

### Homework 6 Problems (#25-#35)

25. E&R 5.16

3.75 moles of an ideal gas with  $\bar{C}_V = 3/2 R$  undergoes the transformations described in the following list from an initial state described by  $T = 298\text{K}$  and  $P = 4.50\text{ bar}$ . Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$ , and  $\Delta S$  for each process.

- The gas undergoes a reversible adiabatic expansion until the final pressure is one third its initial value.
- The gas undergoes an adiabatic expansion against a constant external pressure of 1.50 bar until the final pressure is one third its initial value.
- The gas undergoes an expansion against a constant external pressure of zero bar until the final pressure is equal to one third of its initial value.

(*part c is ambiguous as written. It should have been stated: "...undergoes an adiabatic (and also???) expansion against a constant external pressure of zero bar until the final pressure is equal to one third of its initial value".*)

26. (from "Basic Chemical Thermodynamics", by J. Waser, pub by Benjamin)

- One mole of ideal gas at 300K and 1 atm is compressed reversibly and isothermally to half its volume. Calculate  $\Delta S$  for this process?
- One mole of ideal gas at 300K and 1 atm is heated reversibly to 600K at constant volume and then cooled reversibly to 300K at constant pressure. Calculate  $\Delta S$  for this process?
- How do the final states of the gas in parts a and b compare? How does  $\Delta S$  compare for the two paths?

27.\* (optional) A non-ideal gas obeys the following equation of state:

$$\bar{V} = RT \left[ \frac{1}{P} + \frac{a}{P^2} \right] \text{ where } a \text{ is a function of only temperature: } a(T)$$

For an isothermal compression of one mole of this gas from  $P_1$  to  $P_2$

$$\text{Show that } \Delta S = R \ln \frac{P_1}{P_2} + \left[ aR + RT \left( \frac{\partial a}{\partial T} \right)_P \right] \left[ \frac{1}{P_2} - \frac{1}{P_1} \right]$$

28. E&R P5.33

A refrigerator is operated by a 0.25-hp (1 hp = 746 watts) motor. If the interior is to be maintained at 4.50°C and the room temperature on a hot day is 38°C, what is the maximum heat leak (in watts) that can be tolerated? Assume that the coefficient of performance is 50% of the maximum theoretical value. What happens if the leak is greater than your calculated maximum value?

29. Suppose two blocks of iron, each having 1 mol of iron atoms, are at differing temperatures and are then brought together in an otherwise isolated system. One of the blocks is at 273.15K and the other is at 373.15K and the process is carried out at 1 bar pressure..
- Would you expect  $\Delta S_{\text{sys}} < 0$ ,  $\Delta S_{\text{sys}} = 0$ ,  $\Delta S_{\text{sys}} > 0$  ?
  - Using common sense and high school physics (and perhaps the First Law), what is the common final temperature of the two blocks?
  - Calculate  $\Delta S_{\text{sys}}$  for the process (use Table 4.1 for any needed molar heat capacities needed, and assume that the molar heat capacities are independent of T).
  - What is  $q$  for the isolated system? How does this value of  $q$  and the result of part C relate to the Clausius inequality:  $\Delta S \geq \int_{\text{initial}}^{\text{final}} \frac{\delta q}{T}$  ?
  - Interpret this change in entropy in terms of the ordering-disordering effects involved in the transfer of given amount of heat from a block at higher temperature to one at a lower temperature (i.e. the disordering effect of adding a given  $q$  to the cooler block vs the ordering effect of removing the same  $q$  from the hotter block).
30. [Adapted from Raff #4.30] Using the data in E&R Appendix A, calculate  $\Delta S^\circ$  for the following relations:
- $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
  - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
  - $\text{C}_4\text{H}_{10}(\text{g})$  [*n-butane*] +  $\frac{13}{2} \text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{g})$
  - Discuss the results of each reaction in terms of order-disorder in regard to both the sign of  $\Delta S^\circ$  for each reaction and the relative magnitudes of  $\Delta S^\circ$  for the three reactions.

31.

- a. Prove, in general (but  $\bar{d}w_{other} = 0$ ;  $dn = 0$ ), the relationship in equation 3.19 E&R)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

- b. Evaluate  $\left(\frac{\partial U}{\partial V}\right)_T$  for an ideal gas.

