5.112 Extra Problems - Exam II - Fall, 2005

Here are some extra problems that you can work as preparation for Wednesday's exam. Study the material before you attempt these problems. Approach each problem as an exam problem. Many of these problems are former exam problems. If you usually panic when you first read an exam problem, then panic when you first read these problems and then practice how to calm yourself down. Rephrasing the problem in your own words or drawing a sketch of the problem often helps crystallize the physical concept behind the problem. Once you understand the physical principle behind the problem, the equations necessary to work the problem will come to you easily. Remember, there are a limited number of physical principles being tested here. Don't rely on a fixed, memorized procedure or memorized equation to solve a problem. You can't always make a problem fit into the procedure or equation that you have memorized. You have to modify the procedure or the equation to fit the problem. Don't modify the problem to fit the equations.

Also, don't deny yourself the opportunity to intellectually engage and mentally wrestle with these problems by looking at the solutions first. You won't have this opportunity on the exam. Remember, looking at a map before you start driving is a very different experience than actually driving the roads!

Periodic Trends

1. Write the initial and final electron configurations for the process corresponding to IE_4 (the fourth ionization energy) of Be.

2. The five successive ionization energies of B (i.e IE_1 through IE_5) are 800, 2420, 3660, 25020 and 32820 kJ/mole. **a)** Write equations for these ionization processes giving the electron configuration before and after the ionization. **b)** Write equations for these ionization processes seen in the photoelectron spectrum of B, giving the electronic configuration before and after the ionization.

3. In the second period of the periodic table, there are atoms with a negative electron affinity. Identify two of these atoms and explain why the electron affinity is negative.

4. Consider the systems Li, Be and Li^+. **a)** Give the order of size for these three. Explain. **b)** Which has the highest IE_1? Explain. **c)** Which has the largest EA? Explain.

5. Arrange the following in order of size from the smallest to the largest: I^-, Br^-, Cl^-, Cl, Mg^{2+}, Ne.

6. Consider the following ions: He^+, Li^{2+}, F^{8+}. **a)** Which has the smallest radius? Explain. **b)** Which has the highest IE_1? Explain. **c)** Which has the largest EA? Explain.

7. Arrange the following seven atoms or ions in order of size: K, F^+, Rb, Co^{25+}, Br, F, Rb^-.

8. Predict the larger ion in each of the following pairs. Give reasons for your answers.

a) O^-, S^{2-} **b)** Mn^{2+}, Mn^{4+} **c)** CO^{2+}, Ti^{2+} **d)** Ca^{2+}, Sr^{2+}

9. Consider the atoms As, Cl, K and S.

a) Which atom has the greatest electron affinity? **b)** Which atom has the lowest electron affinity?

10. The first ionization energy of helium is 2370 kJ mol^{-1}, the highest for any element.

a) Define *ionization energy* and discuss why that for He should be so high.

b) Which element would you expect to have the highest *second* ionization energy? Why?

c) Suppose that you wished to ionize some helium by shining electromagnetic radiation on it. What is the maximum wavelength you could use?

11. Without consulting any tables, arrange the following substances in order and explain your choice of order:

a) Mg^{2+}, Ar, Br^{-}, Ca^{2+} in order of increasing radius.

b) Na, Na^{+}, O, Ne in order of increasing ionization energy.

c) H, F, Al, O in order of increasing electronegativity.

Ionic Bonds

1. For the ionic molecule LiF, calculate the value of r* at which the harpoon mechanism becomes energetically allowed. The IE of Li is 519 kJ/mol and the EA of F is 328 kJ/mol.

2. In a gaseous RbF molecule, the bond length is 2.274×10^{-10} m. Using data from Appendix 2, estimate the dissociation energy of gaseous RbF into Rb and F atoms (in kilojoules per mole).

