

Oct. 16 2002: Lecture 16:

Entropy Content in Materials

Last Time

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

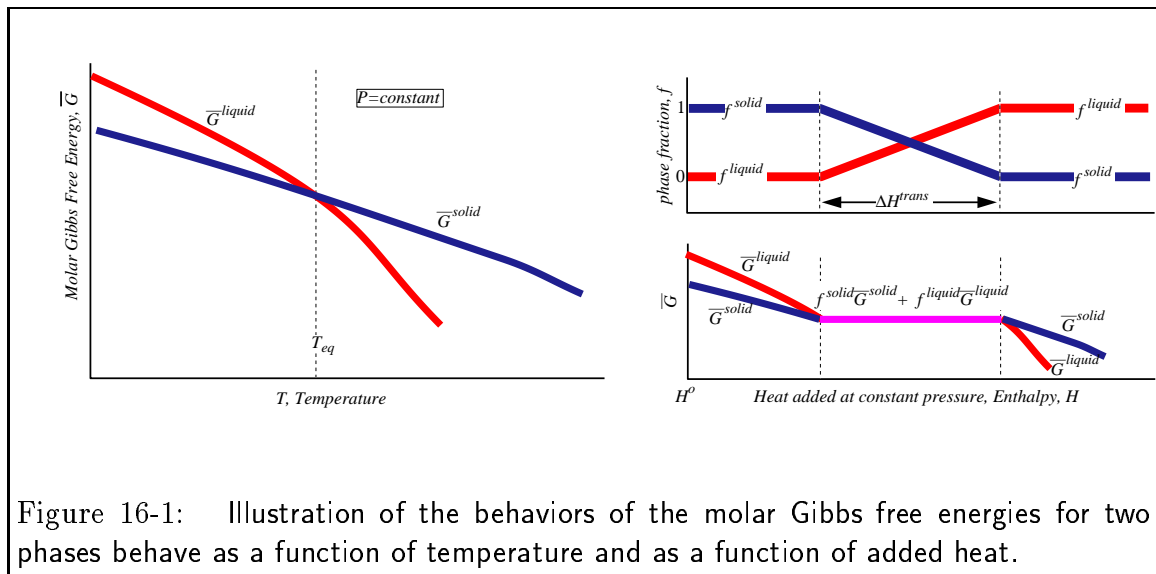
Equilibrium at Constant P and T processes: $\Delta G_{\text{system}} = 0$

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

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

Behavior of Gibbs Free Energy near a Phase Change

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



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

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.

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_2O at 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)	$184.2 \frac{\text{J}}{\text{mole}^\circ\text{K}}$

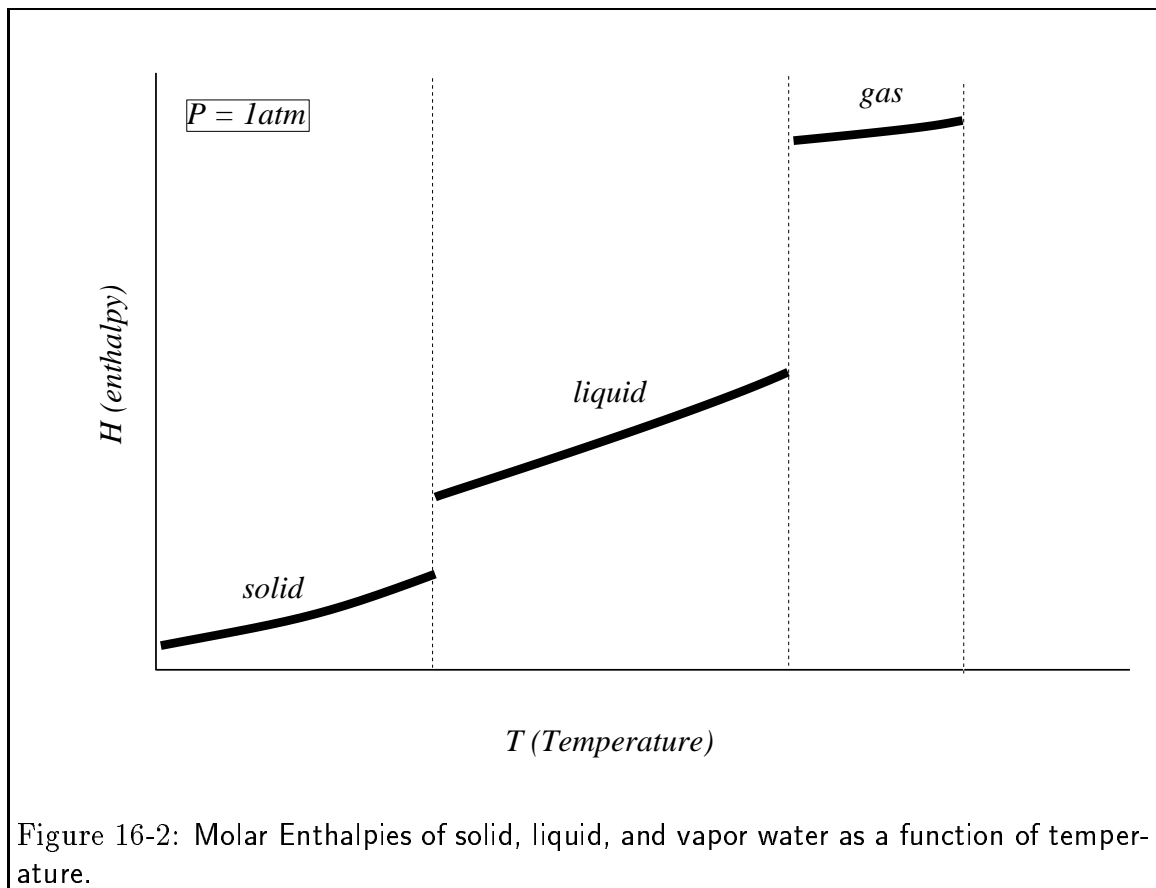
The molar entropies rise with stability at higher temperature.

