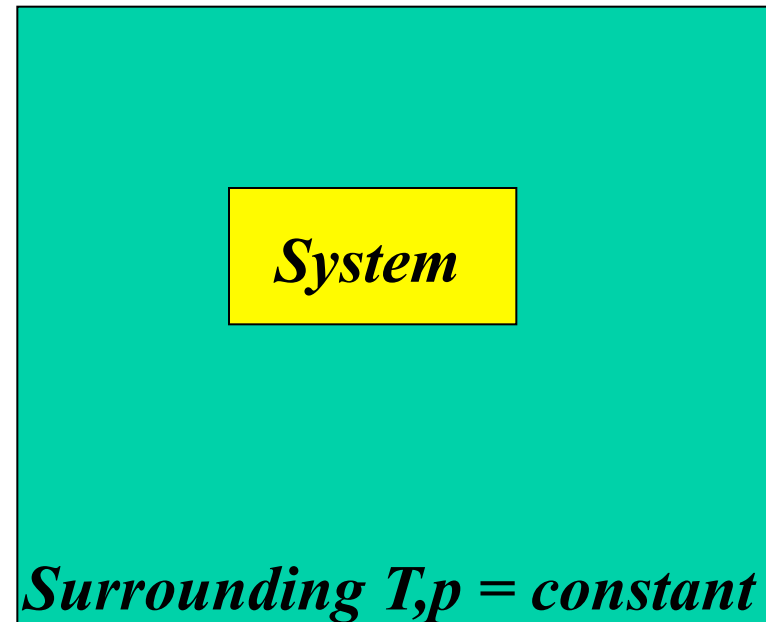


The Second Law of Thermodynamics allows to determine which processes are spontaneous.

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

The problem with applying such criteria is that you must account for the whole Universe.

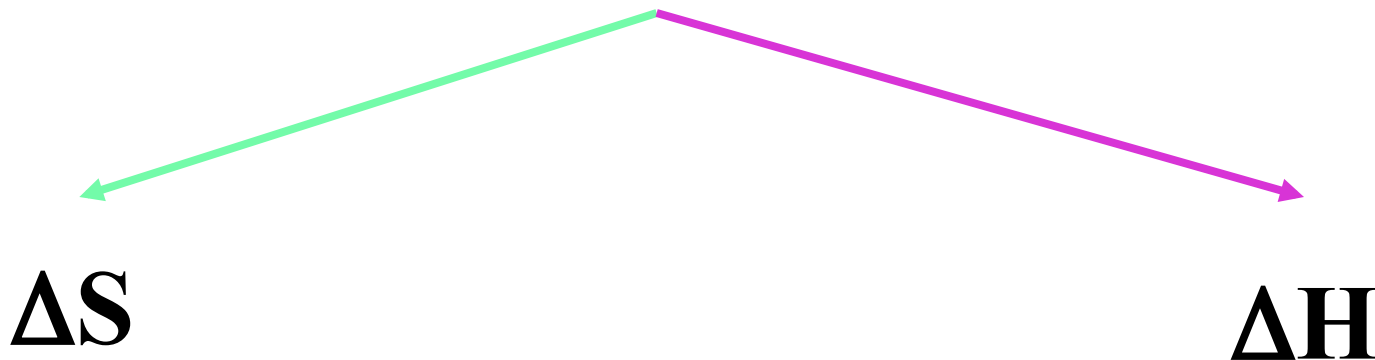
Surrounding stays in equilibrium at temperature T and pressure p.