Thermodynamics

1. Given the following data at 298.15 K, compute ΔH^o for (a) and (b):

$OH(g) = 1/2\ H_2(g) + 1/2\ O_2(g)$ $\quad \Delta H^o = -42.26$ kJ

$H_2O(g) = H_2(g) + 1/2\ O_2(g)$ $\quad \Delta H^o = 241.8$ kJ

$H_2(g) = 2H(g)$ $\quad \Delta H^o = 436.0$ kJ

$O_2(g) = 2O(g)$ $\quad \Delta H^o = 494.5$ kJ

a) The bond energy of O-H, i.e. OH(g) = H(g) + O(g)

b) The sum of the two O-H bond energies in water, i.e. $H_2O(g) = 2H(g) + O(g)$

2. Consider the following molecules, all with empirical formula C_4H_6:

[1] $H_3C\text{-}C{\equiv}C\text{-}CH_3$ **[2]** $H_2C{=}HC\text{-}HC{=}CH_2$

[3]
```
H-C=C-H
  |  |
H2C-CH2
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Bond	Bond Enthalpy [kJ/mol]
C—H	414
C—C	347
C = C	615
O=O	495

Bond	Bond Enthalpy [kJ/mol]
C = O	730
O - H	464
C≡C	811

a) Using the bond enthalpy table above, compute the enthalpy change for the isomerization of molecule **[3]** to molecule **[2].**

b) Using the bond enthalpy table above, compute the enthalpy change in the following reaction: **[2]** + (11/2) $O_2 \Rightarrow 4\ CO_2 + 3\ H_2O$

c) If ΔH^o for the reaction in (b) is actually -1743.2 kJ mol^{-1}, calculate ΔH_f° for compound **[2]** .

3. Consider the equilibrium gas phase reaction of n-butane to isobutane

$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3 \Leftrightarrow H\text{-}C\text{-}(CH_3)_3$$

[n-butane] ⇔ [isobutane]

	ΔH_f^o (298K)	S°(298K)
n-butane	-126.1 kJ/mol	310.0 J/mol K
isobutane	-134.4 kJ/mol	294.64 J/mol K

a) Compute the ΔH^o and ΔS^o for the reaction at 298 K.

b) Compute ΔG^o for the reaction at 298 K.

c) Calculate the value of the equilibrium constant at 298 K.

d) Suppose the partial pressure of isobutane is 5.00 bar and that of butane is 1.00 bar. Calculate ΔG at 298 K.

4. Consider the molecule NF_3(g) with a ΔG°_f = -90.6 kJ/mol and ΔH°_f = -132.1 kJ/mol.

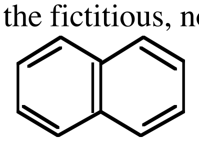
a) Calculate ΔG° and ΔH° for the following reaction at 298 K.

$$N_2(g) + 3F_2(g) \leftrightarrow 2NF_3(g)$$

b) Calculate the value of the equilibrium constant K at 298K of the above reaction.

5. Naphthalene, $C_{10}H_8$, is stabilized by resonance.

(a) Use the tables of bond enthalpies and standard molar enthalpies of formation to estimate the value of ΔH_f° for the fictitious, non-resonance-stabilized molecule (hydrogens not drawn).



	ΔH°/kJ•mol^{-1}
C-H	414
C-C	347
C=C	615
H-H	435

	ΔH_f°/kJ•mol^{-1}
H(g)	218.0
C(g)	716.7
H_2(g)	?
C(graphite)	?

$$10C\ (\text{graphite, 298K}) + 4H_2\ (\text{g, 298K, 1atm}) \Rightarrow C_{10}H_8\ (\text{g, 298K, 1atm})$$

(b) The measured value of ΔH_f°($C_{10}H_8$, g, 298K, 1atm) = 151.0 kJ/mol. What is the resonance stabilization enthalpy for naphthalene?

6. The enthalpy change of the following reaction at standard conditions and 298.15 K is –114.38 kJ. The free energy change of the following reaction at standard conditions and 298.15 K is –75.92 kJ.

$$4HCl(g) + O_2(g) \Leftrightarrow 2Cl_2(g) + 2H_2O(g)$$

Some additional information is given in the following table.

	ΔH_f° (298.15K)
H_2O (l)	-285.83 kJ/mol
H_2O (g)	-241.82 kJ/mol

a) Calculate the enthalpy change if the H_2O product were in the liquid phase, $H_2O(l)$.

b) Suppose the partial pressures (in bar) of the reactants and products of the above reaction are as shown below. Calculate Q.

