BONDING

These questions cover several topics presented in class – use them as a checklist to highlight areas that need more work.

1. What is the wavelength of a photon that has an energy of 1 eV ?
2. Describe the concept of linear superposition, and what we mean by destructive interference.
3. What is the wavefunction for a free electron in 3 dimensions ? Show that it satisfies either the stationary Schroedinger equation, or, if you write also the time-dependent term, that it satisfies the full, time-dependent Schroedinger equation.
4. What is the momentum, and what is the wavelength of an electron that has a kinetic energy of 1 eV ?
5. How can you derive the stationary Schroedinger equation from the time-dependent Schrodinger equation ?
6. What are the eigenfunctions and the eigenstates of an electron confined in 3-dim in a square box of radius a ?
7. How does the STM works ?
8. What is a linear operator ?
9. What is an expectation value ?
10. What is the surface of the earth, if its radius is 6,400,000 m ?
11. What is, in cartesian coordinates, the angular momentum operator ? Derive explicitly its three components
12. Describe in broad terms how we derive the radial Schrodinger equation in a central potential.
13. An electron in an atom has 4 quantum numbers. Why ? What are they ?
14. What is the expectation value of the potential energy for an electron in the 2p ground state of the hydrogen atom ?
15. What is the atom with the smallest radius ?
16. What is the variational principle ? Can you derive it ? How does it lead to the "linear combination of atomic orbitals" ?

THERMODYNAMICS

1. **Why is it hard to make measurements at constant volume?** We have discussed in class that experimentally, C_v is difficult to measure due to thermal expansion. Let's quantify this difficulty: Suppose you have 1 mole of iron that has a volume of 7.31 cm^3 at 293 K. Determine the pressure that would have to be applied after this material is heated to 298 K (only 5 degrees warmer!) to compress it to the volume it had at 293K- thus maintaining constant volume.

Data for Fe: $\alpha = 6.3 \times 10^{-5}$ K^{-1}

                       $\kappa = 1.10 \times 10^{-6}$ atm^{-1} at 298K

2. **Thermal properties of gases.** Calculate the thermal expansion coefficient and isothermal compressibility of an ideal gas.

3. **Cooking with a sealed pot.** Engel and Reid problem P3.5, p. 59.

4. **Irreversibility of a free expansion**. Recall in lecture 2 that we discussed irreversible processes, and gave several examples- one of these example irreversible processes was the expansion of a gas to fill a vacuum. All irreversible processes only occur in one direction spontaneously because it is in this direction that the entropy of the universe is increased, in accord with the second law. Let's show this for the irreversible expansion: consider the diagram below. An ideal gas is initially contained in one half of a chamber with adiabatic walls, the volume of the half of the chamber containing the gas is V_o. The partition between the right and left halves is suddenly removed, and the gas expands isothermally and adiabatically to fill the entire space ($V_f = 2V_o$). Show that this process fulfills the requirements of the second law for spontaneity by calculating the entropy change in the gas, the surroundings, and the universe, and show that for the process to run in reverse (spontaneous collapse of the gas back to one half of the chamber) will violate the second law.