There are two natural tendencies behind spontaneous processes:

- the tendency for a *lower energy state*
- the tendency toward a *more energy dispersed state*

Spontaneity involves



Heat that flows into or out of the system changes the entropy of the surroundings.

$$\Delta S_{\text{surr}} \Big|_{T=\text{const}} = \frac{-q_{\text{surr}}}{T}$$

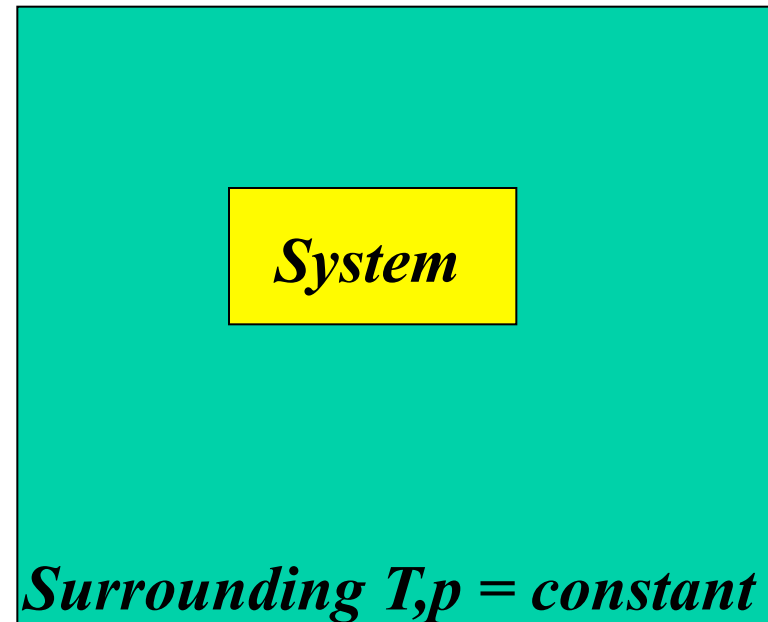
$$q_{\text{surr}} \Big|_{p=\text{const}} = -q_{\text{p}} = \Delta H_{\text{sys}}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{surr}}}{T} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{-\Delta H_{\text{sys}}}{T}$$

$$-T\Delta S_{\text{univ}} = -T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}$$



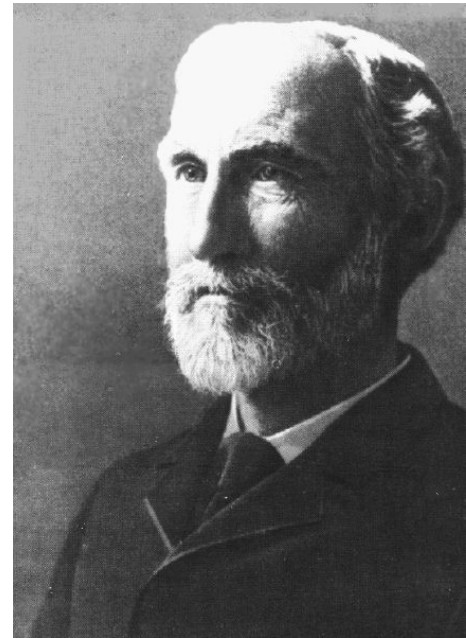
Definiton of a new function - *Gibbs free energy* - it allows to focus on the system.

$$\Delta G_{\text{sys}} = -T\Delta S_{\text{univ}}$$

$$\Delta G_{\text{sys}} = -T\Delta S_{\text{sys}} + \Delta H_{\text{sys}}$$

At constant p and T , ΔG_{sys} can be used in the place of $\Delta S_{\text{universe}}$ to predict the direction of a process.

The surrounding enters only in a generic, anonymous way, through one number, its temperature T .



Gibbs
1839-1903
Professor of
Mathematical
Physics, Yale
University

The enthalpic part of Gibbs free energy is a measure of the average potential energy of interaction between molecules, and the entropic part is a measure of the order or intermolecular correlations.

Gibbs free energy

Extensive property

State function

ΔG allows us to predict whether a process is spontaneous or not (under constant T and p):

$\Delta G < 0 \Rightarrow$ spontaneous in forward direction

$\Delta G > 0 \Rightarrow$ non-spontaneous in forward direction

$\Delta G = 0 \Rightarrow$ at equilibrium

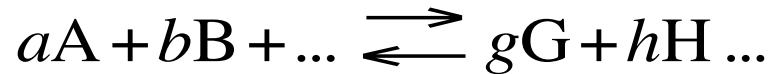
ΔG is the energy which is “free” to do work.

