<u>A bluffer's guide to Thermodynamic Equilibrium</u>... entropy, enthalpy, free energy and compensation effects:

There is a natural tendency for all things (even atoms & molecules) to roll downhill to fall to lower energy.

 Δ H tends to want to be negative



This is opposed (at the molecular level) by the equally natural tendency for thermal/Brownian motion (otherwise known as "entropy") to make things go the other way...

... and this effect gets bigger as the temperature increases.

 $T.\Delta S$ tends to want to be positive



Thermodynamic Equilibrium, expressed in terms of the Gibbs Free Energy change, reflects just the balance between these opposing tendencies...

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

Equilibrium is reached when these two forces just balance ($\Delta G = 0$).

The <u>standard</u> free energy change, ΔG° , is just another way of expressing the equilibrium constant, or affinity (K) for any process, on a logarithmic scale...

$$\Delta G^{\circ} = -RT.lnK$$

<u>Entropy-Enthalpy compensation</u> is a natural consequence of this: systems with higher enthalpy tend also to have higher entropy, but these tend to compensate to give relatively much smaller changes in free energy.

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