
The differences come from the differences in the definitions of the zero in $S^\circ$ which is given by the third law of thermodynamics and $\Delta f \bar{H}^\circ$ and $\Delta f \bar{G}^\circ$ where the values are zero for elements in their standard states at 0 K.

If instead of comparing $\Delta f \bar{G}^\circ = -394.359 \text{ kJ mol}^{-1}$ to

$$\Delta f \bar{H}^\circ - T \Delta f \bar{S}^\circ = -393.509 - 298 \times 0.21374 = -457.20 \text{ kJ mol}^{-1}$$

we use,

$$\Delta f \bar{G}^\circ = \Delta f \bar{H}^\circ - T \Delta f \bar{S}^\circ$$

where

$$\Delta f \bar{S}^\circ = \bar{S}^\circ(\text{CO}_2) - \bar{S}^\circ(\text{C}) - \bar{S}^\circ(\text{O}_2)$$

$$= 213.74 - 5.74 - 205.138 = 2.862 \text{ J mol}^{-1} \text{ K}^{-1}.$$ 

Using this value for $\Delta f \bar{S}^\circ$,

$$\Delta f \bar{H}^\circ - T \Delta f \bar{S}^\circ = -393.509 - 298 \times 0.002862 = -394.36$$

which is in good agreement with $\Delta f \bar{G}^\circ$

2. Chang, problem 6.15 (page 6.38)

For a reaction to be spontaneous, $\Delta_r G$ must be smaller than zero. Therefore, the minimum value of entropy necessary for the reaction to occur at $72^\circ \text{ C} = 345 \text{ K}$ when $\Delta_r H = 19 \text{ kJ}$ is

$$\Delta_r H - T \Delta_r S < 0$$

$$\Delta_r S > \frac{\Delta_r H}{T}$$

$$> \frac{19000}{345} = 55 \text{ J mol}^{-1} \text{ K}^{-1}.$$ 

3. Chang, problem 6.16 (page 6.38)

NO! All that $\Delta G$ tells us is if a reaction is thermodynamically favored. It does not tell us how long the reaction will take.
4. The thermodynamic data for transitions from ordered, helical conformations of polypeptides and polinucleotides to disordered states gives entropy and enthalpy changes that are positive, as expected. Heat is absorbed in these transitions and entropy (or disorder) increases. However, when the synthetic polypeptide, polybenzyl-L-glutamate undergoes a transition from an ordered helix to a disordered coil in an ethylene dichloride-dichloroacetic acid solvent at 39°C and 1 atm, \( \Delta_r H = -4.0 \text{ kJ (per mol amide)} \) and \( \Delta_r S = -12 \text{ J/K (per mol amide)} \).

(a) Give a possible explanation for the experimental result that heat is released and entropy is decreased for this transition. Does increasing the temperature favor the helix-coil transition?

Both of these observations can be explained by the interactions of the two forms of the polypeptide with the solvent. If more solvent molecules are bound to the coiled form than the helix then the reaction will be exothermic (products are at lower internal energy than the reactants) and the products are more ordered. Since \( \Delta_r S < 0 \), increasing the temperature will make \( \Delta_r G \) less negative, making the helix-coil transition less favorable.

(b) Is the reaction spontaneous at 39°C? What thermodynamic criterion did you use to reach this conclusion?

Since \( \Delta_r H < T \Delta_r S \) at this temperature, \( \Delta_r H - T \Delta_r S < 0 \) and the reaction is spontaneous at 39°C.

(c) At what temperature (°C) will the helix-coil reaction be reversible? This temperature is often called the “melting” temperature for the helix. Assume that \( \Delta H^0 \) and \( \Delta S^0 \) are independent of temperature. [60° C]

\[
\frac{\Delta_r H - T \Delta_r S}{T} = 0
\]

\[
T = \frac{\Delta_r H}{\Delta_r S} = \frac{-4000}{-12} = 333 \text{ K} = 60^\circ \text{C}
\]

(d) Can a reaction occur in an isolated system which leads to a decrease in the entropy of the system? If it can, give an example; if it cannot, state why not.

No. For an isolated system, \( q = 0 \) which means that \( \Delta S_{\text{sur}} = 0 \) and \( \Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{sur}} < 0 \) which violates the second law of thermodynamics!

