3.2.4: Free Energy and Equilibrium

The balance between reactants and products in a reaction will be determined by the free energy difference between the two sides of the reaction. The greater the free energy difference, the more the reaction will favor one side or the other. The smaller the free energy difference, the closer the mixture will get to equal parts reactants and products (loosely speaking).

Exactly where the balance lies in an equilibrium reaction is described by the equilibrium constant. The equilibrium constant is just the ratio of products to reactants, once the reaction has settled to equilibrium. That's the point at which the forward and reverse reactions are balanced, so that the ratio of products to reactants is unchanging.

- A reaction has reached equilibrium when the reaction has stopped progressing (i.e., no change in concentrations although at a microscopic level both forward and reverse reactions occur), so that the amount of reactants that have turned into products remains constant, and the amount of reactants left over stays constant.
- The equilibrium constant is the ratio of products to reactants when the reaction has reached equilibrium.

The equilibrium constant could be a large number (like a thousand). That means that there are much more products than reactants at equilibrium. It could also be a very small fraction (like one millionth). That would indicate that the reaction does not proceed very far, producing only a tiny amount of products at equilibrium.

- Every reaction has an equilibrium constant
- A very large equilibrium constant (in the millions or billions) means the reaction goes "to completion", with all reactants essentially converted into products
- A tiny equilibrium (very close to zero) constant means the reaction hardly moves forward at all.
- A modest equilibrium constant (close to one, or as close to one as numbers like 0.01 or 100) is considered to be a true equilibrium reaction, in which there is a significant amount of both products and reactants.

The equilibrium constant is related to the free energy change of the reaction by the expression:

$$K = e^{-\Delta G/RT} \tag{3.2.4.1}$$

or

$$\ln K = -\frac{\Delta G}{RT} \tag{3.2.4.2}$$

in which T is the temperature in Kelvin and R is the "gas constant" (1.986 cal/K mol). Remember, e is just a number that occurs frequently in mathematical relationships in nature (sort of like π); it has a value of about 2.718. This expression for K does make some assumptions about the conditions that we won't worry about; we are using a slightly simplified model.

Relating Gibbs energy and the equilibrium

Let's look at the form of this relationship between free energy and the equilibrium constant. First, we will see how we deal with endergonic versus exergonic reactions. The free energy changes in opposite directions in these two cases, and we usually deal with opposites by giving one quantity a positive sign and one quantity a negative sign. A reaction in which the free energy increases is given a positive value for its free energy. On the other hand, if free energy decreases over the course of the reaction, we show that by using a negative number for the value of the free energy.

If ΔG is negative, the exponent in the relationship becomes positive (because it is multiplied by -1 in the expression). Since e to a positive power will usually be a number greater than one, the relationship suggests there are more products than reactants. That's good, because the reaction is exergonic, and we expect the reaction to go forward. What's more, the larger the value of ΔG, the more product-favored the reaction will be.

- $10^{\text{large number}}$ is a large number.
- $10^{\text{small number}}$ is a smaller number.

However, if ΔG is a positive number, then the exponent in the relationship becomes negative. An number with a negative exponent, by the rules of exponents, is the same as the inverse of the number with a positive exponent of the same size.

In other words, $10^{-2} = 1 / 10^2$.

- $10^{\text{negative number}}$ is a fraction.

That means if ΔG is positive, the equilibrium constant becomes a fraction. That's because that positive value of ΔG is multiplied by -1 in the expression, becoming negative, and then it's placed in the exponent. That's good, because a positive value of ΔG corresponds to an endergonic reaction, which does not favor product formation.

Other factors

There are other factors in the expression relating ΔG to the equilibrium constant. One of them, R, is just a "fudge factor"; it's the number that, when placed in the expression, makes the relationship agree with reality.

Moreover, it is a constant, so it does not change. However, the other factor is temperature, which does change. That means that the equilibrium constant **may** change with different temperatures. Overall, the effect of temperature is to make the exponent in the expression a smaller number. That's because the free energy is divided by the temperature and the gas constant; the resulting number becomes the exponent in the relationship. At the extreme, a high temperature could make the exponent into a very, very small number, something close to zero. What happens then?

- $10^0 = 1$
- $e^0 = 1$

As the exponent gets smaller and smaller, the equilibrium constant could approach 1. That means there would be more or less equal amounts of products and reactants in our simplified approach.

However, the fact that there is a temperature factor in the expression for ΔG itself means that there is a limit to how small K will get as the temperature increases. At some point, the two values for temperature cancel out altogether and the expression becomes K = e (ΔS/R). At that point, the equilibrium constant is independent of temperature and is based only on internal entropy differences between the two sides of the reaction.

This relationship is useful because of its predictive value. Qualtitatively, it confirms ideas we had already developed about thermodynamics.

- Highly exergonic reactions (large, negative/decreasing ΔG) favor products.
- Highly endergonic reactions (large, positive/increasing ΔG) favor reactants.
- Reactions with small free energy changes lead to equilibrium mixtures of both products and reactants.

Problems

TD6.1. Arrange the following series of numbers from the largest quantity to the smallest, from left to right.

A. 10^5 10^4 10^6
B. 2^3 2^6 2^2
C. 3^3 3^0 3^2
D. e^2 e^1 e^4
E. 10^{-1} 10^{-5} 10^{-3}
F. 1 / 10 1 / 25 1 / 50
G. $2^{0.5}$ $2^{0.1}$ $2^{0.9}$

Problem TD6.2. Given the following free energy differences, arrange the corresponding equilibrium constants from largest to smallest.

A. 25 kcal/mol 17 kcal/mol 9 kcal/mol
B. 16 kcal/mol 19 kcal/mol 21 kcal/mol
C. 7 kcal/mol 22 kcal/mol 13 kcal/mol
D. -17 kcal/mol -3 kcal/mol -8 kcal/mol
E. -17 kcal/mol 3 kcal/mol -8 kcal/mol

Problem TD6.3: What is the value of the equilibrium constant at 300K in the following cases? (1 kcal = 1000 cal)

A. ΔG = 3 kcal /mol
B. ΔG = -2 kcal/mol
C. ΔG = -5 kcal /mol
D. ΔG = 15 kcal/mol
E. ΔG = -10 kcal/mol

F. The free energy increases by 8 kcal/mol over the reaction.
G. The free energy decreases by 1 kcal/mol over the reaction.

Problem TD6.4. In which of the cases in TD6.3. do you think there would be significant amounts of both products and reactants at equilibrium?

Problem TD6.5. The mathematical expression for the equilibrium constant says that K will get smaller at higher temperatures. Explain this phenomenon without the mathematical expression in terms of what you know about temperature and energy.

Contributors and Attributions

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