Chapter 6::Chemical equilibrium

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Gibbs energy

Abstract

We would like to determine the spontaneity of a reaction mixture to approach equilibrium, along with deriving the thermodynamic equilibrium constant K_p and equilibrium concentraations of reactants and products in a mixture of reactive ideal gases. We define Gibbs energy (ΔG), which expresses spontaneity in terms of properties of the system alone.

Suppose we have an arbitrary system σ in thermal equilibrium with the surroundings. What determines the directions of a spontaneous change? Well, it would be the tendency of a system to minimize energy.

$$-dq_\sigma = dq_{surr} \implies dS_\Omega + dS_{surr} \geq 0 \implies dS_\sigma + \frac{dq_{surr}}{T} \geq 0$$

Definition

$$\Delta G_\sigma = \Delta H_\sigma - T\Delta S_\sigma \implies dG_\sigma = dH_\sigma - TdS_\sigma$$

If we graph this relation, we notice that ΔG is a function of T. ΔH would be ΔG_0 and the slope would be ΔS.

Gibbs energy holds the following properties::

- $\Delta G < 0 \implies \sigma \equiv spont \implies exergonic$

- $\Delta G > 0 \implies \sigma \equiv \neg spont \implies endergonic$

- Gibbs energy is an extensive property, and is a state function.

When a problem concerns Gibbs energy, we only care about **what happens in the system, not the surroundings**.

Differential forms of U, H, and G

For an infinitessimal process::

$$G = H + TS \implies dG = dH - TdS - SdT$$

According to the first law::

$$dH = dU + PdV + VdP \implies dU = dq + dw \implies dU = dq - PdV$$

For a reversible process::

$$dq_{rev} = TdS, dU = TdS - PdV$$

So,

$$dH = TdS + VdP, dG = VdP - SdT, dU = TdS - PdV$$

This only applies for **expansion** work.