- c. Evaluate  $\left(\frac{\partial \bar{U}}{\partial \bar{V}}\right)_T$  for a Van der Waals gas  $\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$

- d. Interpret your (correct!) results for parts (b) and (c).

- e. Prove, in general (but  $\bar{d}w_{other} = 0$ ;  $dn = 0$ ), the relationship in equation 3.44 E&R:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

32. ★ (optional) E&amp;R P5.38

The heat capacity of  $\alpha$ -quartz is given by

$$\frac{\bar{C}_P(\alpha\text{-quartz, s})}{\text{J K}^{-1}\text{mol}^{-1}} = 46.94 + 34.31 \times 10^{-3} \frac{\text{T}}{\text{K}} - 11.30 \times 10^{-5} \frac{\text{T}^2}{\text{K}^2}$$

The coefficient of thermal expansion is given by  $\beta = 0.3530 \times 10^{-4} \text{ K}^{-1}$  and

$\bar{V} = 22.6 \text{ cm}^3 \text{ mol}^{-1}$ . Calculate  $\Delta \bar{S}$  for the transformation

$\alpha$ -quartz (15.0°C, 1 atm)  $\rightarrow$   $\alpha$ -quartz (420. °C, 925 atm).

(assume that  $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$  is a constant independent of T and P).

33. (Adapted from Tinoco, Sauer, Wang, and Puglisi; *Physical Chemistry*; Prentice-Hall, publishers) The denaturation of a globular protein from state  $\alpha \rightarrow$  state  $\beta$  occurs reversibly at  $T_m = 70^\circ\text{C}$  and  $P = 1 \text{ atm}$ . At this temperature  $638 \text{ kJ mol}^{-1}$  are absorbed for the transition. For this denaturation
- $$(\bar{C}_p)_\beta - (\bar{C}_p)_\alpha = -8.37 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ and } \Delta\bar{V} = 3 \text{ mL mol}^{-1}.$$
- What is  $\Delta\bar{S}$  for this transition at  $70^\circ\text{C}$  and  $1 \text{ atm}$ ?
  - What are  $\Delta\bar{H}$  and  $\Delta\bar{S}$  for this transition at  $37^\circ\text{C}$  and  $1 \text{ atm}$ ?
  - Assuming that the  $\alpha$  and  $\beta$  forms have identical coefficients of thermal expansion ( $\Delta\bar{V} = \text{constant, independent of } T$ ), calculate  $\Delta H$  for the denaturation at  $70^\circ\text{C}$  and  $1000 \text{ atm}$ ?
  - From thermodynamic arguments, which form is more disordered,  $\alpha$  or  $\beta$ ? Why?
34. A  $3 \text{ L}$  container is partitioned into two sections,  $2 \text{ L}$  and  $1 \text{ L}$ . The  $2 \text{ L}$  section contains  $\text{N}_2$  at  $T = 300 \text{ K}$ ,  $1 \text{ atm}$ , and the  $1 \text{ L}$  contains  $\text{O}_2$  at  $T = 300 \text{ K}$ ,  $1 \text{ atm}$ . If the temperature of the container is maintained at  $T = 300 \text{ K}$ , what is the change of entropy when the partition is removed (assume ideal gasses)? [Express the result in  $\text{J K}^{-1}$ ]
35. The molar enthalpy of fusion of water is  $6.03 \text{ kJ mol}^{-1}$  at  $273 \text{ K}$  and the molar heat capacities of liquid water and ice are  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $37.9 \text{ J K}^{-1} \text{ mol}^{-1}$  respectively.

For the process  $1 \text{ mole } \text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{s})$

- Will this be a spontaneous process at  $263 \text{ K}$ ?
- What is  $\Delta H$  at  $263 \text{ K}$ ?
- What is  $\Delta S$  at  $263 \text{ K}$ ?
- Is  $\left(\frac{\Delta H}{T}\right)_{263 \text{ K}} = \Delta S_{263 \text{ K}}$ ? Why or why not?
- (quickly) Repeat the calculations of parts b and c for  $\Delta H$  and  $\Delta S$  at  $T = 283 \text{ K}$ .
- From the results of b,c,d calculate the quantities:
  - $[\Delta H - T\Delta S]_{263}$
  - $[\Delta H - T\Delta S]_{273}$  (you should have obtained  $\Delta S_{273}$  in part c)
  - $[\Delta H - T\Delta S]_{283}$