$$V_o \qquad\qquad 2V_o$$
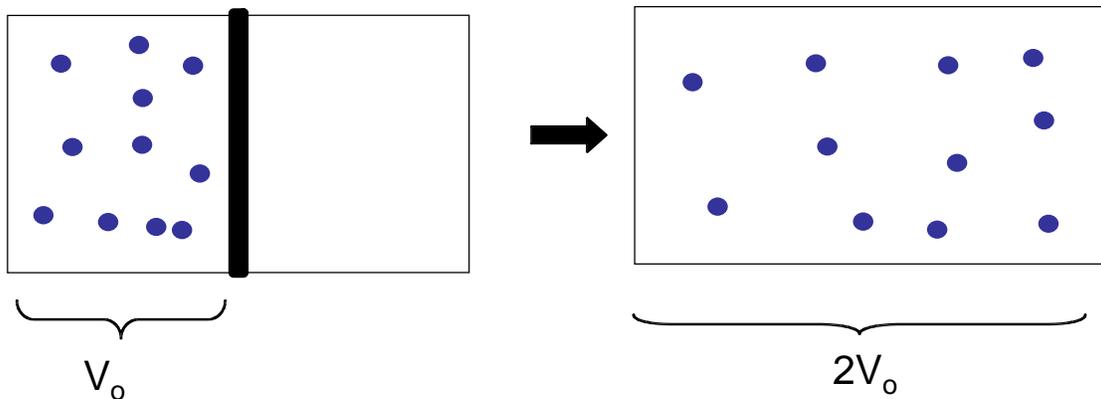
5. Let's revisit the liquid bismuth adiabatic cooling problem we examined on the last problem set. The physical situation is described again below, and the physical data for the system is also given. From your calculations on the last problem set, you showed that the alumina crucible and bismuth equilibrate at a final temperature of 433 K. Demonstrate that this process (cooling of the bismuth, warming of the alumina crucible) obeys the second law of thermodynamics, by calculating the total entropy change of the universe for the process.

Twenty kg of liquid bismuth at 600 K is introduced into a 10 kg alumina (Al_2O_3) crucible (initial temperature 298K), filling the crucible to the top; the crucible and bismuth are then surrounded by adiabatic walls (illustrated below) and the system is allowed to equilibrate. At equilibrium, according to the zeroth law, the temperatures of the bismuth and alumina crucible must be equal. Use the following thermodynamic data:

$$\overline{C}_p^{\,alu\,min\,a,solid} = 106.6 + 0.0178T \frac{J}{K \cdot mole} \qquad\qquad T_m^{alu\,min\,a} = 2327K$$

$$\overline{C}_p^{\,Bi,solid} = 18.8 + 0.023T \frac{J}{K \cdot mole} \qquad\qquad T_m^{Bi} = 544K$$

$$\overline{C}_p^{\,Bi,liquid} = 20 + 0.00615T \frac{J}{K \cdot mole} \qquad\qquad \Delta\overline{H}_m^{Bi} = 10{,}900 \frac{J}{mole}$$

Bi (*l*)

Al$_2$O$_3$ (s)
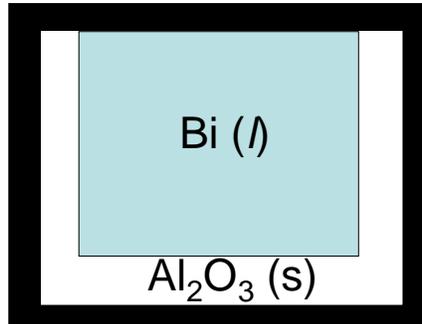
6. **Confirming your intuition using the second law**. Using your ability to calculate entropy and enthalpy changes at phase transitions and the data given below for nickel, consider the following possible processes and confirm your intuition by a calculation showing whether the process is spontaneous or not according to the second law. The key to this problem is to correctly identify what heat is transferring between the system and the surroundings in these processes, and to carefully calculate the entropy changes for the system. Also critical: pay attention to the number of significant figures you carry in your calculation.

   a. One mole of solid nickel at 1716 K isothermally transforms completely to liquid at this temperature. The surroundings are a heat bath at 1716 K, and the process occurs at constant pressure.

   b. One mole of solid nickel at 1736 K isothermally transforms completely to liquid at this temperature. The surroundings are a heat bath at 1736 K, and the process occurs at constant pressure.

$$\overline{C}_p^{\,s} = 16.49 + 0.0187T \frac{J}{K \cdot mole} \qquad\qquad T_m = 1726K \qquad\qquad \Delta\overline{H}_m = 17.47 \frac{kJ}{mole}$$

$$\overline{C}_p^{\,L} = 38.91 \frac{J}{K \cdot mole}$$