

Lecture 15

Gibbs Free EnergyLast Time**Heat of Transformation**

Phase Fractions

Hot Ice Melts and $\Delta S_{\text{universe}} > 0$

Cold Ice Doesn't Melt and the Entropy of the Universe Remains Constant

_____ The Temperature where Universe's Entropy Change is Zero _____

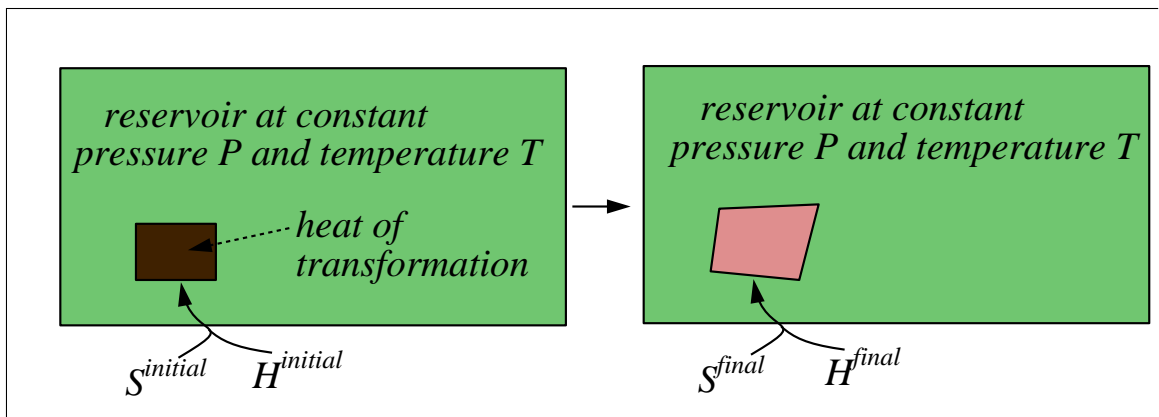


Figure 15-1: Illustration of how the entropy of the universe was calculated for a phase transformation occurring for a body that is kept at constant pressure and temperature. At constant pressure, the heat of transformation is provided by the enthalpy change in the material undergoing a transformation. Application of the first and second laws results in an expression for the entropy change in the universe.

Data for H₂O at 273°K and 1 atm

Quantity	Symbol	Data
Molar Enthalpy of Melting	$\overline{\Delta H_{\text{melt}}}$	$6008 \frac{\text{J}}{\text{mole}}$
Molar Entropy of liquid H ₂ O	$\overline{S_{\text{H}_2\text{O liquid}}}$	$63.2 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
Molar Entropy of solid H ₂ O	$\overline{S_{\text{H}_2\text{O solid}}}$	$41.0 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
Molar Heat Capacity of liquid H ₂ O	$\overline{C_{P_{\text{H}_2\text{O liquid}}}}$	$75.44 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
Molar Heat Capacity of solid H ₂ O	$\overline{C_{P_{\text{H}_2\text{O solid}}}}$	$38.0 \frac{\text{J}}{\text{mole}^\circ\text{K}}$

The data showed that the entropy change in the universe was positive if: 1) the high-temperature phase (liquid) converted to the low-temperature phase (ice) below the equilibrium transition (freezing) temperature; or, 2) The low-temperature phase (ice) converted to the high-temperature phase (liquid) above the equilibrium transition (melting) temperature. Furthermore, the entropy change of the universe would be negative if ice melted below the melting temperature, or if water froze above the freezing temperature.

Similar statements can be written down generally for any phase transformation:

In fact, it only happens that $\Delta S_{\text{universe}} = 0$ for freezing and melting at only one temperature (at fixed pressure), and that is:

$T_{\text{melt}} = T_{\text{freeze}} = 273\text{K}$ for H_2O at 1 atm pressure..

In fact, at that temperature

$$\overline{H}^{\text{liquid}} - T\overline{S}^{\text{liquid}} = \overline{H}^{\text{solid}} - T\overline{S}^{\text{solid}} \quad \text{if } T = T_{\text{melt}} \quad (15-1)$$

and this reintroduces a new thermodynamic function.

Because H was the available thermal energy at constant P (recall the argument that $U+PV$ was subtracting of the available compressive energy),

$$G \equiv H - TS \quad (15-2)$$

must be related to the available energy after the “compressive” term and “thermal” term are removed. This new function must be the internal energy available to do “other kinds of work” at constant P , and T .

G is called the Gibbs free energy.

