

Lecture 19: Gibbs

Helmholtz, Gibbs, Temperature dependence, Thermodynamic Stability

Overall Motivation for Helmholtz and Gibbs

Third Law:

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

Annoying to calculate $\Delta S_{\text{universe}}$ each time to determine spontaneity
Need a new state function!

Helmholtz Derivation

Consider a process at constant T and V

Third Law:

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \geq 0$$

Since we are at constant volume:

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} \geq 0$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} - \frac{\Delta U}{T} \geq 0$$

Rewriting as differentials:

$$dU - T dS \leq 0$$

$$d(U - TS) \leq 0$$

Helmholtz Free Energy

Helmholtz

$$A = U - TS$$

$$\Delta A = \Delta U - T\Delta S$$

$$\Delta A = \Delta U - q_{\text{rev}}$$

ΔA : Amount of non-PV work a system can do at constant T, V

First Law:

$$\Delta U = q + w$$

$$= q_{\text{rev}} + w_{\text{PV}} + w_{\text{non-PV}}$$

$$\Delta A = q_{\text{rev}} + \cancel{w_{\text{PV}}} + w_{\text{non-PV}} - q_{\text{rev}} = w_{\text{non-PV}}$$

$\Delta A < 0$ Does work Spontaneous

$\Delta A > 0$ Needs work Non-spontaneous

Gibbs Derivation

Consider a process at constant T and P

Third Law:

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \frac{q_{\text{surr}}}{T} \geq 0$$

Since we are at constant pressure:

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} - \frac{q_{\text{sys}}}{T} \geq 0$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} - \frac{\Delta H}{T} \geq 0$$

Rewriting as differentials:

$$dH - T dS \leq 0$$

$$d(H - TS) \leq 0$$

Gibbs

$$G = H - TS$$

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

$\Delta G < 0$ spontaneous

$\Delta G = 0$ equilibrium

$\Delta G > 0$ non-spontaneous

$$G = H - TS = U + PV - TS$$

$$dG = dU + PdV - TdS$$

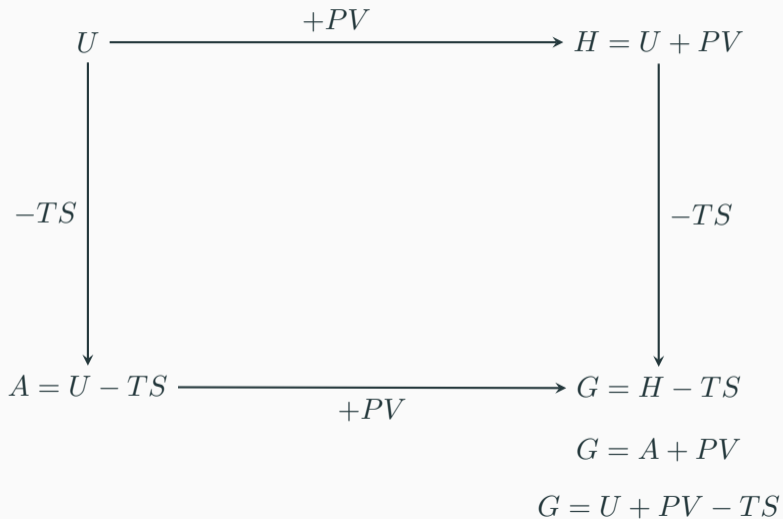
$$dU = TdS - PdV + w_{\text{non-PV}}$$

$$dG = w_{\text{non-PV}}$$

The non-PV work corresponds to:

- Chemical work: μdn
- Electrical work: εdq
- Magnetic work: $H dm$

Symmetry of state functions



Equations involving Gibbs

Equations involving Gibbs

$$\Delta G^\circ = \Delta H^\circ - 298 \text{ K} \cdot \Delta S^\circ$$

$$\Delta G_T = \Delta H^\circ - T\Delta S^\circ$$

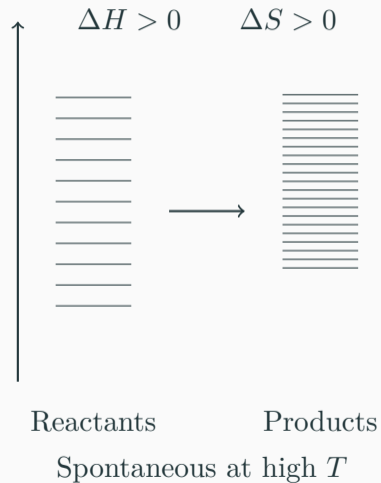
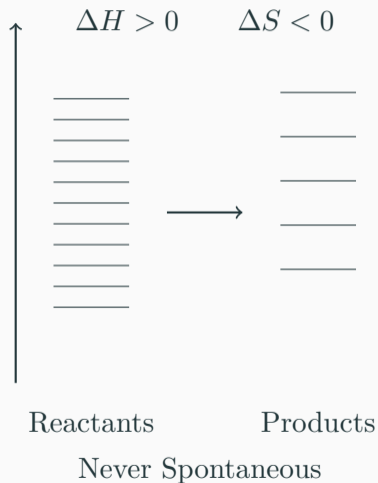
$$\Delta G_{\text{rxn}}^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum n\Delta G_f^\circ(\text{reactants})$$

ΔH	ΔS	Spontaneous?
-	-	low T
-	+	Always
+	-	Never
+	+	high T

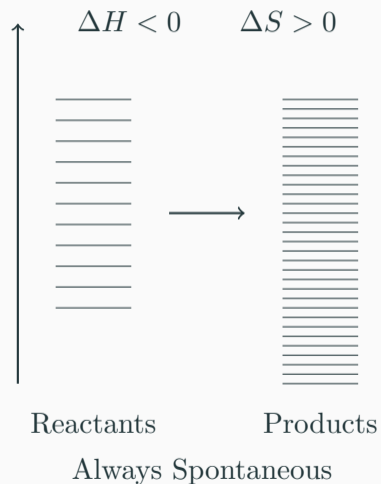
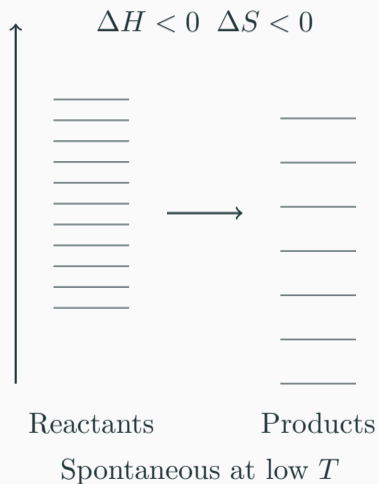
$\Delta G_T = \Delta H^\circ - T\Delta S^\circ$ assumes no temperature dependence of ΔH° , ΔS°

ΔG_f° is standard gibbs free energy of formation, $\Delta G_f^\circ = 0$ for standard state

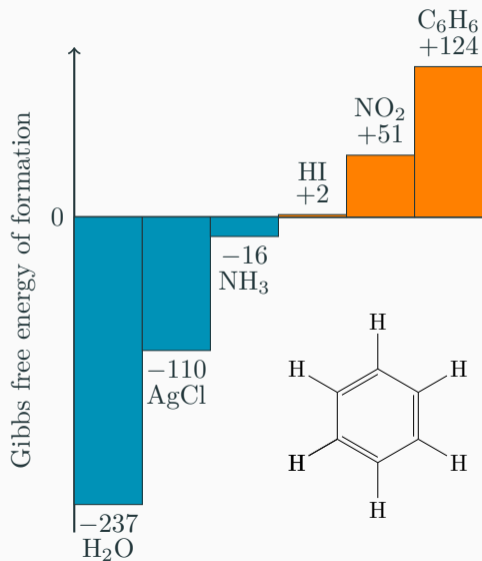
Temperature Dependence of Spontaneity



Temperature Dependence of Spontaneity



Thermodynamic Stability



Unlike ΔH_f where the sign does not have meaning, ΔG_f does have physical meaning

Sign of ΔG_f°

Tells you if a compound exists under standard conditions based on thermo

$\Delta G_f^\circ < 0$: thermodynamically stable

$\Delta G_f^\circ > 0$: thermodynamically unstable

Only considers thermodynamics, completely ignores kinetics