Lecture 16

Entropy Content in Materials

Last Time

Constant P and T processes: $T\Delta S_{\textbf{universe}} = -\Delta G_{\textbf{system}}$

Equilibrium at Constant P and T processes: $\Delta G_{\textbf{system}} = 0$

If $\overline{G}^{\alpha} > \overline{G}^{\beta}$ **then** α **can transform to** β

Constant V and T processes: $T\Delta S_{\textbf{universe}} = -\Delta F_{\textbf{system}}$

Behavior of Gibbs Free Energy near a Phase Change

Consider how the molar Gibbs energy changes near the equilbirum temperature in an environment that is a constant fixed pressure:

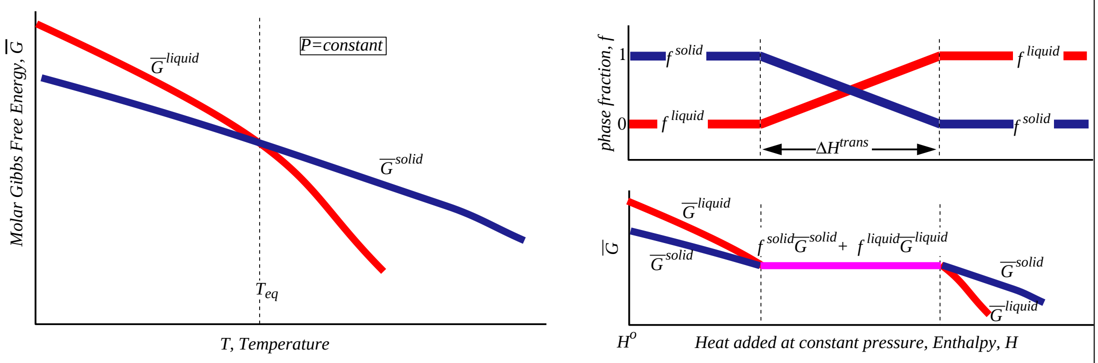

Figure 16-1: Illustration of the behaviors of the molar Gibbs free energies for two phases behave as a function of temperature and as a function of added heat.

The Third Law of Thermodynamics

However, I've slipped something past you. I've given numbers for entropy without saying where they come from. To get entropies of a substance, we need to introduce our fourth, and final law of thermodynamics.[16]

Third Law: The limiting value of the entropy of a system can be taken as zero as the absolute value of temperature approaches zero.

There is really not much interesting to say about this now. Most applications of the the third law appear in statistical mechanics.[17] Except, notice that it allows us to calculate the absolute value of entropy by integrating $\int_{T=0}^{\text{any state}} \frac{dq_{\text{rev}}}{T}$

A Survey of Molar Entropies

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[16] Complicated discussion but potentially useful for your general knowledge of entropy appears in Denbigh, 13.1–2

[17] One interesting thing: entropy has a universal reference state, while energy quantities do not.

Consider the following data:

Material	Molar Entropy at STP ($\frac{\text{J}}{\text{mole}^\circ\text{K}}$)
Diamond	2.5
Platinum	41.2
Lead	64.0
Laughing gas	217.1

What do we observe; what correlations can we make?

Graphite is particularly illustrative of this point. Its molar entropy is in the same ballpark as diamond but higher. This correlates with its rigid bonds within the close-packed planes and weak van der Waals bounds out of plane.

$$\overline{S}_{\text{C(graphite), STP}} = 5.5 \frac{\text{J}}{\text{mole}^\circ\text{K}} \tag{16-1}$$

Consider another list of data:

Material	Molar Entropy at STP ($\frac{\text{J}}{\text{mole}^\circ\text{K}}$)
Copper	2.5
NaCl	71.4
ZnCl_2	108.4

What observations or generalized can be made??

If a substance has several different forms (phases, crystal structures, etc.), then the higher entropy forms tend to be stable at high temperature (Note $\overline{G} = \overline{H} - T\overline{S}$, low $\overline{G}$ correlates with the more stable phases.

In other words, melting and evaporation tend to have positive changes in their entropy values. We already observed for H_2O:

Molar Entropies of H_2Oat STP	
Solid (ice)	41.0 $\frac{\text{J}}{\text{mole}^\circ\text{K}}$
Liquid (wawa)	63.2 $\frac{\text{J}}{\text{mole}^\circ\text{K}}$
Vapor (steam)	184.2 $\frac{\text{J}}{\text{mole}^\circ\text{K}}$

The molar entropies rise with stability at higher temperature.