$P_{HCl} = 2.00 \times 10^{-5}$	$P_{O_2} = 4.5 \times 10^{-1}$	$P_{Cl_2} = 2.5 \times 10^{-3}$	$P_{H_2O} = 4.8 \times 10^{-1}$

c) Is the reaction in part (b) at equilibrium at 298.15 K? Show your calculations that support your conclusion. Your calculations must be precise within two significant figures.

7. Consider the following reaction.

$$Cl_2(g) \Leftrightarrow 2Cl(g)$$

a) Is ΔH°□at 298.15 K for this reaction positive, negative or zero? Justify your answer.

b) Is ΔS° at 298.15 K for this reaction positive, negative or zero? Justify your answer.

c) Is ΔG° for this reaction less than zero at all temperatures? Justify your answer.

Bonding

1. On a single x-y graph, draw the interaction potential, of the kind that we drew for H_2, for the NN bond in each of the following molecules: N_2, N_2H_4, and N_3^{-1}. Clearly label the quantities that you are plotting on each axis. Label the equilibrium bond distance for each NN bond. Label the quantity equivalent to the bond strength for each NN bond. The relative values of the bond distances and strengths must be correct. Set the separated atom limit at zero energy. (HINT: Draw the most stable Lewis structure of each molecule before you draw the interaction potentials.)

Kinetic Theory

1. Calculate the "local" pressure (the pressure due to a single atom's collision, the pressure due to our f_i in class) that a He atom exerts on the wall of a container. Consider the unit area of the surface to be given by the collision diameter of the He atom, 2.59 Å. The speed of the He atom is 1.26×10^3 m/sec. Consider the collision length to be the diameter of the He atom.

2. A gaseous mixture containing 2.00 g of CO_2, 2.00 g of H_2O, and 2.00 g of CH_4 is kept in a 1.0 □ bulb at 10.0 atm. Calculate the temperature.

3. Consider a sample of N_2 gas at 273 K.

a) For every 1000 molecules traveling at a speed of 500 m/s, how many travel at 1000 m/s?

b) What is the equivalent ratio at 373 K?

4. A gas molecule escaping the earth's gravity is like an electron ejecting from an atom or molecule upon ionization, except that the potential energy of interaction is $U(r)=-GMm/r$, where M is the mass of the earth (5.98×10^{24} kg), m is the mass of the molecule and G is the universal gravitation constant, 6.672×10^{-11} N m^2 / kg^2. The threshold escape velocity is determined by the value of the velocity at which the kinetic energy is equal to the potential energy of the interaction.

(a) Compute a value for the escape velocity for a distance r equal to that of the radius of the earth, 6730 km.

(b) Find the temperature of the atmosphere that is required for the v_{rms} of N_2 to equal that of the escape velocity.

5. Calculate the root mean square speed of a hexane and methane molecule at 273 K. Calculate the root mean square speed of a mole of hexane and a mole of methane at 273 K. Calculate the average kinetic energy of a hexane and a methane molecule at 273 K. Calculate the average kinetic energy of a methane molecule and a hexane molecule per mole of each at 273 K.

6. Chlorine dioxide (ClO_2) is used for bleaching wood pulp. In a gaseous sample held at thermal equilibrium at a particular temperature, 35.0% of the molecules have speeds exceeding 400 m/s. If the sample is heated slightly, will the percentage of molecules with speeds in excess of 400 m/s be greater than or less than 35%?