Wait a minute!

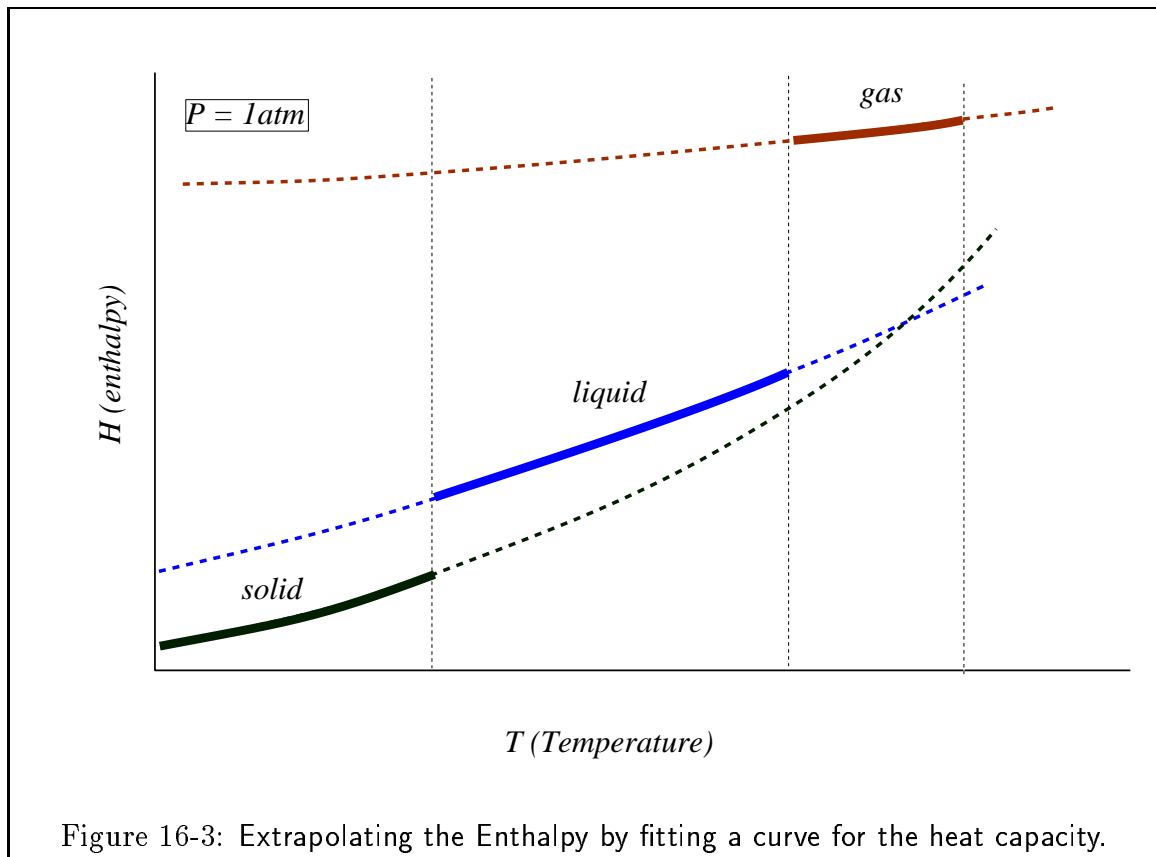
Vapor is not stable at STP! (Neither is ice . . .)

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

Consider our original enthalpy diagram:



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



$$\overline{H}(T) - \overline{H}(T_0) = \int_{T_0}^T \overline{C}_p dT \quad (\text{constant pressure}) \quad (16-2)$$

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,

$$\overline{S}(T) - \overline{S}(T_0) = \int_{T_0}^T \frac{\overline{C}_p}{T} dT \quad (\text{constant pressure}) \quad (16-3)$$

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.

