

CHEM 3410: Physical Chemistry I — Fall 2009

Homework 4— Solutions

1. (a) Before doing any calculations, we know that for a reversible process $\Delta S_{universe} = 0$ which means $\Delta S_{surr} = -\Delta S_{sys}$. We need to find the heat flow for the system to find the entropy. Since the process is reversible and isothermal, we can find q much like in Problem 2.

$$q = -w = nRT \ln \frac{V_2}{V_1} = (1 \text{ mole}) \left(8.314 \frac{\text{J}}{\text{mole} \cdot \text{K}} \right) \ln \left(\frac{2}{1} \right)$$

$$q = 1717.3 \text{ J}$$

$$\Delta S_{sys} = \int \frac{\partial q_{rev}}{T}$$

For a constant temperature process this becomes:

$$\Delta S_{sys} = \frac{1}{T} \int \partial q_{rev} = \frac{q_{rev}}{T} = \frac{1717.3 \text{ J}}{298 \text{ K}}$$

$$\boxed{\Delta S_{sys} = 5.763 \text{ J/K}}$$

For ΔS_{surr} we use the actual heat flow into our out of the surroundings. In this case, it is $-q_{rev}$ since we are actually doing the reversible process.

$$\Delta S_{sys} = \int \frac{\partial q_{surr}}{T} = \frac{-1717.3 \text{ J}}{298 \text{ K}}$$

$$\boxed{\Delta S_{surr} = -5.763 \text{ J/K and } \Delta S_{univ} = 0}$$

- (b) For the irreversible path (constant pressure in this case), the entropy change for the system is the same as in part (a) since entropy is a state function.

$$\boxed{\Delta S_{sys} = 5.763 \text{ J/K}}$$

For the change in entropy of the surroundings we need to find the actual heat flow into or out of the surroundings since it will end up in a different state than in part (a). To do this, we can find w which is $-q$ in this case since $\Delta U = 0$ for an isothermal process.

$$q_{sys} = -w = PdV = (12.2 \text{ atm})(2 \text{ L} - 1 \text{ L}) \left(\frac{8.314 \text{ J}}{0.0821 \text{ L} \cdot \text{atm}} \right) = 1235.5 \text{ J}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-1235.5}{298} = -4.146 \text{ J/K}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 5.763 - 4.4146 = 1.617 \text{ J/K}$$

$$\boxed{\Delta S_{surr} = -4.416 \text{ J/K and } \Delta S_{univ} = 1.617 \text{ J/K}}$$

This makes sense because the expansion described in part (b) is spontaneous.

2. (a) To find the final temperature, we need to find out how much heat is required to raise the temperature in each phase and each phase temperature. The best way to do this is in steps.

- i. First ask if there is enough heat coming into the system to raise the temperature from the initial temperature (298 K) to the first transition temperature ($\alpha \rightarrow \beta$, 993 K). The heat required to raise the temperature this much is:

$$q = n \int_{298}^{992} C_p^\alpha dT = 2 \int_{298}^{992} \left(21.6159 \frac{J}{mole \cdot K} \right) dT = (2)(21.6159)(993 - 298) = 30046 J$$

We have a total of 100698 J of heat available. Therefore we have enough to raise the temperature to the first transition (from α to β) and have $100698 - 30046 = 70652$ J of heat remaining.

- ii. Now do we have enough heat available to complete the transition from the α to the β phase:

$$\Delta H_{trans}^{\alpha \rightarrow \beta} = (2 \text{ moles})(2010 J/mole) = 4020 J$$

We have 70652 J remaining from (i), so we can completely transform to the β phase, leaving $70652 - 4020 = 66632$ J of heat remaining.

- iii. Now can we raise the temperature from 993 K to the transition temperature for β to γ at 1373K?

$$q = n \int_{993}^{1373} C_p^\beta dT = 2 \int_{993}^{1373} \left(34.9028 \frac{J}{mole \cdot K} \right) dT = (2)(34.9028)(1373 - 993) = 26526 J$$

Yes we can! This leaves us with $66632 - 26526 = 40106$ J leftover. So we can continue!

- iv. Now do we have enough heat available to complete the transition from the β to the γ phase:

$$\Delta H_{trans}^{\beta \rightarrow \gamma} = (2 \text{ moles})(2300 J/mole) = 4600 J$$

This leaves us $40106 - 4600 = 35506$ J leftover.

- v. Now can we raise the temperature from 1373 K to the transition temperature for γ to δ at 1409?

$$q = n \int_{1373}^{1409} C_p^\gamma dT = 2 \int_{1373}^{1409} \left(44.8 \frac{J}{mole \cdot K} \right) dT = (2)(44.8)(1409 - 1373) = 3226 J$$

Yes we can! This leaves us with $35506 - 3226 = 32280$ J leftover. So we can continue!