7. The ClO_2 from problem 6 is heated further until it explodes, yielding Cl_2, O_2, and other gaseous products. The mixture is then cooled until the original temperature is reached. Is the percentage of Cl_2 with speeds in excess of 400 m s^{-1} greater than or less than 35%?

8. Do Ar atoms move faster or slower than hydrogen molecules at the same temperature? By what factor do the root mean square speeds differ?

9. Vessel A contains CO_2 gas at about 0 C and 1 atm. Vessel B contains HCl gas at 20 C and 0.5 atm. The two vessels have the same volume. **a)** Which vessel contains more molecules? **b)** Which contains more mass? **c)** In which vessel is the average kinetic energy higher? **d)** In which vessel is the rms speed of molecules higher?

10. Deuterium (^2H), when heated to sufficiently high temperature, undergoes a nuclear fusion reaction that results in the production of helium. The reaction proceeds rapidly at a temperature *T*, at which the average kinetic energy of the deuterium atoms is 8×10^{-16} J. (At this temperature, deuterium molecules dissociate completely into deuterium atoms.)

a) Calculate *T* in K (atomic mass of $^2H = 2.015$).

b) For the fusion reaction to occur with ordinary hydrogen atoms, the average energy of the atoms must be about 32×10^{-16} J. By what factor does the root mean square speed of the ^1H atoms differ from that of the ^2H atoms of part (a)?

11. A sample of 2.00 mol of argon is confined at low pressure in a volume at a temperature of 50°C. Describe quantitatively the effects of each of the following changes on the pressure, the average energy per atom in the gas, the root-mean-square speed, the frequency of Ar–Ar collisions, and the mean free path:

a) The temperature is decreased to –50°C.

b) The volume is doubled.

c) The amount of argon is increased to 3.00 mol.

Internal Modes

1. The Li_2 molecule (^7Li isotope) shows a very weak infrared line in its vibrational spectrum at a wavelength of 2.85×10^{-5} m. Calculate the force constant for the Li_2 molecule.

2. The vibrational frequencies of $^{23}Na^1H$, $^{23}Na^{35}Cl$, and $^{23}Na^{127}I$ are 3.51×10^{13} s^{-1}, 1.10×10^{13} s^{-1}, and 0.773×10^{13} s^{-1}, respectively. Their bond lengths are 1.89 Å, 2.36 Å, and 2.71 Å. What are their reduced masses? What are their force constants? If NaH and NaD have the same force constant, what is the vibrational frequency of NaD? D is ^2H.

3. a) The fundamental frequency of Ar_2 is 25.74 cm^{-1}. Calculate the time it takes for Ar_2 to complete one vibrational cycle when Ar_2 is in the v=2 vibrationally excited state.

b) If the well depth of the Ar_2 interaction is 1.654×10^{-21} J, calculate the experimentally measured energy necessary to dissociate Ar_2 in the ground vibrational state.

c) Calculate the value of the quantum number of the vibrationally excited state that has sufficient energy to allow Ar_2 to dissociate.

d) Calculate the moment of inertia of Ar_2. The value of r_e is 3.40×10^{-10} m. (HINT: For a homonuclear diatomic molecule, $\mu = m_1/2$ or $\mu = m_2/2$.)

e) Calculate the value of J necessary for Ar_2 to have at least as much rotational energy as in one quantum ($E_{v=1} - E_{v=0}$) of vibrational energy.