Wait a minute!

Vapor is not stable at STP! (Neither is ice . . .)

Question: How can we write down a number for something that isn't stable?

Consider our original enthalpy diagram:

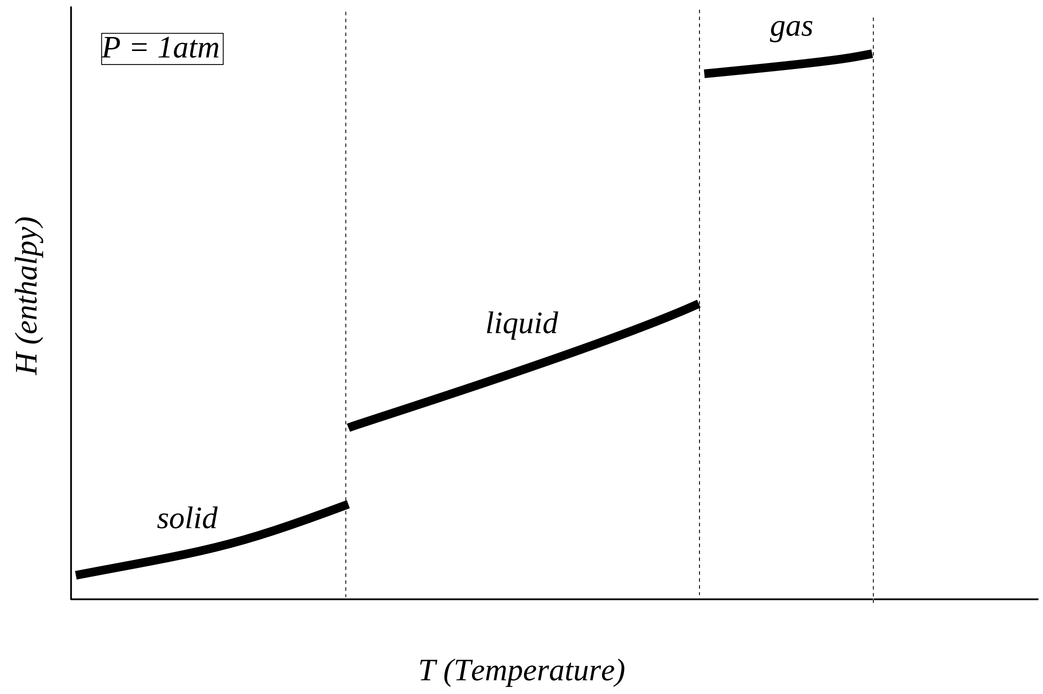

Figure 16-2: Molar Enthalpies of solid, liquid, and vapor water as a function of temperature.

We extrapolate the enthalpy by fitting a curve for the heat capacity:

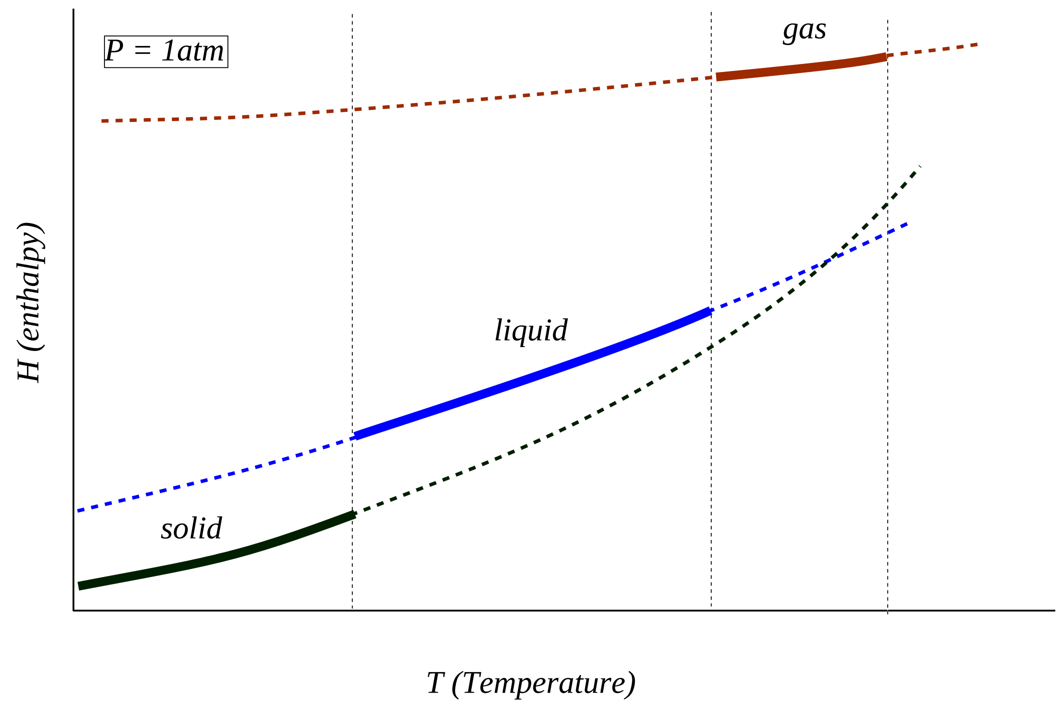

Figure 16-3: Extrapolating the Enthalpy by fitting a curve for the heat capacity.

$$\overline{H}(T) - \overline{H}(T_\circ) = \int_{T_\circ}^{T} \overline{C_p} dT \quad \text{(constant pressure)} \tag{16-2}$$

Furthermore, we can use the definition of entropy to integrate the entropy so enthalpies are measured with regard to standard state.

Or, if it is known at some other state,

$$\overline{S}(T) - \overline{S}(T_\circ) = \int_{T_\circ}^{T} \frac{\overline{C_p}}{T} dT \quad \text{(constant pressure)} \tag{16-3}$$

Microscopic Origins of Entropy in Materials

In pure substances, entropy may be divided into three parts.

1. Translational degrees of freedom (e.g., monatomic ideal gas molecules have these).
2. Rotational degrees of freedom (e.g., non-spherical molecules in fluids have these).
3. Vibrational degrees of freedom (e.g., non-spherical fluid molecules and solids have these).

In non-pure substances (e.g. a solution of A-B) another degree of freedom arises which relates to the ways that the system can be mixed up. Entropy tends to decrease with addition of a solute—this will be discussed when we consider solutions.

Statistical Mechanical Definition of Entropy
Extra (i.e., not on test) but Potentially Instructive Material

Ludwig Boltzmann is credited with the discovery of microscopic definition of entropy. The definition is remarkably simple—however, it is not at all simple to show that Boltzmann's microscopic definition of entropy is the same one as we use in continuum thermodynamics: $dS = dq_{rev}/T$.

Boltzmann's definition relates the entropy of a system to the number of different ways that the system can store a fixed amount of energy:

$$S(U) = k \log \Omega(U) \tag{16-4}$$

where U is the internal energy of a system and Ω is the number of distinguishable ways that the system can be arranged with a fixed amount of internal energy. The proportionality constant is the same one that relates kinetic energy to temperature—it is called Boltzmann's constant and is the ideal gas constant R divided by Avogadro's number.

One way to interpret equation 16-4 is that if an isolated system (i.e., fixed U) can undergo some change such that the number of states increases, it will do so. The interpretation of this is that if all observations are equally probable, the state of the system with the most numerable observations is the one that is *most likely* to be observed. This is a slight change from our continuum definition of the second law which stated that an observation of decreased universal entropy is impossible. The statistical mechanical definition says that an observation of universal increased entropy is *not probable.*

Every course in statistical mechanics will have a section that demonstrates out that—for all but the very smallest systems—the probability of an observation of entropy decrease is so small that it virtually never occurs.

Why should there be a logarithm in equation 16-4? Remember that entropy is an extensive quantity. The number of different states of two systems A and B increase when those state are considered together is the product $\Omega_A \Omega_B$.[a] Therefore, if $S_{total} = S_A + S_B$ then a function is needed that when the product of the number of states occurs then the function is added. The logarithm has this behavior: $\log \Omega_{AB} = \log \Omega_A + \log \Omega_B$.

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[a] To demonstrate this consider the number of states that a coin (heads (h) or tails (t)—$\Omega_{coin} = 2$) and a die (die is the singular of dice, $\Omega_{die} = 6$) can occupy when the coin and die are considered together. The possible states are $\overbrace{h1}, \overbrace{h2}, \ldots \overbrace{h6}, \overbrace{t1}, \ldots \overbrace{t6}$ and there are $2 \times 6 = 12$ different states.

Figure 16-4: Ludwig Boltzmann's ground state and, apparently, the formula for which he wished to be remembered with....