- vi. Now do we have enough heat available to complete the transition from the γ to the δ phase:

$$\Delta H_{trans}^{\gamma \rightarrow \delta} = (2 \text{ moles})(1800 J/mole) = 3600 J$$

This leaves us $32280 - 3600 = 28680$ J leftover.

- vii. Now that we are in the *delta* phase, no additional phase transitions are possible (according to our data). Therefore, the remaining heat coming into the system will go into raising the temperature of the δ phase. We can then solve for the final T knowing how much heat is leftover from the previous steps:

$$28680 J = \int_{1409}^{T_{final}} nC_p^\delta dT = (2)(47.3)(T_{final} - 1409)$$

Solving for T_{final} we find:

$$\boxed{T_{final} = 1712 \text{ K}}$$

- (b) Since we are working at constant pressure, $q_p = \Delta H$, therefore:

$$\boxed{\Delta H = 100698 \text{ J}}$$

- (c) To find the entropy change, we need to take into consideration each of our heating steps and phase transformations from part (a). For the heating steps, the change in entropy can be written as:

$$\Delta S = \int_{T_1}^{T_2} \frac{\partial q_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

ensuring that for each different phase we use the correct value for C_p . Note that we have assumed that the heat capacities are independent of temperature since we are given not data to contradict this.

For the phase transformations, the entropy change is just:

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

Putting this together:

$$\Delta S = (2 \text{ moles}) \left[C_p^\alpha \ln \frac{993}{298} + \frac{\Delta H_{trans}^{\alpha \rightarrow \beta}}{993 \text{ K}} + C_p^\beta \ln \frac{1373}{993} + \frac{\Delta H_{trans}^{\beta \rightarrow \gamma}}{1373 \text{ K}} + C_p^\gamma \ln \frac{1409}{1373} + \frac{\Delta H_{trans}^{\gamma \rightarrow \delta}}{1409 \text{ K}} + C_p^\delta \ln \frac{1712}{1409} \right]$$

$$\Delta S = (2 \text{ moles}) [26.0177 + 2.0242 + 11.3093 + 1.6752 + 1.1595 + 1.2775 + 9.2132] \left(\frac{\text{J}}{\text{mole} \cdot \text{K}} \right)$$

$$\boxed{\Delta S = 105.4 \text{ J/K}}$$

(d) As we found in part (a), at the final temperature we are completely in the δ phase.

3. We know for a reversible, adiabatic process that the entropy change for the system must be zero since no heat is transferred into or out of the system.

We can break up the adiabatic process into two parts: (1) an isothermal expansion from V_1 to V_2 at T_1 and (2) a constant volume process from T_1 to T_2 at V_2 . We know how to write the entropy changes for both these types of process.

- (1) Isothermal process from V_1 to V_2 at T_1

For this process $q = -w = -nRT_1 \ln \frac{V_2}{V_1}$. The entropy change is then:

$$\Delta S_1 = \frac{\int \partial q}{T_1} = \frac{q}{T_1} = nR \ln \frac{V_2}{V_1}$$

- (2) Constant volume process from T_1 to T_2 at V_2 Since the volume is constant, $w = 0$ and $\Delta U = q = nC_v dT$. The entropy change for this part of the process is then:

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_v \ln \frac{T_2}{T_1}$$

We know for the overall process, $\Delta S = 0$. Therefore, the entropies calculated for part (1) and (2) must be equal and opposite in sign. We can prove this using the relationship between aT and V for an adiabatic process (section 2.10):

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1} \right)^{1-\gamma}$$

where $\gamma = \frac{C_p}{C_v}$. Substituting this into our expression from part (2) above:

$$\Delta S_2 = nC_v \ln \frac{T_2}{T_1} = nC_v \ln \left(\frac{V_2}{V_1} \right)^{1-\gamma} = nC_v (1-\gamma) \ln \left(\frac{V_2}{V_1} \right) = nC_v \left(1 - \frac{C_p}{C_v} \right) \ln \left(\frac{V_2}{V_1} \right)$$

Remembering that $C_p - C_v = R$ for an ideal gas, we can write:

$$\Delta S_2 = -n(C_p - C_v) \ln \frac{V_2}{V_1} = -nR \ln \frac{V_2}{V_1}$$

We have now shown that:

$$\boxed{\Delta S_1 = -\Delta S_2 \text{ and that the entropy change for this adiabatic process is indeed zero}}$$