Chemistry 4A, Exam II
October 4, 1999
Professor R.J. Saykally

Name ______

TA ______

1. (20) 13 + 0 = 13
2. (25) 10 + 13 = 23
3. (30) 5 + 10 + 10 = 25
4. (25) 0 + 20 = 20

TOTAL EXAM SCORE (100) 81

Rules:
- Work all problems to 2 significant figures
- No lecture notes or books permitted
- No word processing calculators
- Time: 50 minutes
- Show all work to get partial credit
- Periodic Table, Tables of Physical Constants, Conversion Factors, Activity Coefficients included

Inches 1 2 3 4 5 6

Periodic Table of the Elements

Atomic number — 27 58.93 Co Cobalt — Atomic mass
name
symbol:
Black naturally occurring
White synthetically prepared
most stable isotope

Metals
Metalloids
Nonmetals
Noble gases

H [illegible]																	2 4.003 He Helium
3 6.94 Li Lithium	4 9.01 Be Beryllium											B [illegible]	C [illegible]	N [illegible]	O [illegible]	F [illegible]	10 20.18 Ne Neon
11 22.99 Na Sodium	12 24.31 Mg Magnesium											13 26.98 Al Aluminum	Si [illegible]	P [illegible]	S [illegible]	Cl [illegible]	18 39.95 Ar Argon
19 39.10 K Potassium	20 40.08 Ca Calcium	21 44.96 Sc Scandium	22 47.90 Ti Titanium	23 50.94 V Vanadium	24 51.996 Cr Chromium	25 54.94 Mn Manganese	26 55.85 Fe Iron	27 58.93 Co Cobalt	28 58.70 Ni Nickel	29 63.55 Cu Copper	30 65.37 Zn Zinc	31 69.72 Ga Gallium	Ge [illegible]	As [illegible]	Se [illegible]	Br [illegible]	36 83.80 Kr Krypton
37 85.47 Rb Rubidium	38 87.62 Sr Strontium	39 88.91 Y Yttrium	40 91.22 Zr Zirconium	41 92.91 Nb Niobium	42 95.94 Mo Molybdenum	43 (98) Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.40 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium	49 114.82 In Indium	50 118.69 Sn Tin	Sb [illegible]	Te [illegible]	I [illegible]	54 131.30 Xe Xenon
55 132.91 Cs Cesium	56 137.33 Ba Barium	57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.95 Ta Tantalum	74 183.85 W Tungsten	75 186.21 Re Rhenium	76 190.20 Os Osmium	77 192.22 Ir Iridium	78 195.09 Pt Platinum	79 196.97 Au Gold	80 200.59 Hg Mercury	81 204.37 Tl Thallium	82 207.19 Pb Lead	83 208.98 Bi Bismuth	Po [illegible]	At [illegible]	86 (222) Rn Radon
87 (223) Fr Francium	88 226.03 Ra Radium	89 227.03 Ac Actinium	104 (261) Rf Rutherfordium	105 (262) Ha Hahnium	106 (266) Sg Seaborgium	107 (262) Ns Nielsbohrium	108 (265) Hs Hassium	109 (266) Mt Meitnerium	110 (271)	111 (272)	112 (277)	(113)	(114)	(115)	(116)	(117)	(118)

Lanthanide series ▶	58 140.12 Ce Cerium	59 140.91 Pr Praseodymium	60 144.24 Nd Neodymium	61 (145) Pm Promethium	62 150.40 Sm Samarium	63 151.96 Eu Europium	64 157.25 Gd Gadolinium	65 158.93 Tb Terbium	66 162.50 Dy Dysprosium	67 164.93 Ho Holmium	68 167.26 Er Erbium	69 168.93 Tm Thulium	70 173.04 Yb Ytterbium	71 174.97 Lu Lutetium
Actinide series ▶▶	90 232.04 Th Thorium	91 231.04 Pa Protactinium	92 238.03 U Uranium	93 237.05 Np Neptunium	94 (244) Pu Plutonium	95 (243) Am Americium	96 (247) Cm Curium	97 (247) Bk Berkelium	98 (251) Cf Californium	99 (252) Es Einsteinium	100 (257) Fm Fermium	101 (260) Md Mendelevium	102 (259) No Nobelium	103 (262) Lr Lawrencium

Note: Atomic masses shown here are the 1983 IUPAC values (maximum of six significant figures).

