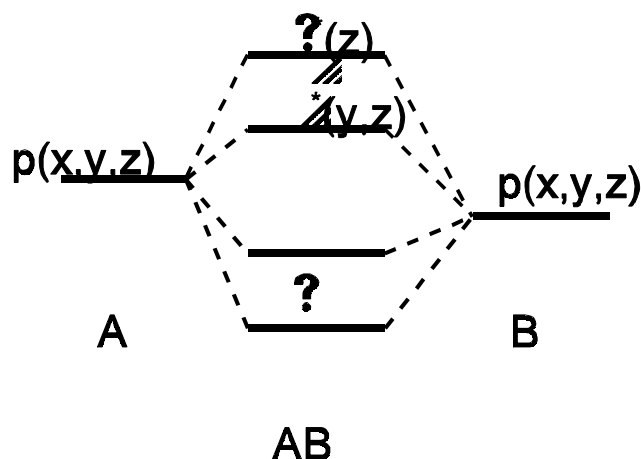


Georgetown University
Department of Chemistry

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 KClO₃ to generate O₂ gas. What is the maximum number of moles of O₂ 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?

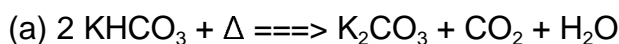
How many grams of KCl were formed as a result ?
 [Vapor pressure of water at 23°C = 21 torr] [10 points]

$$P(\text{O}_2) = 747 - 21 = 726 \text{ torr} = 726/760 = 0.955 \text{ atm.}$$

$$n = RT/PV = 0.08206(296)/0.955(3.00) = 0.118 \text{ mol O}_2 \text{ produced}$$

$$\text{mol KCl produced} = 2/3 \times \text{mol O}_2 = 0.0783 \text{ mol or 5.86 grams}$$

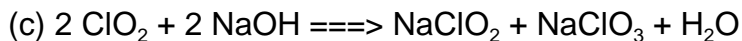
3. State whether or not each of the following equations is an oxidation-reduction reaction. In those cases where redox occurs, (i) specify the changes in oxidation number and (ii) give the correct chemical names for the oxidizing agent and the reducing agent [5 points]



not redox



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



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



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]

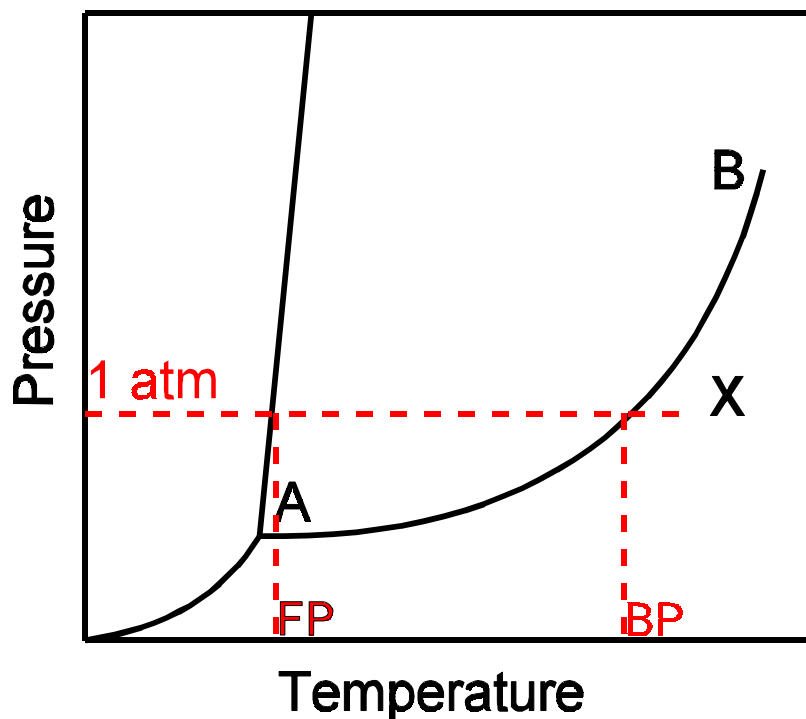


Figure for Question 4

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]

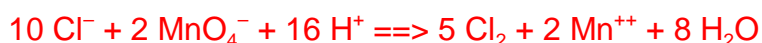
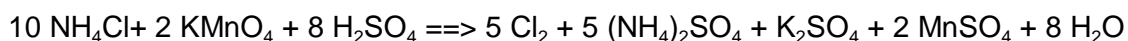
6. (a) Write balanced chemical equations *in molecular form* that illustrate *real*

examples of each of the following types of reaction

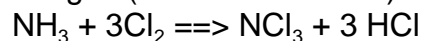
[15 points]

- (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**



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



[7 points]

$$3/22.4 = 0.134 \text{ mol Cl}_2 \quad 1/17 = 0.059 \text{ mol NH}_3$$

$$0.134 \text{ mol HCl formed} = 4.89 \text{ g}$$

- (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 $a = 7.130 \text{ L}^2\text{-atm/mol}^2$ and $b = 0.05992 \text{ L/mol}$. Calculate the pressure exerted by 2.000 mol methylamine confined to a volume of 1.000 L at 227°C.

$$P = 64.7 \text{ atm}$$

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

$$P = 82.1 \text{ atm}$$

[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

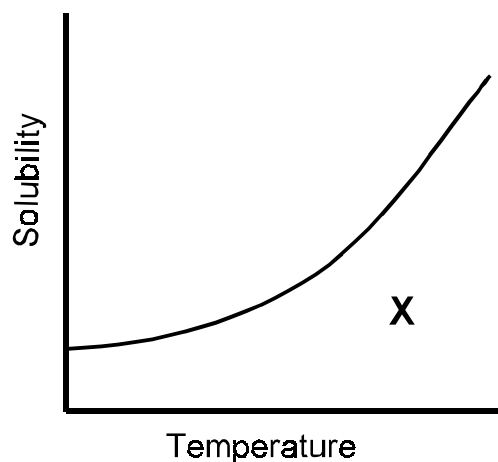
0.815 M

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

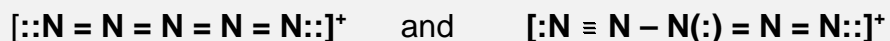
(iv) hybrid atomic orbital

(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



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

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

$$R = 0.08206 \text{ L-atm/mol-K}$$

$$R = 8.3145 \text{ J/mol-K}$$

$$1 \text{ atm} = 101.3 \text{ kPa} = 760 \text{ torr}$$

$$\text{specific heat of water} = 4.184 \text{ J/g-K}$$

kinetic theory equation

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

$$\text{Avogadro's no. } 6.02 \times 10^{23}$$

$$\text{Planck's constant: } 6.63 \times 10^{-34} \text{ J-s}$$