Thermodynamics – why does a reaction occur?

2.0 intro to thermo and G

Gibbs free energy (G) - energy for a reaction to occur at a constant temp and pressure.

- When G is negative, the reaction is **spontaneous/exergonic** (energy releasing) and will occur without any input of energy; This is also called a forward reaction where reactants form products/ products favored.
- When G is positive, the reaction is **non-spontaneous/endergonic** (energy consuming) and would require an input of energy; This is also called a reverse reaction where products form reactants/ reactants favored.
- When G equals 0, the reaction is considered to be **at equilibrium** because neither the forward nor reverse reactions are favored.

2.1 equilibrium

$$\Delta G = \Delta G^0 + RT\ln Q$$

Equation 2.1

ΔG is the non-standard Gibbs free energy (J/mol), ΔG° is the standard Gibbs free energy (J/mol), R is the ideal gas constant (8.314 J/mol*K), T is the temperature (K), and Q is the reaction quotient (unitless).

Standard conditions (what does the ° mean?)

- ΔG° is ΔG when the conditions are standard, meaning the pressure is 1 atm and the concentration is 1 M (mol/L). However standard conditions are rare to come by, thus other factors allow us to quantify the change in G (i.e. RTlnQ).

Reaction Quotient (Q) - ratio of initial concentration of products to initial concentration of reactants

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

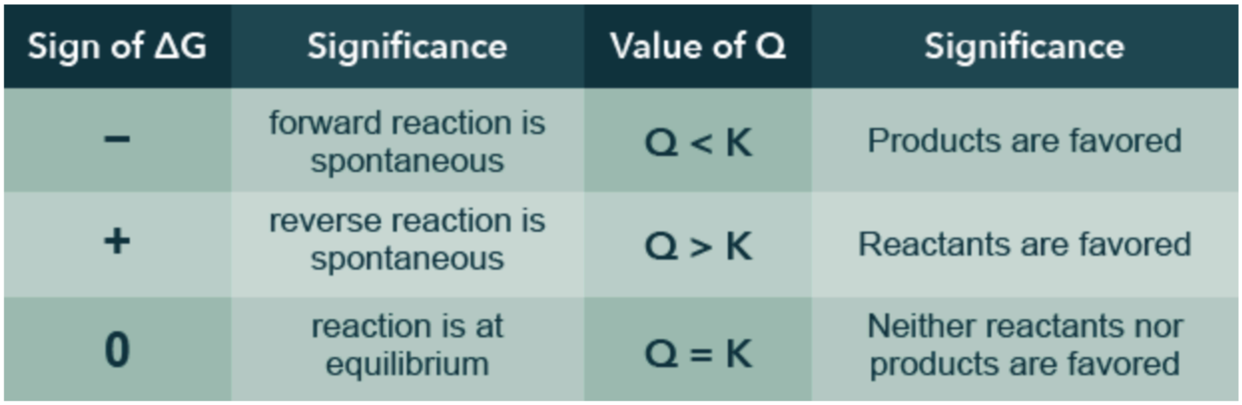
When there are stoichiometric coefficients (a,b,c,d), Q is calculated using.

- Reactants appear in the reaction quotient differently, when they are pure substances:
  - Gases (denoted with a g) are included using its pressure in atmospheres (atm) rather than concentration
  - Solids (denoted with an s) and liquids (denoted with an l) contribute a value of 1

G at equilibrium

- K_{eq} is Q at equilibrium, and defines reaction when there is no spontaneous change.