Physical Constants

Standard acceleration of terrestrial gravity	$g = 9.80665$ m s^{-2} (exactly)
Avogadro's number	$N_0 = 6.022137 \times 10^{23}$
Bohr radius	$a_0 = 0.52917725$ Å$=5.2917725 \times 10^{-11}$ m
Boltzmann's constant	$k_B = 1.38066 \times 10^{-23}$ J K^{-1}
Electron charge	$e = 1.6021773 \times 10^{-19}$ C
Faraday constant	$\mathcal{F} = 96{,}485.31$ C mol^{-1}
Masses of fundamental particles:	
Electron	$m_e = 9.109390 \times 10^{-31}$ kg
Proton	$m_p = 1.672623 \times 10^{-27}$ kg
Neutron	$m_n = 1.674929 \times 10^{-27}$ kg
Ratio of proton mass to electron mass	$m_p/m_e = 1836.15270$
Permittivity of vacuum	$\epsilon_0 = 8.8541878 \times 10^{-12}$ C^2 J^{-1} m^{-1}
Planck's constant	$h = 6.626076 \times 10^{-34}$ J s
Speed of light in a vacuum	$c = 2.99792458 \times 10^8$ m s^{-1} (exactly)
Universal gas constant	$R = 8.31451$ J mol^{-1} K^{-1}
	$= 0.0820578$ L atm mol^{-1} K^{-1}

Values are taken from "Quantities, Units and Symbols in Physical Chemistry," International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, 1988.

Conversion Factors

Standard atmosphere	1 atm = 1.01325×10^5 Pa = 1.01325×10^5 kg m^{-1} s^{-2} (exactly)
Atomic mass unit	1 u = 1.660540×10^{-27} kg
	1 u = 1.492419×10^{-10} J = 931.4943 MeV (energy equivalent from $E = mc^2$)
Calorie	1 cal = 4.184 J (exactly)
Electron volt	1 eV = $1.6021773 \times 10^{-19}$ J = 96.48531 kJ mol^{-1}
Foot	1 ft = 12 in = 0.3048 m (exactly)
Gallon (U.S.)	1 gallon = 4 quarts = 3.78541 L (exactly)
Liter-atmosphere	1 L atm = 101.325 J (exactly)
Metric ton	1 metric ton = 1000 kg (exactly)
Pound	1 lb = 16 oz = 0.45359237 kg (exactly)

Table 8-1

Activity coefficients for aqueous solutions at 25° C

Ion	Ion size (α, pm)	0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, H_2citrate$^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2						
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, Hcitrate^{2-}	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3						
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
citrate^{3-}	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4						
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

a. Lanthanides are elements 57–71 in the periodic table.
SOURCE: J. Kielland, *J. Am. Chem. Soc.* **1937**, *59*, 1675.

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EXAMPLE

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SOLUTION

In Table 8-1, I
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How to Int

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y = 0.83 when

x value: 10
y value: 0.6

1. (5+5+5+5 points)

A) Compare the magnitude of the individual intermolecular forces operating in gaseous H_2O or gaseous NO_2 (both polar molecules with the same van der Waals "a" constant).

Force	Larger (NO_2 or H_2O)
✓ Electrostatic (Ionic)	✓ ~~Nonexistant~~
~~Dipole - dipole~~	✓ H_2O (due to H bonding)
✓ Induced dipole (dispersion forces)	~~0 insignificant b/c both are~~ polar
✓ Repulsion	✓ NO_2

(3)

B) List the following substances in order of increasing normal boiling points T_b, and explain your reasoning: NO, NH_3, Ne, RbCl.

(5)

Ne, NO, NH_3, RbCl.

Ne is a noble gas with only dispersion forces to keep atoms together. NO is a polar molecule w/ dipole forces to attract, but NH_3 has Hydrogen bonding which is a stronger dipole attraction. RbCl has ionic bonds which provide an electrostatic force (Coulombic), the strongest attraction force. The larger the attraction, the more resist less vapor it forms. T_b is the pt when P_{vapor} = P_{atm}

C) Write down the most accurate equation of state for a real gas.

