamine, CH_3NH_2

dispersion; dipole-dipole; hydrogen bonds

(b) The van der Waals parameters for methylamine are a = 7.130 L^2-atm/mol^2 and b = 0.05992 L/mol. Calculate the pressure exerted by 2.000 mol methylamine confined to a volume of1.000 L at 227°C.

P = 64.7 atm

(c) What would be the pressure in part (b) if methylamine behaved as an ideal gas ?

P = 82.1 atm

[10 points]

9. (a) A solution containing 1.600 g NaOH was titrated with a solution of sulfuric acid, and required 24.55 mL of acid for complete neutralization. Determine the molarity of the sulfuric acid. [5 points]

0.040 mol NaOH require 0.02 mol H_2SO_4

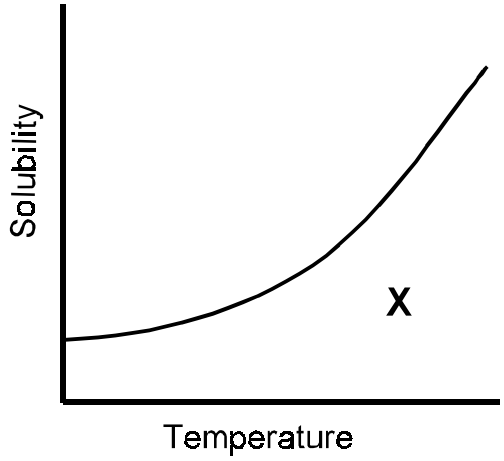
0.815 M

9. (b) A solution of 5.00 g of lauryl alcohol in 100.0 g benzene freezes at 4.1°C. If the freezing point of pure benzene is 5.5°C and its freezing point constant is 5.12, determine the molecular weight of lauryl alcohol. [5 points]

molality = 1.4/5.12 = 0.273

Molwt = 5.00/0.0273 = 183

10. (a) Sketch a solubility *vs* temperature curve for a substance with an endothermic enthalpy of solution. Label both axes, and indicate with "X" a point representing an unsaturated solution. [4 points]



(b) Define, or otherwise explain what you understand by **ANY THREE** of the following terms. Give an example where appropriate: [6 points]

(i) hydrogen bond

(ii) state function

(iii) colligative property of a solution

(iv) hybrid atomic orbital

(v) polarizability

(vi) dynamic equilibrium

Extra Credit Question for Exam 03:

(a) About one year ago chemists reported an ionic compound that contained the never-before-observed N_5^+ cation. Two possible Lewis structures for this cation are

[::N = N = N = N = N::]$^+$ and **[:N ≡ N – N(:) = N = N::]$^+$**

Which one of these is less likely to be a significant resonance form ? Why ? What shape do you predict for N_5^+ ? [6 points]

left hand structure

three adjacent N atoms with positive formal charges

bent at central N atom

(b) The lattice energy of LiCl can be computed starting with the standard enthalpy of formation, ΔH_f . However although **ΔH_f** of LiCl is ***less than*** that of KCl , but the **lattice energy** of LiCl is ***greater than*** that of KCl . What is the reason for this ? [4 points]

the higher ionization energy of Li (Born Haber cycle)

van der Waals equation

$$(P + \frac{n^2a}{V^2})(V - nb) = nRT$$

kinetic theory equation

$$PV = \frac{1}{3}nmu^2$$

R = 0.08206 L-atm/mol-K
R = 8.3145 J/mol-K
1 atm = 101.3 kPa = 760 torr
specific heat of water = 4.184 J/g-K

Avogadro's no. 6.02×10^{23}
Planck's constant: 6.63×10^{-34} J-s