We can rewrite Equation 15-1 in terms of the new function:

In fact this,

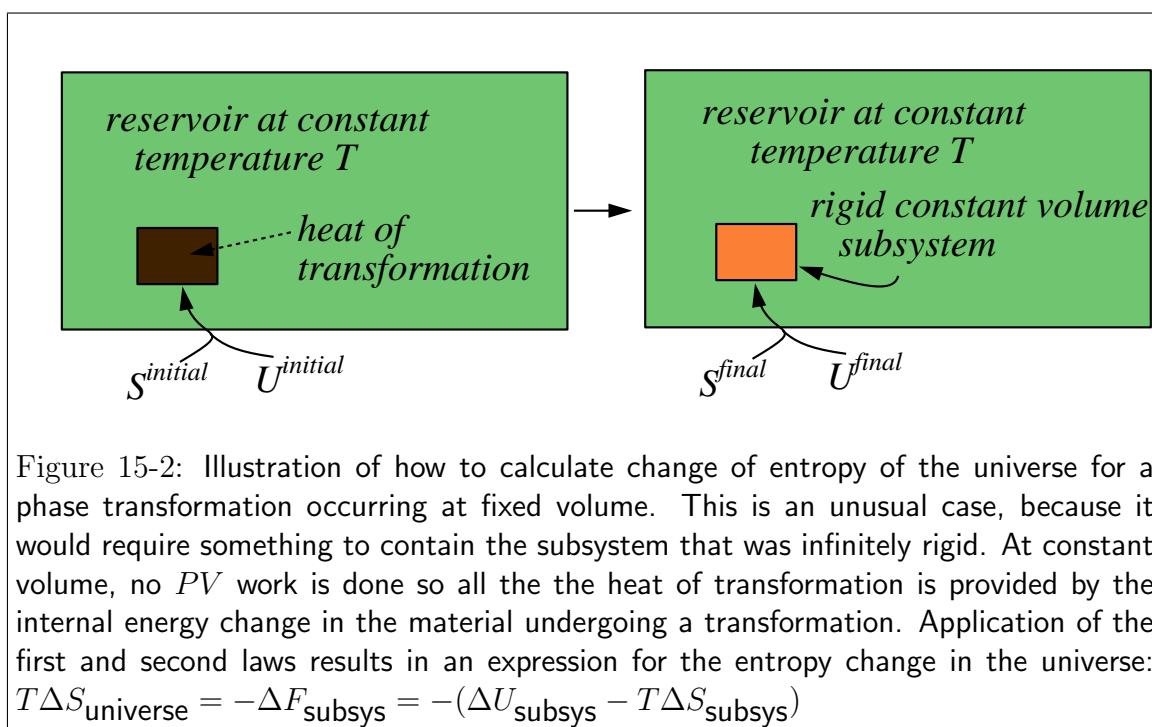
will become our most favorite criteria for equilibrium at constant P and T .

Note that there are several equivalent ways to write the Gibbs free energy in terms of the other thermodynamic functions that we have introduced.

Some of the relations for the *molar* Gibbs free energy are:

$$\bar{G} = \bar{H} - T\bar{S} = \bar{F} + P\bar{V} = \bar{U} - T\bar{S} + P\bar{V} \quad (15-3)$$

Note that if we had considered a phase change that takes place at constant volume:



Summary of Equilibrium Conditions		
Change	Special Condition	Utility
$\Delta S_{\text{universe}} = 0$	All cases	Fundamental criterion for reversible process or equilibrium by the second law of thermodynamics. Must be applied to every possible subsystem affected by a process.
$\Delta G_{\text{system}} = 0$	System at constant P and T	Fundamental criterion for reversible process or equilibrium for typical experimental conditions. Calculation need only consider the system undergoing change—but extra conditions, i.e., constant P and T must be assumed.
$\Delta F_{\text{system}} = 0$	System at constant V and T	Fundamental criterion for reversible process or equilibrium for isothermal constant volume phase transition. This will not differ much from ΔG for systems that have a small ΔV associated with the transformation.

Nature Prefers Low Enthalpies at Low T

and Large Entropies at High T

The behavior of G during a phase change.

Consider how the molar Gibbs energy changes when ice melts:

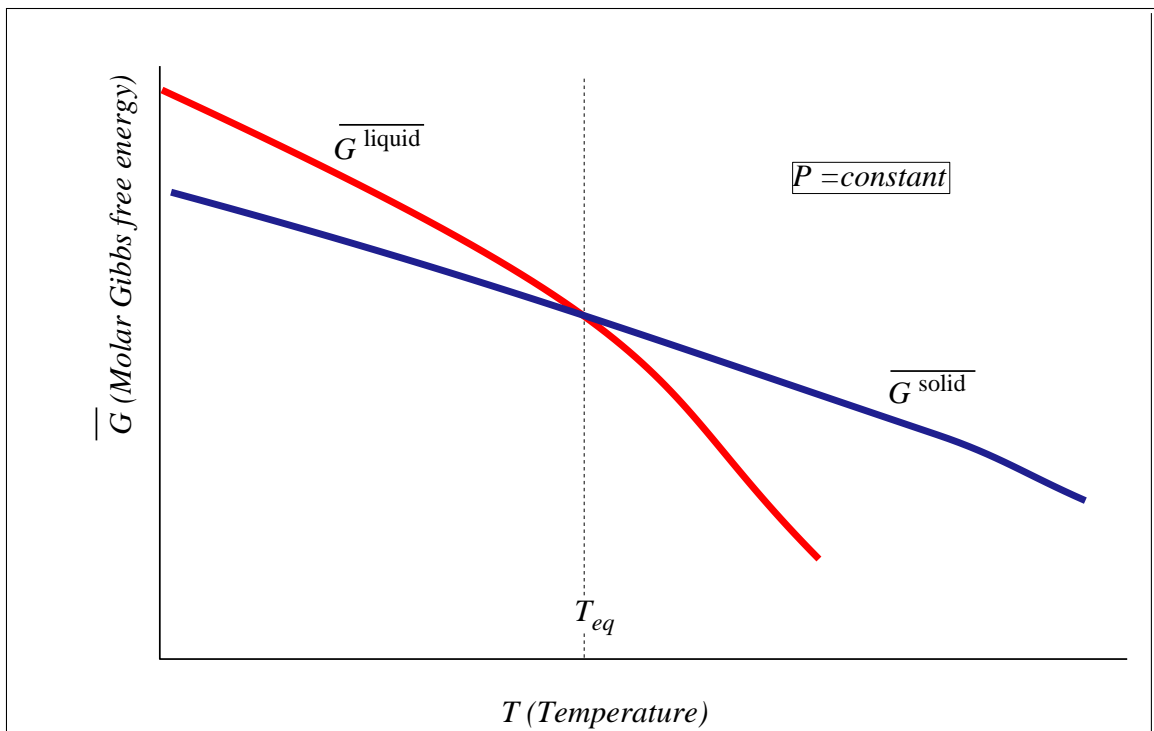


Figure 15-3: Plot of molar free energy of solid and liquid phases against temperature. **The curve with the lowest value of G indicates which phase is most stable at that particular temperature.**

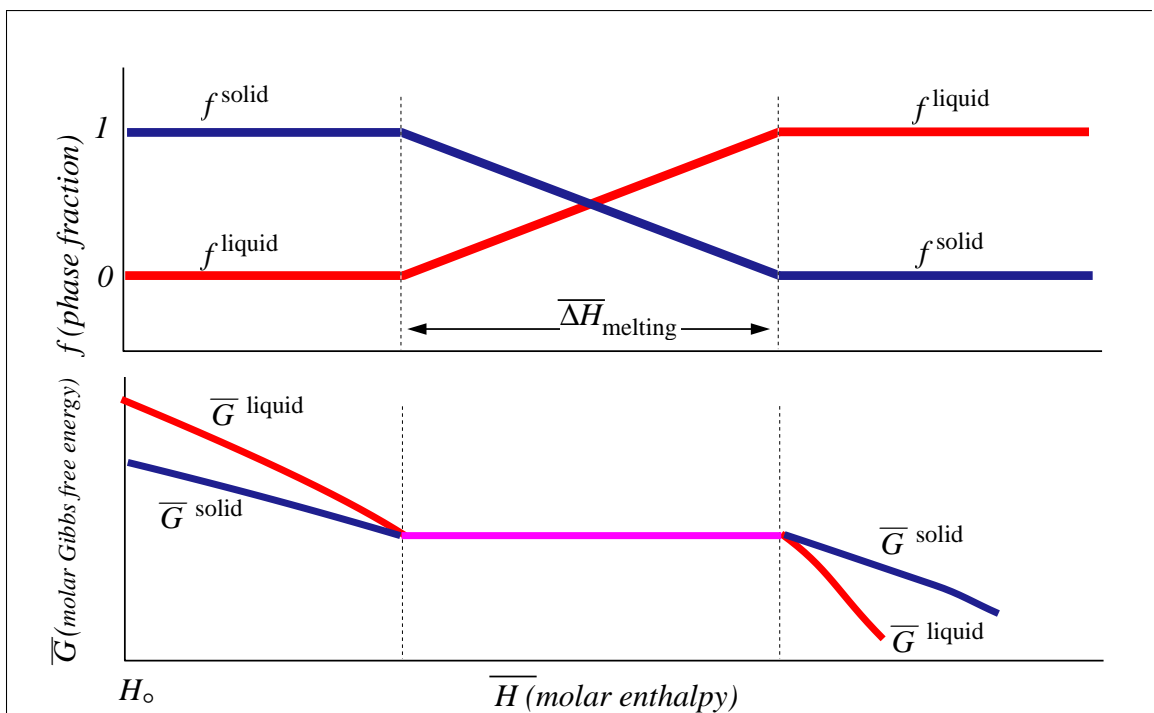


Figure 15-4: Plot of phase fractions of the molar free energy of solid and liquid phases against enthalpy. **The molar Gibbs free energy of each phase is equal during the transformation regardless of how much material is present.**