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



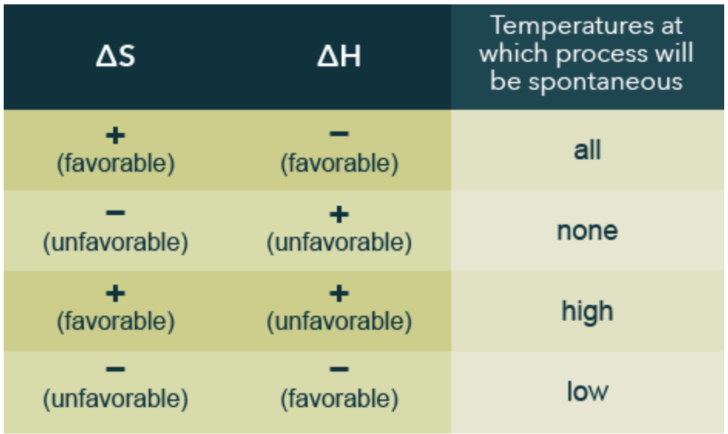
Sign of ΔG	Significance	Value of Q	Significance
–	forward reaction is spontaneous	Q < K	Products are favored
+	reverse reaction is spontaneous	Q > K	Reactants are favored
0	reaction is at equilibrium	Q = K	Neither reactants nor products are favored

2.2 Balance of Enthalpy and Entropy

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

where ΔG is the change in Gibbs free energy (J or J/mol), T is the temperature (K), ΔS is the change in entropy of the system (J/K or J/mol*K), and ΔH is the change in enthalpy of the system (J or J/mol).

Enthalpy (H) - the flow of heat during a reaction
Entropy (S) - measure of the distribution of energy in a reaction. The more molecules, the more entropy.



ΔS	ΔH	Temperatures at which process will be spontaneous
+ (favorable)	− (favorable)	all
− (unfavorable)	+ (unfavorable)	none
+ (favorable)	+ (unfavorable)	high
− (unfavorable)	− (favorable)	low

Table 2.3

2.3 standard Gibbs free energy

- In standard conditions, the Q is 1 thus:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT\mathit{ln}Q\\ &= \Delta G^\circ + RT\mathit{ln}(1)\\ &= \Delta G^\circ + RT(0)\\ &= \Delta G^\circ\end{aligned}$$

  -

$$\Delta G^\circ_{rxn} = \Sigma(n \times \Delta G^\circ_{f,prod}) - \Sigma(n \times \Delta G^\circ_{f,react})$$

Equation 2.6

the sum of all the ΔG°_f values of the reactants are subtracted from all the ΔG°_f values of the products. The *n* terms in the equation represent the stoichiometric coefficients of each reactant and product in the reaction

2.4 enthalpy

Enthalpy (H) is the heat flow at constant pressure.

$$\Delta H^\circ_{rxn} = \Sigma(n\times\Delta H^\circ_{f,prod}) - \Sigma(n\times\Delta H^\circ_{f,react})$$

Equation 2.7

-

<u>2.5 entropy</u>

Entropy - distribution of energy in reaction

- Molecules can translate, vibrate, and rotate; they have 3N total modes of motion, called **degrees of freedom**.
  - N is number of atoms in compound

Microstate - one possible arrangement of energy in a system (i.e. vibrate, translate, rotate). Which produces a macrostate.

Macrostate - is the collection of measured properties of system (temp, pressure, position, momenta of molecules and atoms) > you don't have to understand this just know, 3N gives degrees of freedom.

- Microstates make up different macrostates; sometimes different microstates can make up the same macrostate

<u>2.5A The Boltzmann Equation</u>

- Entropy is given by:

$$S = k_B \ln W$$

Equation 2.8

  -

where S is the entropy of the system (in units of J/K), kB is the Boltzmann constant (1.381×10−23 J/K), and W is the number of microstates corresponding to the measured macrostate of the system. The Boltzmann constant is equal to the gas constant R (8.3145 J/mol·K) divided by Avogadro's constant (6.022 × 1023 mol–1)

- Entropy increases as the number of microstates increases.

<u>2.5B Predicting the Relative Magnitude of Entropy</u>

- Molecules with greater molar mass tend to have larger entropies

<u>2.5C changes in entropy of Chemical Reactions</u>

$$\Delta S^{o}_{rxn} = \sum nS^{o}_{prod} - \sum nS^{o}_{react}$$

-