

yet more

Quick review of classical thermodynamics, part 2

Chemistry 422/522, Spring 2021

To repeat, from the first lecture: please read Chapters I and II in the Slater handout, and look at Chapters 3, 6, and 10 in the Dill and Bromberg book.

1 Free energy minimization

Consider dividing the universe to two parts, the "system" of interest, and everything else (also called the "bath"). See pp. 132-133 of MDF.



$$dU_{system} + dU_{bath} = 0 \quad \text{first law} \quad (1)$$

$$dS_{total} = dS_{system} + dS_{bath} \geq 0 \quad \text{second law} \quad (2)$$

$$dU = TdS - pdV + \bar{\mu}dN \Rightarrow dS_{bath} = \frac{dU_{bath}}{T} = -\frac{dU_{sys}}{T} \quad (3)$$

if the bath is at constant T, V and N. Combining the last two equations, we can get an expression just in terms of the system:

$$dU_{sys} - TdS_{sys} \equiv dA_{sys} \leq 0 \quad \star \quad (4)$$

here, for the system at constant T, V and N. This proves our little lemma, that maximizing the entropy of universe corresponds to minimizing the free energy of the system.

2 H and S as functions of T

Question: why are heat capacities so important in thermodynamics? Let's go to constant pressure for a moment:

$$C_p = \left(\frac{\partial q_{rev}}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad (5)$$

$$\Delta H \equiv H(T_2) - H(T_1) = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T} \right)_p dT = \int_{T_1}^{T_2} C_p(T) dT = C_p \Delta T \quad (6)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \quad (7)$$

This leads to a hierarchy of approximations: (a) treat H as independent of temperature; (b) treat C_p as independent of temperature; (c) treat dC_p/dT as independent of temperature, etc.

$$C_p(T) = a + bT + \frac{1}{2}cT^2 + \dots$$

$$G(T)$$

One needs to be careful not to ignore the temperature dependence of thermodynamic quantities like H , G , etc. Suppose you were asked about the temperature dependence of $G = H - TS$. You might be tempted to treat H and S as constants and do the following (everything here is assumed to be at constant pressure and composition):

$$\frac{\partial(G/T)}{\partial T} = \frac{\partial(H/T - S)}{\partial T} = H \left(\frac{\partial(1/T)}{\partial T} \right) = -\frac{H}{T^2} \quad \text{wrong!} \quad (8)$$

This is insidious, because the the answer is actually correct, but the derivation is wrong. You should do the following, treating $G(T)$, $H(T)$, and $S(T)$ as functions of temperature:

$$\frac{\partial(G/T)}{\partial T} = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right) - \frac{G}{T^2} = -\frac{1}{T^2} \left[G - T \left(\frac{\partial G}{\partial T} \right) \right] = -\frac{G + TS}{T^2} = -\frac{H}{T^2} \quad (9)$$

3 Phase transitions and chemical equilibria

Staying at constant pressure and temperature, for a two component system:

$$dG = -SdT + Vdp + \sum_{i=1}^2 \mu_i dn_i = \sum_i \mu_i dn_i = \mu_1 dn_1 + \mu_2 dn_2 \quad (10)$$

But we must have $dn_1 = -dn_2$ or $dG = (\mu_1 - \mu_2)dn_1$. At equilibrium G is minimized, hence $dG = 0$ and $\mu_1 = \mu_2$. The chemical potential μ is an "escaping tendency": the higher its value the more molecules want to leave.