Second law restated for a system

For any spontaneous process or reaction:

$$\Delta G_{sys} < 0$$

Gibbs Free Energy of reaction



$$\Delta G = G(\text{final state}) - G(\text{initial state})$$

$$\Delta G = g \mu_G + h \mu_H + \dots - a \mu_A - b \mu_B - \dots \quad \text{from } \mu_i = \mu_i^0 + RT \ln C_i \text{ it follows:}$$

$$\Delta G = g \mu_G^0 + h \mu_H^0 + \dots - a \mu_A^0 - b \mu_B^0 - \dots + RT \ln \frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots}$$

The direction of the reaction depends upon

- *Energy content of participants*
- *Reactant-to-product ratio*

ΔG does not indicate the rate of the process.

A reaction in an equilibrium

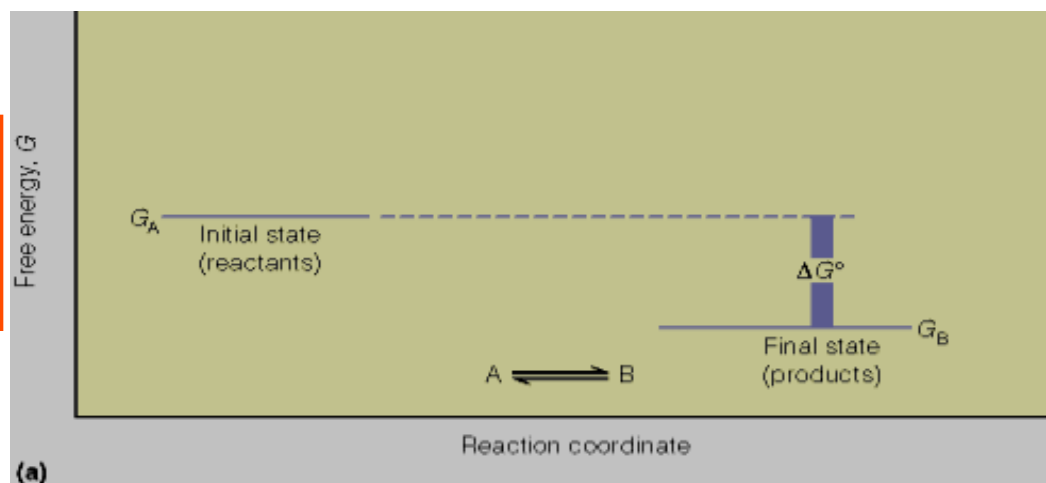
$$0 = \Delta G^0 + RT \ln \left(\frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} \right)_{\text{Eq}}$$

$$\Delta G^0 = -RT \ln \left(\frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} \right)_{\text{Eq}} = -RT \ln K$$

The **standard free-energy of reaction (ΔG^0)** is the free-energy change for a reaction when it occurs under standard-state conditions.

ΔG^0 , the standard free energy change for a reaction determines *the relative concentrations of reactants and products that will be found at thermodynamic equilibrium.*

$$K = \left(\frac{[G]^g [H]^h \dots}{[A]^a [B]^b \dots} \right)_{\text{Eq}} = \exp \left(\frac{-\Delta G^0}{RT} \right)$$

