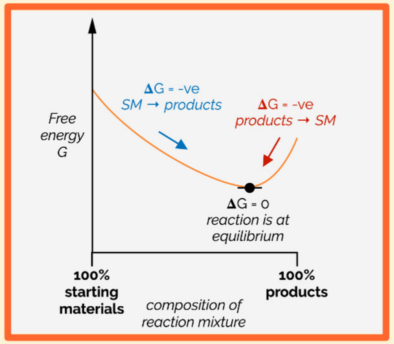
HIGHLIGHTS

- What is an equilibrium reaction?
- What is the position of the equilibrium & how do you determine the equilibrium constant K_c?
- How is the equilibrium constant K_c related to the free-energy change?
- What terms control the magnitude of the free-energy change?
- Enthalpy & entropy.



Many synthetic chemists forget that reactions are equilibrium processes.

A reaction reaches equilibrium when the rate of the forward and backward transformations are the same. The concentrations of the starting materials & products do not have to be equal. The position of the equilibrium is given by the ***equilibrium constant K_c***, the ratio of starting material to product.

The size of the equilibrium constant is related to the ***Gibbs free-energy change of reaction***, and for a reaction to proceed, it must be ***negative***, meaning energy is released. The free-energy change is made up of two terms with ***enthalpy*** relating to the stability of the reactants & products while ***entropy*** is a measure of disorder.

This summary was written from a synthetic chemists viewpoint & simplifies the subject greatly so don't expect the mention of activities, standard states & all that malarky.

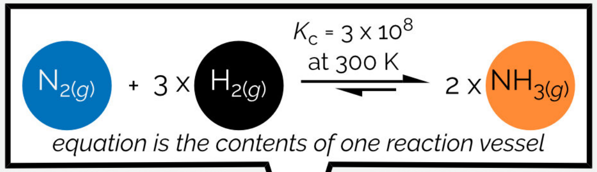
CHEMISTRY CLASSICS

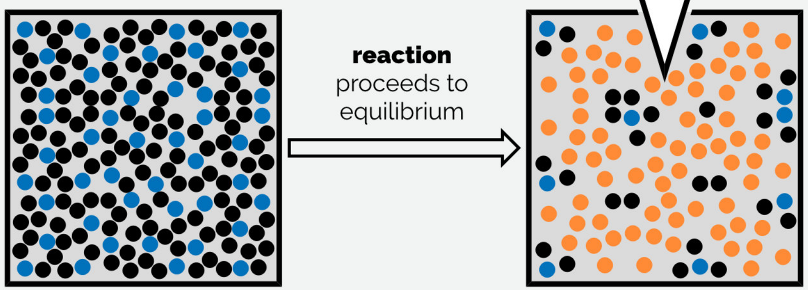
EQUILIBRIA

BY A SYNTHETIC CHEMIST

Equilibria (by a synthetic chemist)

1. Equilibrium Reactions





initial mixture
before reaction

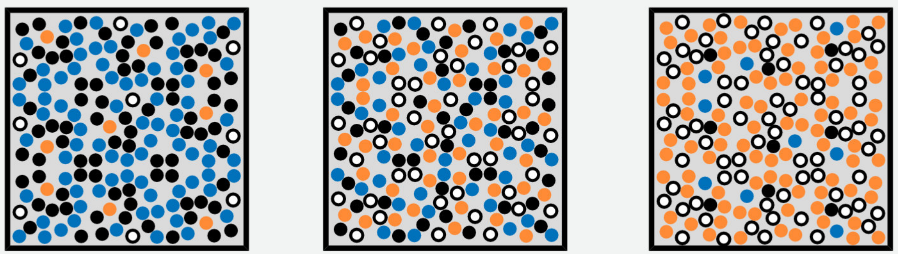
equilibrium mixture
(no indication of rate/time)

At equilibrium, the rate of the forward reaction, forming products, equals the reverse process that gives starting materials. The concentration of each can be different.

$$a\,\mathrm{A} + b\,\mathrm{B} \underset{\text{at ? °C}}{\overset{K_c}{\rightleftharpoons}} c\,\mathrm{C} + d\,\mathrm{D} \qquad K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

Position of the equilibrium given by ***K***, the ***equilibrium constant***, at a given temperature. For simplicity, use K_c, equilibrium constant of ***concentration*** & not activity (activity approx. equal to concentration for dilute solutions).

2. Meaning of K_c



K_c < 1
favours ***left***-hand side
$K_c < 10^{-2}$
1% products

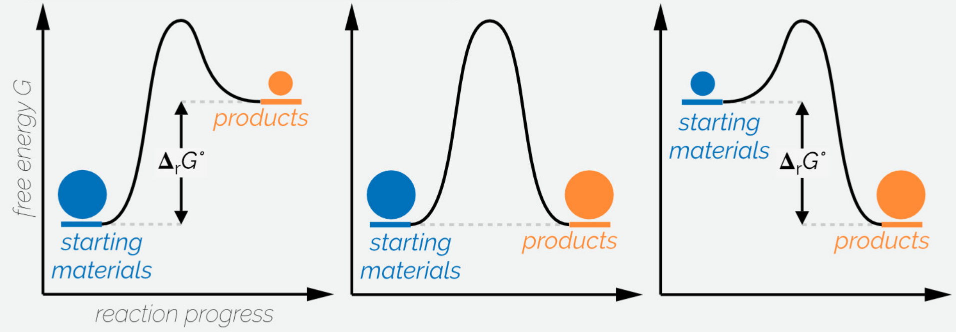
K_c = 1
50:50 mixture of
starting material:product

K_c > 1
favours ***right***-hand side
$K_c < 10^2$
99% products

3. The Position of K_c & Gibbs Free-Energy Change

$\Delta_rG° = G°_{products} - G°_{starting\ materials}$
$\Delta_rG°$ negative forward reaction favoured

$\Delta_rG° = -RT \ln K_c$ or $K_c = e^{(-\Delta_rG°/RT)}$
R = gas constant 8.314 J K^{-1} mol^{-1}; T = temp. (in K)



K_c < 1
ΔG° is positive
favours left-hand side

K_c = 1
ΔG° is 0

K_c > 1
ΔG° is negative
favours right-hand side

The amount of product (& SM) is related to the Gibbs free-energy change, ΔG°, which is equal to the difference in free energy between the products & starting materials.

4. Gibbs Free-Energy

starting materials → products
ΔG negative
forward reaction spontaneous

ΔG = ΔH – TΔS
ΔH = change in enthalpy
ΔS = change in entropy

Gibbs free-energy is made up of two terms: ***enthalpy*** & ***entropy***. The change in ***enthalpy***, ΔH relates to the ***stability*** of the products or the difference in strength between the bonds broken and formed in the reaction. ***Entropy*** a measure of disorder/randomness (simplistic definition).

The sign of ΔG can tell you if the reaction, as written, is ***spontaneous*** or not. If ΔG is ***negative*** the reaction is spontaneous.