

Thermodynamics: Entropy and Free Energy

Inspired by Paul Groves

A BLUFFER'S GUIDE

1. There are two driving forces for reactions. Reactions tend toward:

minimum **Enthalpy**, ΔH (heat energy)

$\Delta H -$, $\Delta H < 0$, downhill

maximum **Entropy**, ΔS (randomness)

$\Delta S +$, $\Delta S > 0$, uphill

2. Recognize whether $\Delta S > 0$ or < 0

Entropy increases, $\Delta S +$, $\Delta S > 0$:

- from solid to liquid to gas
- fewer moles (g) to more moles (g)
- simpler molecules to more complex molecules
- smaller molecules to longer molecules
- ionic solids with strong attractions to ionic solids with weaker attractions
- separate solute & solvent to solutions
- gas dissolved in water to escaped gas

3. Product or Reactant favored reactions depend on ΔH , ΔS , and absolute Temp

ΔH	ΔS	Product-Favored...
+	+	at higher temperatures
-	-	at lower temperatures
-	+	at all temperatures
+	-	never (reactant-favored at all temps)

	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	Spontaneous at all T ($\Delta G < 0$)	Spontaneous at high T (when $T\Delta S$ is large)
$\Delta S < 0$	Spontaneous at low T (when $T\Delta S$ is small)	Non-spontaneous at all T ($\Delta G > 0$)

5. Many books use the term "spontaneous" for "product-favored."

A spontaneous reaction does not necessarily mean a fast reaction.

The SPEED of a reaction is Kinetics...we are discussing whether a reaction CAN OCCUR which is Thermodynamics.

6. Gibbs Free Energy, ΔG , puts the effects of ΔH , ΔS , and Temperature together.

$$\Delta G = \Delta H - T\Delta S$$

$\Delta G < 0$, $\Delta G -$, product-favored reaction

$\Delta G > 0$, $\Delta G +$, reactant-favored reaction

$\Delta G = 0$, reaction is at equilibrium

Note that ΔH is usually in kJ/mol

ΔS is usually in J/mol·K

$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = \Delta G_{\text{sys}}$			
ΔH	ΔS	ΔG	At...
- <i>exothermic</i>	+ <i>more disorder</i>	- <i>ALWAYS spont.</i>	Any temp
+ <i>endothermic</i>	- <i>less disorder</i>	+ <i>NEVER spont.</i>	Any temp
- <i>exothermic</i>	- <i>less disorder</i>	- <i>spont.</i>	Low Temp
- <i>exothermic</i>	- <i>less disorder</i>	+ <i>NOT spont.</i>	High Temp
+ <i>endothermic</i>	+ <i>more disorder</i>	- <i>spont.</i>	High Temp
+ <i>endothermic</i>	+ <i>more disorder</i>	+ <i>NOT spont.</i>	Low Temp