Text Problems

1. 1.77 AJ
2. 1.79 AJ
3. 1.85 AJ
4. 4.67 AJ
5. 4.69 AJ
6. 5.1 AJ
7. 5.3 AJ
8. 5.7 AJ
9. 5.9 AJ
10. 5.11 AJ
11. 6.53 AJ
12. 6.57 AJ
13. 6.59 AJ
14. 6.61 AJ
15. 6.63 AJ
16. 7.47 AJ
17. 7.51 AJ
18. 7.53 AJ
19. 7.57 AJ
20. 7.59 AJ
21. 7.61 AJ
22. 7.71 AJ
23. 9.11 AJ
24. 9.13 AJ
25. 9.15 AJ
26. 9.17 AJ
27. 9.31 AJ
28. 9.41 AJ
29. 9.95 AJ
30. 9.97 AJ

After you have studied for the exam and worked the problems above, you should be able to work the following 5 problems in 50 minutes.

1. IONIC BONDING

a) The energy from the bottom of the well of the KCl molecule to the separated ion limit, K^+ and Cl^-, is 521 kJ/mol. Calculate the equilibrium bond length of KCl.

b) Calculate the energy, in kJ/mol, required to dissociate KCl into K and Cl. The ionization energy of K is 418 kJ/mol and the electron affinity of Cl is 349 kJ/mol.

c) Suppose the electron on K were to jump to Cl at a distance of 3.02×10^{-9} m. Calculate the barrier to that reaction. That is, calculate how much energy, in kJ/mol, would have to be supplied to the system in order for the electron jump to occur at that distance. The ionization energy of K is 418 kJ/mol and the electron affinity of Cl is 349 kJ/mol.

2. KINETIC THEORY

a) Which gas has a wider distribution of molecular velocities: Cl_2 at 439 K or BH_3 at 321 K? Or is the width of these distributions equivalent? Why?

b) In a Maxwell-Boltzmann distribution of Cl_2 gas at 439 K, some molecules have a velocity of $(RT/M)^{1/2}$. Will their numbers increase, remain the same or decrease as the temperature is raised? Why?

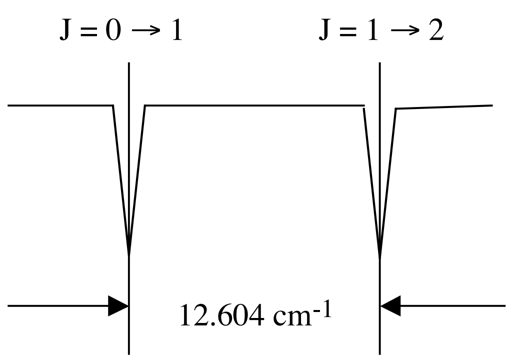
c) How many translational, vibrational and rotational modes does BH_3 have?

3. VIBRATIONS AND ROTATIONS

Consider the rotational spectrum and the vibrational spectrum of AlH and AlD.

a) Convert 12.604 cm^{-1} into J.

b) In a microwave absorption spectrum of AlH, two transitions are observed as shown below. The transition at the lower frequency is a transition between J=0 to J=1 and the transition at higher frequency is a transition between J=1 to J=2. The difference in frequency between the two transitions is 12.604 cm^{-1}. Calculate the value of I, the moment of inertia, of AlH.



c) The v=0 to v=1 transition of this same molecule, AlH, occurs at 5.0442 x 10^{13} Hz in the infrared range of the electromagnetic spectrum. At what frequency would the v=1 to v=2 transition occur?

d) The experimentally measured AlH bond energy is 4.886 x 10^{-19} J. Calculate the well depth, from the bottom of the well to the dissociation limit, of the AlH interaction potential.

e) Using the information in part (c) and knowing that the force constants for AlH and AlD are equal, calculate the frequency at which the v=0 to v=1 transition occurs in AlD. The mass of Al is 26.98153 amu, H is 1.007825 amu and D is 2.01355 amu. Do not use any approximations.

4. THERMOCHEMISTRY

Use the following bond enthalpies to calculate ΔH_f^o (298.15 K) for NH_3.

Bond	**Enthalpy kJ/mol**
H-H	436
H-N	389
N-N	163
N=N	418
N≡N	946

5. PERIODIC PROPERTIES

a) Order the elements S, Cl, Ar, K, Ca, Sc, Ti from lowest to highest ionization energy.

b) Order the elements S, Cl, Ar, K, Ca, Sc, Ti from lowest to highest second ionization energy.