Gibbs (Free) energy

A proxy for the total entropy change

Relationship between S and H

- For a given energy change (ΔH at constant pressure), the change in entropy (ΔS) will be greater at **lower** temperatures
- We can relate them by:
- Units of S are J/K, and H are J.

$$\Delta S = \frac{\Delta H}{T}$$

Total entropy change – hard to

- Use a proxy – Gibbs Free energy ΔG
- We will express the changes that take place only in terms of the system – not the surroundings.

ΔG uses only system terms

- $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
- And we know that $\Delta S = \Delta H/T$
- $\Delta S_{total} = \Delta S_{system} + \Delta H_{surroundings}/T$
- $\Delta H_{system} = -\Delta H_{surroundings}$
- $\Delta S_{total} = \Delta S_{system} - \Delta H_{system}/T$
  - (multiply by –T)
- $-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system}$

- $\Delta G = \Delta H - T\Delta S$
- Use ΔG (or ΔG° - at standard state – 298K) to find out if the process will "go" (be spontaneous)
- Enthalpy (ΔH) tells us about thermal energy – but during every change some energy is lost – spreads out – and becomes useless
- ΔG tells us what is left – available – free to do work

Free energy

- When ΔG is negative - equivalent to ΔS (for the universe) being positive.
  - Criterion for a process to "go"
  - Often termed "spontaneous" but this it misleading – many spontaneous reactions take a long time to happen.
- But ΔG is temperature dependent – so we have to look at both ΔH and ΔS to predict the sign of ΔG

ΔG and temperature

ΔH	ΔS	ΔG
Negative (exothermic)	Positive (system entropy increases)	Negative at all temperatures – (always thermodynamically favored
Positive (endothermic)	Negative (system entropy decreases)	Positive at all temperatures (never thermodynamically favored)
Negative (exothermic)	Negative (system entropy decreases)	Depends on the temperature, as T increases ΔG will become more **positive** and the reaction will
Positive (endothermic)	Positive (system entropy increases)	Depends on the temperature, as T increases ΔG will become more **negative** and the reaction will