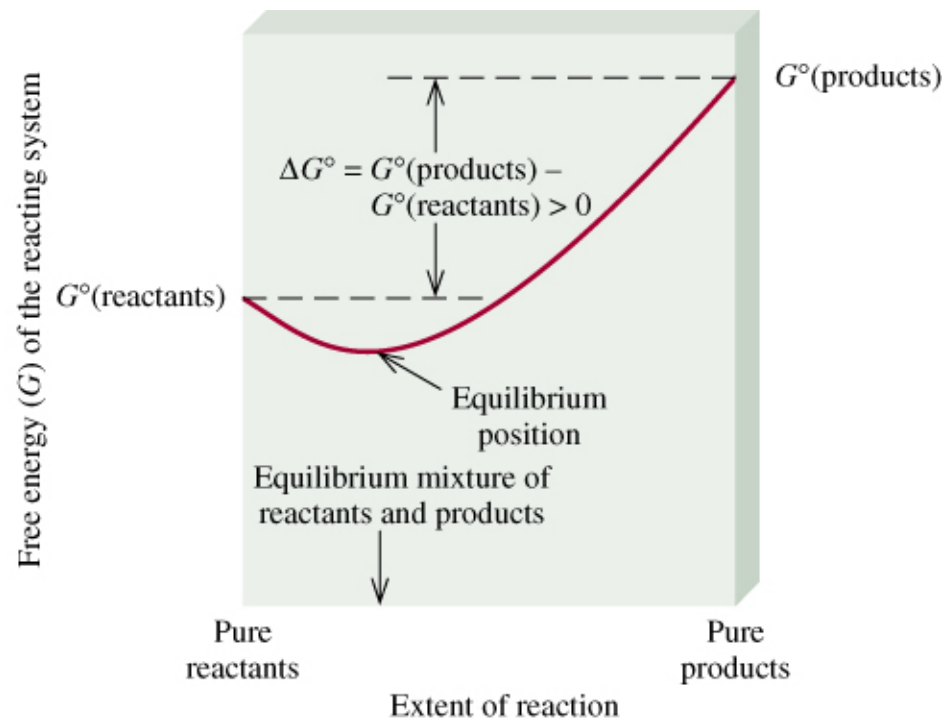
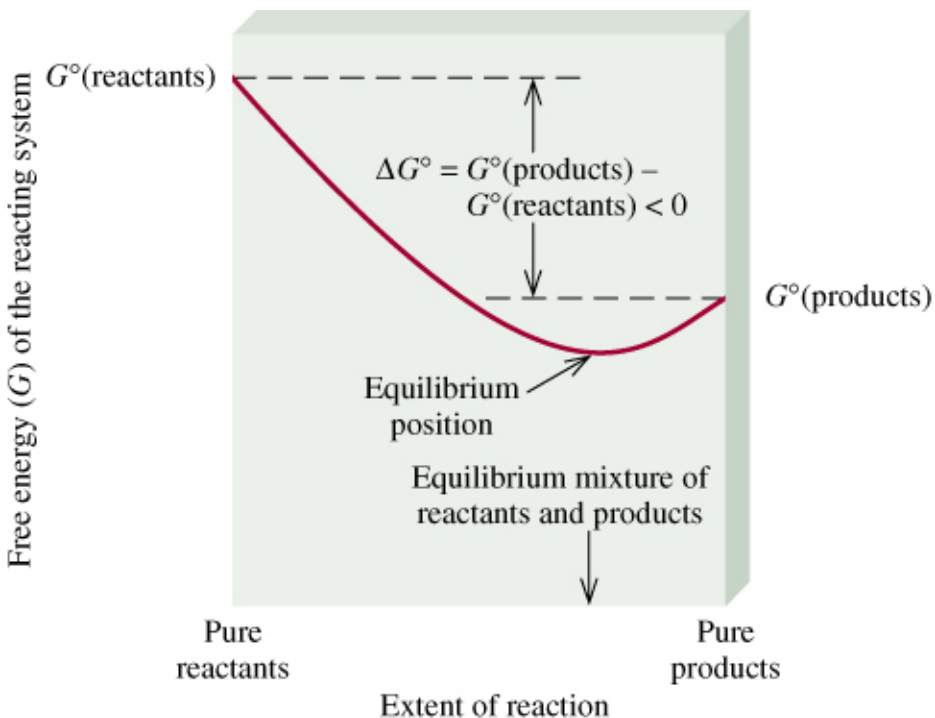