5. An electrochemical battery is used to provide 1 milliwatt of power for a (small) light. The chemical reaction in the battery is:

\[
\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightarrow \text{NH}_3(g)
\] (1)

(a) What is the free energy change for the reaction at 25°C, 1 atm?

\[
\Delta_r G^\circ = \Delta_f G^\circ (\text{NH}_3) - \frac{1}{2} \Delta_f G^\circ (\text{N}_2) - \frac{3}{2} \Delta_f G^\circ (\text{H}_2)
\]

\[
= \Delta_f G^\circ (\text{NH}_3) = -16.45 \text{ kJ mol}^{-1}
\]

(b) Calculate the change in Gibbs free energy for this reaction at 50°C, 1 atm. State any assumptions made in the calculation.

If we assume that the enthalpy and the entropy are both independent of temperature,

\[
\Delta_r G(323) = \Delta_r G(298) - (323 - 298) \times \Delta_r S
\]

where
\[
\Delta_r S = \overline{S}(\text{NH}_3) - \frac{1}{2}\overline{S}(\text{N}_2) - \frac{3}{2}\overline{S}(\text{H}_2) \\
= 192.45 - \frac{1}{2} \times 191.61 - \frac{3}{2} \times 130.684 = -99.38 \text{ J mol}^{-1} \text{ K}^{-1}
\]

Therefore,

\[
\Delta_r G(323) = -16.45 - 25 \times (-0.09938) = -13.97 \text{ kJ}
\]

(c) The limiting reactant in the battery is 100 g of H\textsubscript{2}. Calculate the maximum length of time (sec) the light can operate at 25°C. \([5.44 \times 10^8 \text{ s}]

From the answer to part (a), the maximum amount of work that can be done by the battery is 16 450 J/ mol NH\textsubscript{3}. For 100 g of H\textsubscript{2},

\[
w = 16 450 \text{ J/mol NH}_3 \times \frac{2}{3} \text{ mol NH}_3/\text{mol H}_2 \times \frac{1}{2.016} \text{ mol H}_2/\text{g H}_2 \times 100 \text{ g H}_2 = 544 000 \text{ J}
\]

Since the battery is operating at 1 mwatt (or \(10^{-3} \text{ J/sec}\)), the battery can run for \(5.44 \times 10^8 \text{ s}\) or 17 years!

6. The earth’s atmosphere behaves as if it is approximately isentropic – the molar entropy of air is independent of the altitude up to about 10 km. It is well known that pressure and temperature vary with altitude.

Calculate the temperature of the atmosphere 10 km above the earth where \(P = 210 \text{ Torr}\). The temperature and pressure at the surface of the earth (0 km) are 25°C and 760 Torr, respectively. You may assume air behaves as an ideal gas with \(C_P = \frac{7}{2} nR\). You may ignore gravitational influences. \([-66.6\, ^\circ\text{C}]\)

To solve this problem, we use the relationship derived in class, taking \(\Delta S = 0\) for an isentropic system.

\[
\Delta S = C_P \ln \left( \frac{T_f}{T_i} \right) - nR \ln \left( \frac{P_f}{P_i} \right) \\
0 = \frac{7}{2} nR \ln \left( \frac{T_f}{T_i} \right) - nR \ln \left( \frac{P_f}{P_i} \right)
\]

\[
\ln \left( \frac{T_f}{T_i} \right) = \ln \left( \frac{P_f}{P_i} \right) \\
T_f = T_i \left( \frac{P_f}{P_i} \right)^{\frac{7}{2}}
\]

\[
= 298 \times \left( \frac{210}{760} \right)^{\frac{7}{2}} = 206 \text{ K} = -66.6\, ^\circ\text{C}
\]

7. At 298 K the standard enthalpy of combustion of sucrose is -5645 kJ/mol and the standard Gibbs free energy of the reaction is -5797 kJ/mol. Estimate the additional non-expansion work that may be obtained by raising the temperature to blood temperature, \(37^\circ\text{C}\).

\[
\Delta_r G(310) = 310 \times \left[ \frac{\Delta_r G(298)}{298} + \left( \frac{1}{310} - \frac{1}{298} \right) \Delta_r H \right] = -5803 \text{ kJ mol}^{-1}
\]

Therefore, the maximum amount of non-PV work is 5803 kJ per mole of sucrose, and the additional non-PV work is 5803-5797 = 6 kJ.