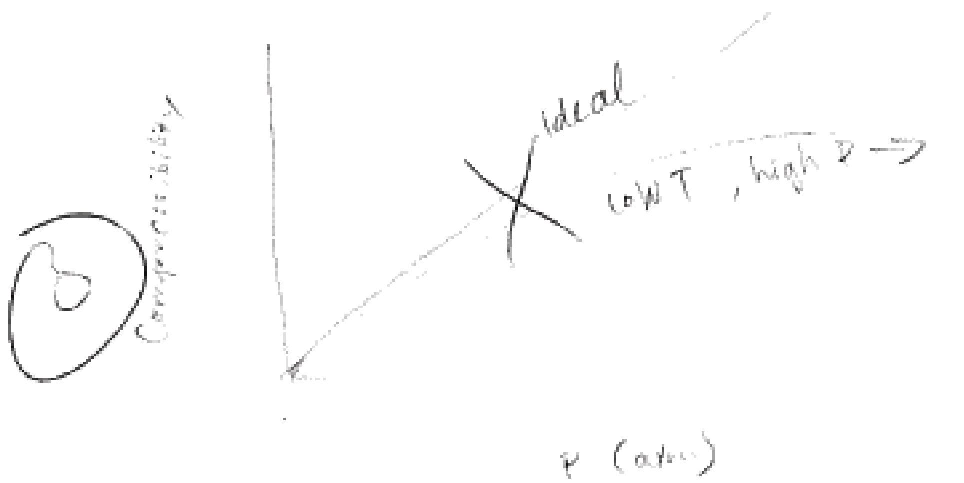
Virial

$$Z = 1 + B(T)\frac{n}{V} + C(T)\frac{n^2}{V^2} \ldots$$

$$B(T) = \left(b - \frac{a}{RT}\right)$$

5

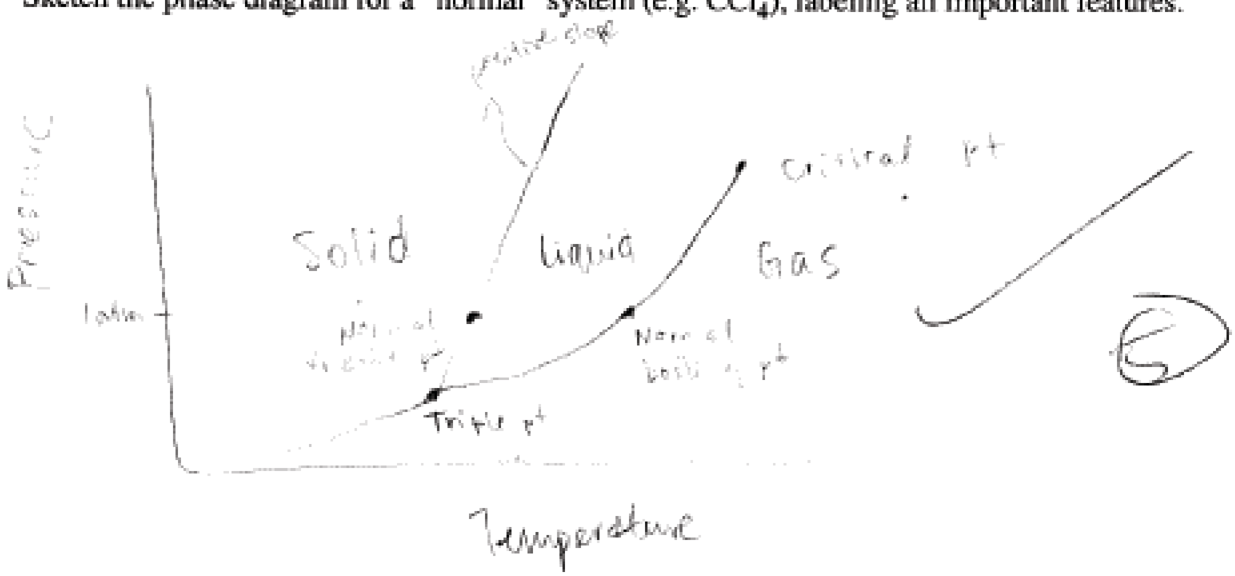
D) Sketch a graph of the compressibility versus P for a gas with a large van der Waals "a" constant at low T.



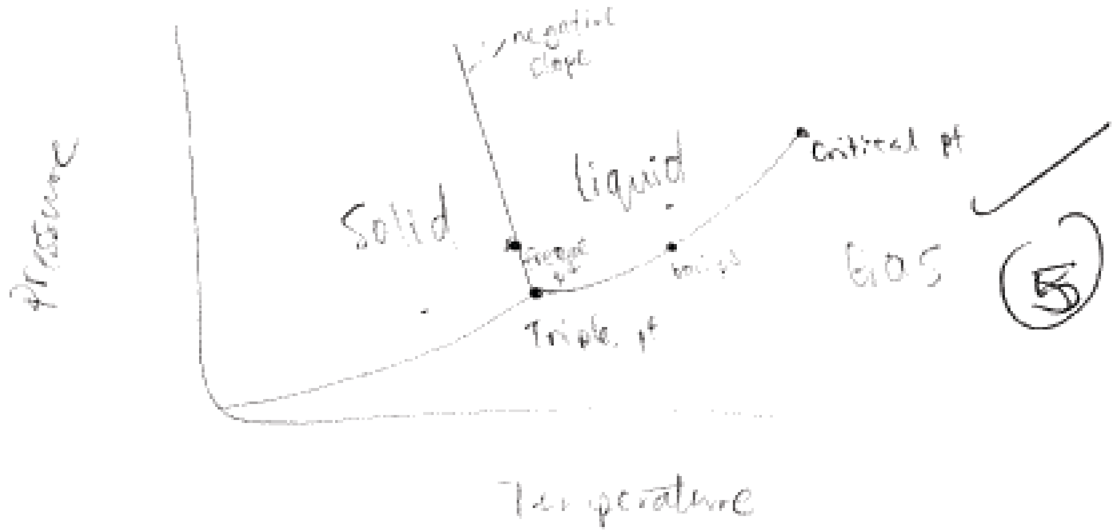
$$Z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a}{RT}$$

