

### Homework 5 Problems (#25-#35)

*Section Questions: none this week*

25. E&R<sub>4th</sub> 5.16

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<sub>4th</sub> P5.46

† the 50% of the maximum efficiency refers to the coefficient of performance of a reversible Carnot refrigerator (Eq 5.69)<sub>4th</sub>

$$(\eta_R)_{\max} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}} \quad \text{and} \quad (\eta_R)_{\text{actual}} = \frac{(q_{\text{cold}})_{\text{actual}}}{w}$$

where 'cold'=the lower  $T_L$  expansion and 'hot'=the upper  $T_U$  compression

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:  $\Delta S \geq \int_{\text{initial}}^{\text{final}} \frac{\bar{d}q}{T}$  ?
  - 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  $\bar{d}w_{\text{other}} = 0$ ;  $dn = 0$ ), the relationship in equation 3.15 E&R<sub>4th</sub>)

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

- 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  $\bar{d}w_{\text{other}} = 0$ ;  $dn = 0$ ), the relationship in equation 3.40 E&R<sub>4th</sub>:

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

32. ★ (optional) E&R<sub>4th</sub> P5.14

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

$$\left(\bar{C}_p\right)_\beta - \left(\bar{C}_p\right)_\alpha = -8.37 \text{ kJ mol}^{-1} \text{ K}^{-1} \text{ and } \Delta\bar{V} = 3 \text{ mL mol}^{-1}.$$

- a. What is  $\Delta\bar{S}$  for this transition at  $70^\circ\text{C}$  and  $1 \text{ atm}$ ?
- b. What are  $\Delta\bar{H}$  and  $\Delta\bar{S}$  for this transition at  $37^\circ\text{C}$  and  $1 \text{ atm}$ ?
- c. 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  $1000 \text{ atm}$ ?
- d. 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 mole  $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{s})$

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