University of Washington
Department of Chemistry
Chemistry 452
Summer Quarter 2014

Lecture 8 7/11/14
ERD: 5.4-5.7
Devoe: 4.5

A. Entropy for Irreversible Processes.

- In past lectures we showed how to calculate the enthalpy change for irreversible processes. Basically we composed a sequence of reversible steps which begin and end in the same states as the irreversible change. Because DH is a state function, the enthalpy change for the real, irreversible change is the same as the enthalpy change calculate for the sequence of reversible steps.
- The strategy is the same for entropy calculations. To calculate the entropy for an irreversible change we can still use $dS = \frac{\delta q_{rev}}{T}$ but we have to compose a reversible path that starts and ends in the same states as the irreversible process.
- It is very important that the properties of reversible and irreversible changes not be confused. A famous example is the entropy change for a reversible / irreversible adiabatic expansion.
  - By definition, for a reversible adiabatic expansion, $q_{rev}=0$. Because $dS = \frac{\delta q_{rev}}{T}$ we can assume ΔS=0 for such a process.
  - For an irreversible adiabatic expansion we have $q_{irrev}=0$. .But this does not mean the entropy change is zero. This can be seen by considering that

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \tag{8.1}$$

  which follows from the fact that U is a state function so ΔU is invariant with respect to whether a reversible or irreversible path is followed.
  - Now we have shown that the work performed by a gas which is undergoing a reversible is greater than the work performed if the same expansion is done reversibly:

$$-w_{rev} > -w_{irrev} \tag{8.2}$$

  - .From equations 8.1 and 8.2 we conclude:

$$q_{rev} > q_{irrev} \tag{8.3}$$

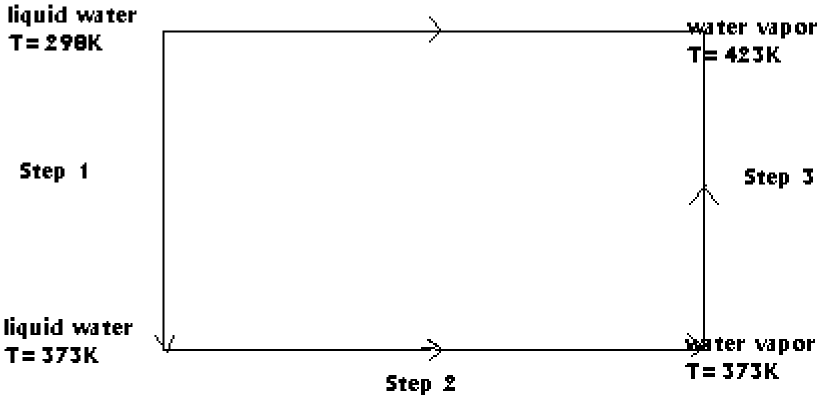
    - So for a irreversible adiabatic expansion even though $q_{irrev}=0$, the entropy change ΔS>0

B. Entropy Problems for Irreversible Processes

Example 1: Entropy Calculation for an Irreversible Vaporization

Suppose 18g of water at 298K are evaporated by falling on a iron crucible that is maintained at 423K. Calculat the entropy change for the water, the crucible and the universe. For liquid water $\bar{c}_P^l = 75.4 J/mole \cdot K$ and for water vapor $\bar{c}_P^v = 36.0 J/mole \cdot K$. Also, assume $\Delta H_{vap} = 40.68 kJ/mole$.

Solution: To calculate ΔS we break the transition from liquid water at T=298K to water vapor at 423K (i.e. in thermal contact with the crucible) into three steps



- Step 1: Heat liquid water from 298K to 373K

$$\Delta S_{water} = n\bar{c}_P \ln\left(\frac{T_2}{T_1}\right) = (1mole)(75.4 J/mole \cdot K)\ln\left(\frac{373}{298}\right) = 16.8 J/K$$

- Step 2: Vaporize the water at 373K

$$\Delta S_{water} = \frac{\Delta H_{vap}}{T} = (1mole)\frac{40{,}680 J/mole}{373K} = 109.1 J/K$$

- Step 3: Heat water vapor from373K to 423K

$$\Delta S_{water} = n\bar{c}_P \Delta T = (1mole)(36.0 J/mole \cdot K)\ln\left(\frac{423}{373}\right) = 4.40 J/K$$