2. (5+5+5+10 points)

A) Sketch the phase diagram for a "normal" system (e.g. CCl_4), labeling all important features.



B) Sketch the phase diagram for water, labeling all important features (you may show only one solid phase).

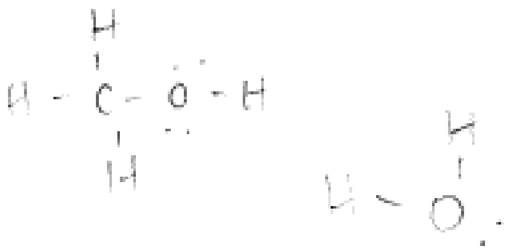


(5)

C) Contrast the H-boding expected for methanol (CH_3OH) with that for water, using Lewis structures. What type of structures do you expect to find in liquid methanol?

(3)

CH_3OH has two acceptor sites (lone pair electrons on the O atom) and H donor (H atom) sites but isn't in the tetrahedral structure that H_2O makes. +1 Therefore in the liquid phase, H_2O will exhibit more structure and possess more H bonds (since it also has the capacity to form 4 H bonds per molecule)



structure?

H_2O is denser than CH_3OH in liquid phase (CH_3OH has less structure & fewer H bonds)

D) Calculate the density change that occurs when gaseous water liquifies at STP.

$\rho_{gas} = \frac{1}{22.4 \frac{L}{mol}} = .0446 \frac{mol}{L} \times \frac{18.02 g}{mol} = .804 \frac{g}{L} \times \frac{L}{10^3 cm^3}$

$\rho_{liq} = 55.5 \frac{mol}{L} \times \frac{18.02 g}{mol} \times \frac{L}{10^3 cm^3} = 1.00 \frac{g}{cm^3}$ ($8.04 \times 10^{-4} \frac{g}{cm^3}$)

$\Delta\rho = .999 \frac{g}{cm^3}$

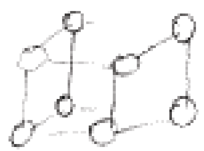
or negative value if going from gas → liq.

10/10

3. (5+5+10+10 points)

A) Describe the structure of the cubic form of ice (ice I_c), and calculate the number of water molecules in the unit cell.

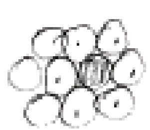
cubic : 1 atom at ea. lattice pt.



since ea. atom is shared by 8 unit cells, but there are 8 atoms per cell, $\frac{1}{8} \times 8 = 1$ molecule H_2O

0/5

B) Sketch the structure of a single layer of close-packed spheres, indicating the number of nearest neighbors. What is the packing fraction of a close-packed lattice?



6 nearest neighbors

packing fraction = .74

5/5

C) At 20°C, the vapor pressure of toluene is 0.0289 atm and the vapor pressure of benzene is 0.0987 atm. Equal chemical amounts (equal numbers of moles) of toluene and benzene are mixed and form an ideal solution. Compute the mole fraction of benzene in the vapor in equilibrium with this solution.

+10

$P_{tol} = X_1 \cdot .0289$ atm

$P_{ben} = X_2 \cdot .0987$

$X_1 = X_2 = .5$

$P_{tol} = .0145$ atm

$P_{ben} = .0494$ atm

$\frac{P_{ben}}{P_T} = \frac{.0494}{.0494 + .0145}$

$= .773$

$X_{ben\ in\ vapor} = \frac{P_{ben}}{P_T}$

✓

D) The structure of aluminum is face-centered cubic and its density is 2.70 g/cm^3. Calculate the nearest neighbor distance (d).