$$\Delta G^0 = \sum n \Delta G^0 (\text{products}) - \sum m \Delta G^0 (\text{reactants})$$

$$\Delta G^0 < 0$$

$$\Delta G^0 = -RT \ln K$$

$$\Delta G^0 > 0$$



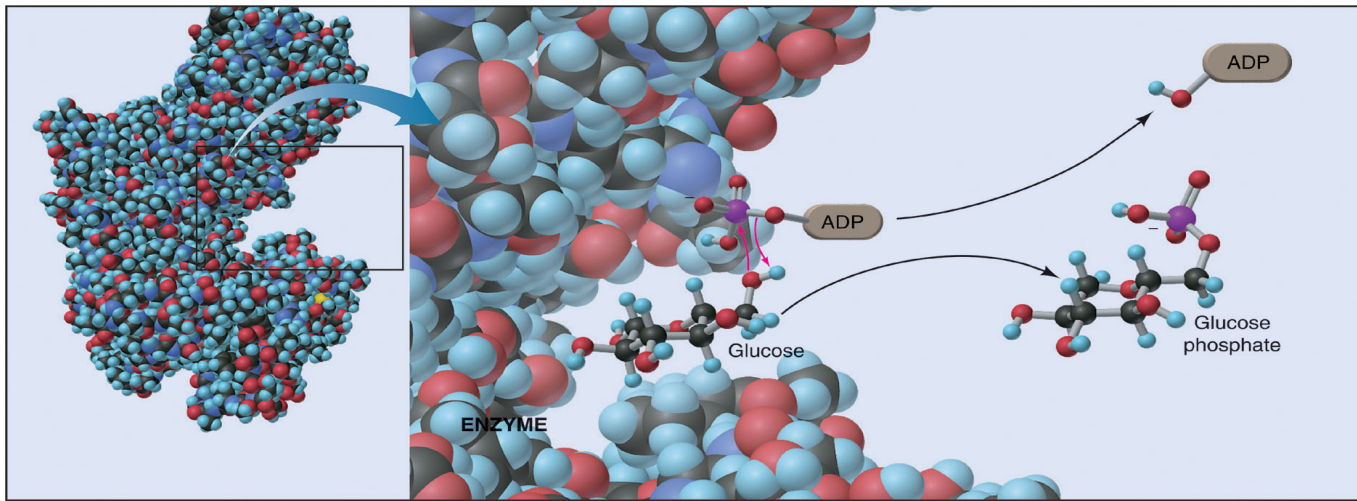
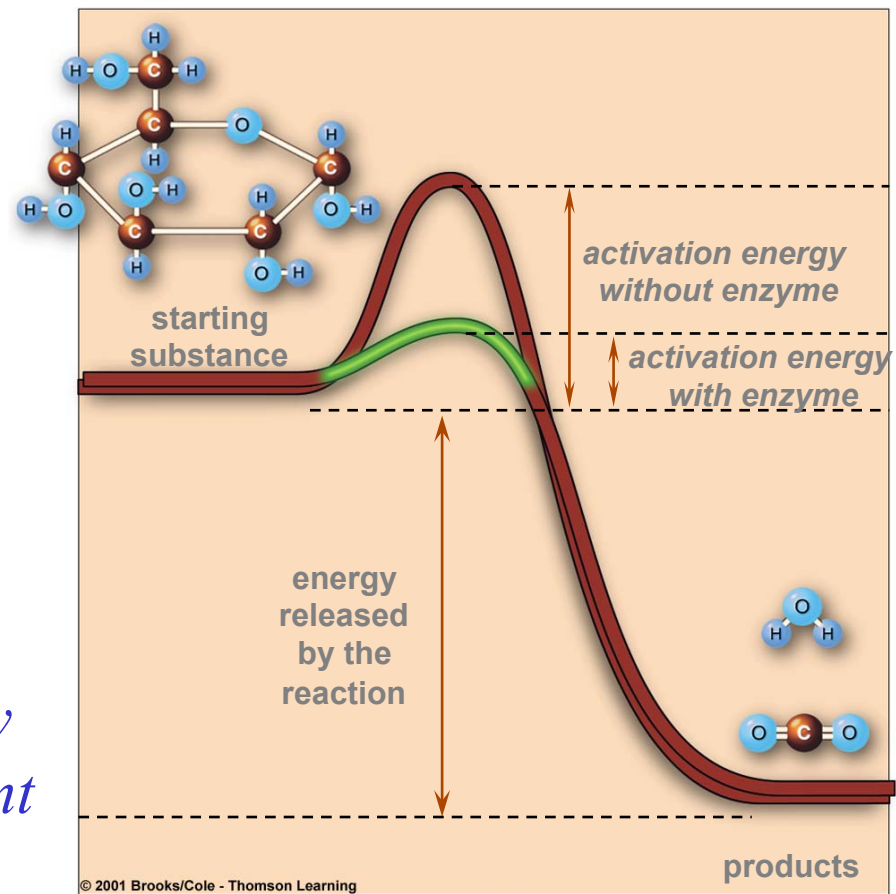
K	$\ln K$	ΔG°	Comments
> 1	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
< 1	Negative	Positive	Reactants are favored over products at equilibrium.