- Total entropy change for the water:

$$\Delta S_{water} = 16.8 J/K + 109.1 J/K + 4.40 J/K = 130.3 J/K$$

- To calculate the entropy change for the surroundings i.e. the crucible, we assume any heat that went into the water came out of the crucible. The heat transfeered from the crucible to the water was done so at constant pressure. The heat leaving the crucible is:

$$q_P = \Delta H_{crucible} = -\left(n\bar{c}_P^l \Delta T_{step1} + n\Delta H_{vap} + n\bar{c}_P^v \Delta T_{step3}\right)$$

$$= -\left((1mole)(75.4J/mole\cdot K)(373K - 298K) + (1mole)(40,680J/mole)\right.$$
$$\left. +(1mole)(36J/mole\cdot K)(423K - 373K)\right) = \text{-48,135J}$$

- To calculate the entropy chane of the crucible you now assume the hea calculated above is transferred at a constant temperature of 423K…

$$\Delta S_{crucible} = \frac{\Delta H_{crucible}}{T} = \frac{-48{,}135J}{423K} = -113.8J/K$$

- The entropy change of the universe is:
  $$\Delta S_{universe} = \Delta S_{water} + \Delta S_{crucible} = 130.5J/K - 113.8J/K = 16.7K/K$$

Example 2. Entropy of Mixing

Assume two ideal gases, initially in separate containers, are mixed at constant temperature. Assume their initial pressures are each 1 atm (i.e. when separate) and the final total pressure $P_T=P_A+P_B$ =1 atm. Calculate the entropy of mixing.

- For the gas A…

$$\Delta S_A = n_A R\ln\left(\frac{V_{2A}}{V_{1A}}\right) = n_A R\ln\left(\frac{P_{1A}}{P_{2A}}\right) = -n_A R\ln\left(\frac{P_{2A}}{P_{1A}}\right) = -n_A R\ln\left(\frac{\chi_A(1atm)}{1atm}\right)$$

where $\chi_A = \dfrac{n_A}{n_A + n_B}$ and where $P_{2A} = \chi_A P_T = \chi_A(1atm)$

- Similarly for gas B…

$$\Delta S_B = n_B R\ln\left(\frac{V_{2B}}{V_{1B}}\right) = n_A R\ln\left(\frac{P_{1B}}{P_{2B}}\right) = -n_B R\ln\left(\frac{P_{2B}}{P_{1B}}\right) = -n_B R\ln\left(\frac{\chi_B(1atm)}{1atm}\right)$$

where $\chi_B = \dfrac{n_B}{n_A + n_B}$

- Add the two results and divide by n_A+n_B to get the entropy of mixing per mole…

$$\Delta\bar{S} = \frac{\Delta S_A + \Delta S_B}{n_A + n_B} = -\frac{n_A}{n_A + n_B}R\ln(\chi_A) - \frac{n_B}{n_A + n_B}R\ln(\chi_B)$$
$$= -\chi_A R\ln(\chi_A) - \chi_B R\ln(\chi_B)$$

  The formula can be generalized to include any number of components. That is, mixing of N gases together has an entropy change of $\Delta\bar{S} = -R\sum_{i=1}^{N}\chi_i\ln(\chi_i)$.

  - Calculate the entropy change when 50 g each of oxygen O_2, nitrogen N_2, and hydrogen H_2 are mixed at 1 atm pressure and 273K.
    Solution:
    - First calculate the moles of each gas mixed

$$moles\,O_2 = \frac{50g}{32g/mole} = 1.56\,moles$$

$$moles\,N_2 = \frac{50g}{28g/mole} = 1.79\,moles$$

$$moles\,H_2 = \frac{50g}{2g/mole} = 25\,moles$$

- Then calculate the mole fractions

$$total\,moles = n_T = 1.56 + 1.79 + 25 = 28.35\,moles$$

$$\chi_{O_2} = \frac{1.56moles}{28.35moles} \approx 0.06$$

$$\chi_{N_2} = \frac{1.79moles}{28.35moles} \approx 0.06$$

$$\chi_{H_2} = \frac{25moles}{28.35moles} \approx 0.88$$

- Calculate the final expression:

$$\begin{aligned}\Delta\overline{S} &= -R\left(\chi_{O_2}\ln\left(\chi_{O_2}\right) + \chi_{N_2}\ln\left(\chi_{N_2}\right) + \chi_{H_2}\ln\left(\chi_{H_2}\right)\right)\\ &= -\left(8.31J/moles\cdot K\right)\left(0.06\ln(0.06) + 0.06\ln(0.06) + 0.88\ln(0.88)\right)\\ &= -\left(8.31J/moles\cdot K\right)\left(-0.34 - 0.11\right) = 3.76\,J/moles\cdot K\end{aligned}$$