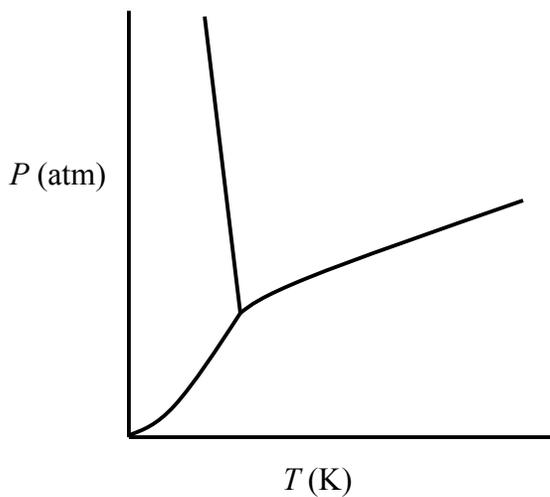


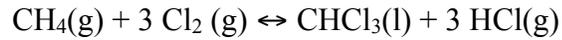
CH353 – Physical Chemistry I  
Spring 2012, Unique 52135

Homework, Week 15

1. Explain the significance of a state function and list six properties that can be determined by state functions.
2. When one mole of an ideal gas is compressed adiabatically and reversibly to one-half its original volume, the temperature of the gas increases from 273 K to 433 K.
  - a) Why does the temperature rise?
  - b) Determine the value of  $C_{V,m}$  for this gas, assuming it is independent of temperature.
  - c) Find  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S_{tot}$  of the compression.
3. The phase diagram of  $H_2O$  is shown below. Label each phase and provide a succinct and clear explanation of the difference in the relative slopes of each phase boundary shown. (You don't need to explain the origin of any curvature in these boundaries.)

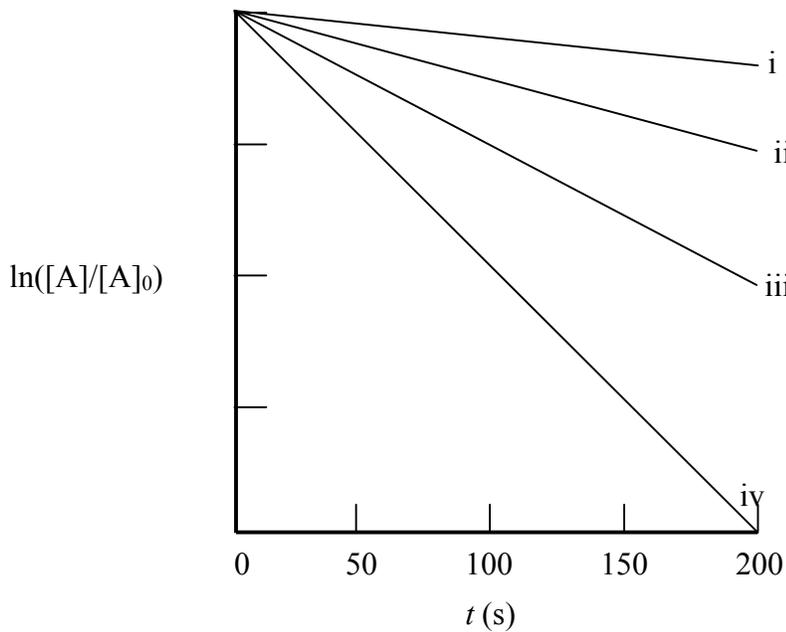


4. Chloroform can be synthesized from natural gas and elemental chlorine according to the following reaction:



Initially the system contains 3 bar  $\text{CH}_4(\text{g})$ , 1 bar  $\text{Cl}_2(\text{g})$ , and 2 bar  $\text{HCl}(\text{g})$ , with some liquid chloroform present. Determine the Gibbs energy,  $\Delta G_{rxn}$  for this system.

5. Consider the following figure:



- What information is being represented on this figure?
- The four curves have slopes of  $-0.0125 \text{ s}^{-1}$ ,  $-0.0250 \text{ s}^{-1}$ ,  $-0.0500 \text{ s}^{-1}$ , and  $-0.1000 \text{ s}^{-1}$ . Assign a slope to each curve.
- Label the magnitude of the y axis (i.e. put a number next to each tick mark and the origin).

6. In each of the following scenarios, determine if  $\Delta S_{\text{sys}}$  is positive. In each case the system is underlined.

- A drop of ink is dispersed in a liter of water.
- Ice melts in your cooler over the course of your afternoon picnic.
- A heat pump cools your room from  $85^\circ\text{C}$  to  $78^\circ\text{C}$ .
- Humpty Dumpty sat on a wall  
Humpty Dumpty had a great fall  
All the king's horses and all the king's men  
Couldn't put Humpty together again.
- One mole of fructose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is combusted in oxygen to form carbon dioxide and water.

7. A singly-degenerate three-state system, has energy levels  $E_1 = 0$ ,  $E_2 = \epsilon$ ,  $E_3 = 2\epsilon$ . This system is filled with 4 molecules.

- How many individual microstates are present in this system?
- How many macrostates are present in this system?
- What is the partition function of the system?
- Plot the probability of each state vs.  $T$ .

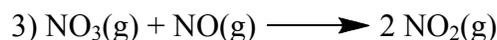
8. Nitric anhydride ( $\text{N}_2\text{O}_5(\text{g})$ ) decomposes to  $\text{NO}_2(\text{g})$  and  $\text{O}_2(\text{g})$ :



with the experimentally observed rate law

$$\frac{d[\text{O}_2]}{dt} = k_{\text{obs}}[\text{N}_2\text{O}_5]$$

The following mechanism has been proposed for this decomposition:



where the steady-state approximation is assumed to apply to both the  $\text{NO}(\text{g})$  and  $\text{NO}_3(\text{g})$  reaction intermediates. Determine whether this mechanism is consistent with the experimentally observed rate law, and if so, express  $k_{\text{obs}}$  in terms of the rate constants for the individual steps of the reaction mechanism.

9. A 2.0 kg block of copper at a temperature of  $0^{\circ}\text{C}$  is placed in an adiabatic container containing 1.0 mol  $\text{H}_2\text{O}(\text{g})$  at  $100^{\circ}\text{C}$  and 1 atm. Assuming that all of the water vapor is condensed to liquid, determine the change in entropy of the water, the change in entropy of the copper, and the change in entropy of the surroundings, and the total change in entropy.

10. Compound 1 at volume  $V_1$  is mixed with compound 2 at  $V_2$  at constant temperature and pressure. Determine  $\Delta V$ ,  $\Delta S$ ,  $\Delta G$ ,  $\Delta A$ , and  $\Delta U$  upon mixing.