4 atoms per unit cell

$\rho = 2.70 \frac{g}{cm^3}$

$2.70 \frac{g}{cm^3} \times \frac{mol}{26.98 g} \times \frac{6.022 \times 10^{23}\ atoms}{mol} \times \frac{}{4\ atoms} = 1.51\ cm^{-3}$

$V = \frac{1}{1.51 (cm^{-3})} = 6.64 \times 10^{-23}\ cm^3$

$a = \sqrt[3]{V} = 4.05 \times 10^{-8}\ cm$

+10 nearest neig. dist $= \frac{a\sqrt{2}}{2}$ = 4.05 Å

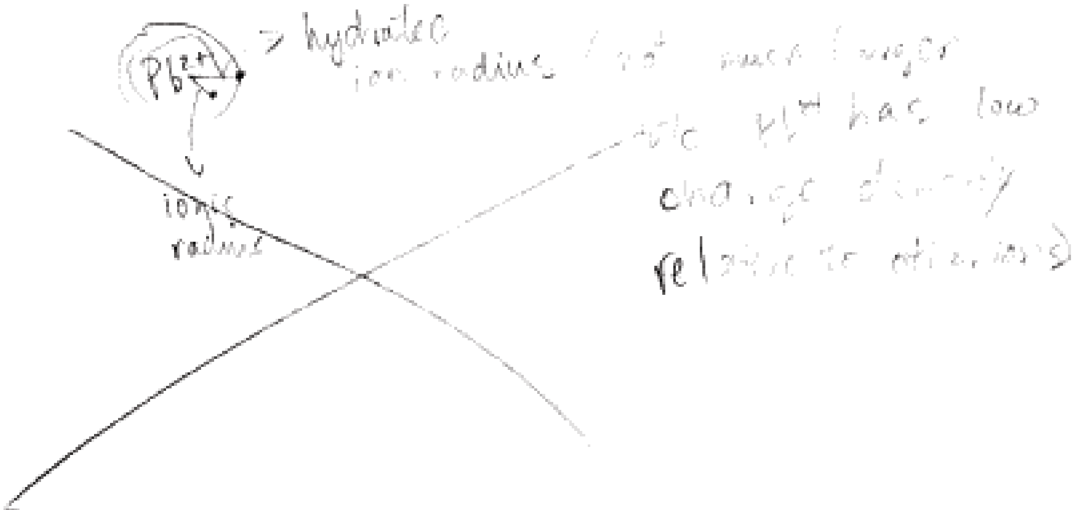
$= \frac{4.05\sqrt{2}}{2} = 2.86$ Å

4. (5+5+5+10 points) Consider the following equilibrium:

$$PbS_{(s)} \leftrightarrow Pb^{2+}_{(aq)} + S^{2-}_{(aq)} \qquad K_{sp} = 3 \times 10^{-28}$$

A) Sketch the structure of the Pb^{2+} solvated by water.

0



B) Determine the activity coefficients for Pb^{2+} and S^{2-} in 0.10 M KNO_3 solution.

$\gamma_{Pb^{2+}} : 0.37 \qquad \gamma_{S^{2-}} : 0.38$

$I = \frac{1}{2}\sum_i (z_i c_i^2)$

$= \frac{1}{2}((.1M)(+1)^2 + (.1M)(-1)^2) = \frac{1}{2}(.2) = .1\ M$

+5

C) Calculate $[Pb^{2+}]$ for a saturated solution of PbS in 0.10 KNO_3 solution, and compare with the result for pure water.

$K_{sp} = 3\times10^{-28} = [Pb^{2+}]\gamma_{Pb^{2+}}[S^{2-}]\gamma_{S^{2-}}$

$[Pb^{2+}] = [S^{2-}]$

$3\times10^{-28} = x(0.37)\,x(0.38)$

$2.13\times10^{-27}\ M^2 = x^2$

$4.62\times10^{-14}\ M = x$

$\frac{x_w}{x} = 37\%$

+5

for pure H_2O: $3\times10^{-28} = [Pb^{2+}][S^{2-}]$

$3\times10^{-28} = x^2$

$x_w = 1.73\times10^{-14}$

D) Explain the reason for the increased $[Pb^{2+}]$ in the KNO_3 solution.

The increased $[Pb^{2+}]$ is due to the K^+ and NO_3^- neutralizing the Pb^{2+} and S^{2-} ions through ion shielding. once Pb^{2+} and S^{2-} ions are contained, more $PbS_{(aq)}$ dissolves ($PbS_{(s)} \rightarrow PbS_{(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + S^{2-}_{(aq)}$) to increase the concentration of active Pb^{2+} and S^{2-} ions in solution. The K^+ and NO_3^- also exert attractive forces on the ionic salt $PbS_{(aq)}$ which pull it apart.

+10