K and ΔG^0 reveal nothing about the rates of process nor information about the height of the barrier between these states.

The rate of a chemical reaction is dependent on the free energy of activation (transition state).

$$\text{rate} = A \cdot e^{-E_a / RT}$$

A catalyst (enzyme) lowers the Energy of activation but does not alter reactant or product free energies.



Protein denaturation

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

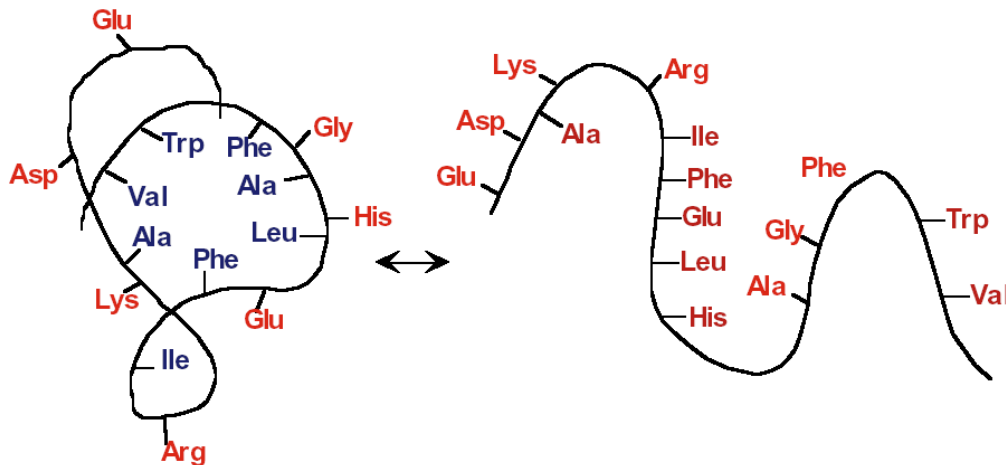
T is the temperature (in Kelvin) where the reaction is at equilibrium.

$$\Delta G = 0$$

$$T = \frac{\Delta H^0}{\Delta S^0}$$

ΔH^0 – includes the components of the binding energy and intra- and inter-molecular interactions

ΔS^0 – includes effect of molecular rearrangement.



Protein denaturates at $T \geq 60^\circ\text{C}$ where the $T\Delta S$ term carries more weight and offsets the large positive ΔH .