Chem 4511
Problem Set 3 Solutions

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

1. Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (a) 0°C, (b) 100°C. Assume that the block is so large that its temperature does not change significantly as a result of the heat transfer. Then

\[ \Delta S = \int_{T_i}^{T_f} \frac{dq_{\text{rev}}}{T} \left[ 3.2 \right] = \frac{1}{T} \int_{T_i}^{T_f} dq_{\text{rev}} \text{ [constant } T] = \frac{q_{\text{rev}}}{T} \]

(a) \( \Delta S = \frac{25 \times 10^3 \text{ J}}{273.15 \text{ K}} = \left[ 92 \text{ J K}^{-1} \right] \)

(b) \( \Delta S = \frac{25 \times 10^3 \text{ J}}{373.15 \text{ K}} = \left[ 67 \text{ J K}^{-1} \right] \).

2. Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is 146.22 J K\(^{-1}\) mol\(^{-1}\) at 298 K.

\[ S_m(T_f) = S_m(T_i) + \int_{T_i}^{T_f} \frac{C_{V,m}}{T} \, dT \left[ 3.19, \text{ with } C_{V,m} \text{ in place of } C_{p,m} \right]. \]

If we assume that neon is a perfect gas then \( C_{V,m} \) may be taken to be constant and given by

\[ C_{V,m} = C_{p,m} - R; \quad C_{p,m} = 20.786 \text{ J K}^{-1} \text{ mol}^{-1} \left[ \text{Table 2.7} \right] \]

\[ = (20.786 - 8.314) \text{ J K}^{-1} \text{ mol}^{-1} \]

\[ = 12.472 \text{ J K}^{-1} \text{ mol}^{-1}. \]

Integrating, we obtain

\[ S_m(500 \text{ K}) = S_m(298 \text{ K}) + C_{V,m} \ln \frac{T_f}{T_i} \]

\[ = (146.22 \text{ J K}^{-1} \text{ mol}^{-1}) + (12.472 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{500 \text{ K}}{298 \text{ K}} \right) \]

\[ = (146.22 + 6.45) \text{ J K}^{-1} \text{ mol}^{-1} = \left[ 152.67 \text{ J K}^{-1} \text{ mol}^{-1} \right]. \]
3. Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ext} = 0$, and (c) an adiabatic reversible expansion.

\[
\Delta S(\text{gas}) = nR \ln \frac{V_f}{V_i} \quad [3.13] = \left( \frac{14 \text{ g}}{28.02 \text{ g mol}^{-1}} \right) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln 2 \\
= +2.9 \text{ J K}^{-1}.
\]

\[\Delta S(\text{surroundings}) = \boxed{-2.9 \text{ J K}^{-1}} \text{ [overall zero entropy production]}.\]

\[\Delta S \text{ (total)} = \boxed{0} \text{ [reversible process]}.\]

(b) \[\Delta S \text{ (gas)} = \boxed{+2.9 \text{ J K}^{-1}} \text{ [S a state function]}.\]

\[\Delta S \text{ (surroundings)} = \boxed{0} \text{ [surroundings do not change]}.\]

\[\Delta S \text{ (total)} = \boxed{+2.9 \text{ J K}^{-1}}.\]

(c) \[\Delta S \text{ (gas)} = \boxed{0} \text{ [}q_{rev} = 0\text{]}.\]

\[\Delta S \text{ (surroundings)} = \boxed{0} \text{ [no heat transferred to surroundings]}.\]

\[\Delta S \text{ (total)} = \boxed{0}.\]
4. Consider the expansion of an ideal gas (n mol) in an isolated system of two rigid containers (with equal volumes \( V_1 \) and \( V_2 \)) at temperature \( T \), with \( P_2 = 0 \) initially. As there is no heat or work exchanged between the system and the surroundings there can be no change in the temperature or the internal energy of the system.

\((P_1, V_1)_{\text{initial}} \rightarrow (P, V_1 + V_2)_{\text{final}}.\)

**Surroundings**

\[ \text{work} \quad \text{heat} \]

In class, we discussed that a gas expanding and filling a vacuum is a spontaneous process, only driven by entropy (because there is no change in \( U \) or \( H \)).

1) Instead of the actual gas expansion with ever increasing \( P_2 \) until the equilibrium is reached, the process can be viewed as the gas expanding with an inflating boundary (see above). Then, the process depicted above is identical to free expansion with \( P_2 = 0 \). In about one sentence, explain why this model correctly predicts \( \Delta U \), \( \Delta H \), and \( \Delta S \). (answer: the same final states, state functions)

2) The isolated system \( (V_1 + V_2) \) receives no heat from the surroundings. We know the definition of \( dS_{\text{system}} \), and we know that entropy must be the only driving force for this spontaneous process. Is \( dS_{\text{system}} = 0 \)? What is going on? Briefly explain your conclusion. (answer: \( q(\text{irr}) = 0 \), but entropy is calculated from \( q(\text{rev}) \))

3) Calculate the entropy changes, \( \Delta S_{\text{system}} \), \( \Delta S_{\text{surr}} \), and \( \Delta S_{\text{total}} \). (answer: \( nR\ln 2 \), 0, \( nR\ln 2 \)).