

## 0.1 Equilibrium Constant and Gibbs Free Energy

### 0.1.1 What is the Equilibrium Constant?

Consider some arbitrary reaction at equilibrium:



We can determine that the forward rate (going from reactants to products) will be:

$$r_F = k_1 \cdot [R_1]^{a_1} [R_2]^{a_2} [R_3]^{a_3} \dots$$

Where:

$[R_n]^{a_n}$  - concentration of reactant raised to some experimentally determined power.

$k_1$  - rate constant for forwards reaction

For the backward reaction (going from products to reactants), the rate law will be:

$$r_B = k_2 \cdot [P_1]^{b_1} [P_2]^{b_2} [P_3]^{b_3} \dots$$

Where:

$[P_n]^{b_n}$  - concentration of product raised to some experimentally determined power.

$k_2$  - rate constant for backwards reaction.

We know that at equilibrium the forward and backward rates of reaction are equal:

$$r_F = r_B$$

Substitute the formulas for the rates above and rearrange to get:

$$k_1 \cdot [R_1]^{a_1} [R_2]^{a_2} [R_3]^{a_3} \dots = k_2 \cdot [P_1]^{b_1} [P_2]^{b_2} [P_3]^{b_3} \dots$$

$$\frac{k_1}{k_2} = \frac{[P_1]^{b_1} [P_2]^{b_2} [P_3]^{b_3} \dots}{[R_1]^{a_1} [R_2]^{a_2} [R_3]^{a_3} \dots}$$

On the left hand side of the equation, all variables are fixed :  $k_1$  and  $k_2$  are constant (assuming the equilibrium occurs with no temperature change).

This implies, that the right hand side of the equation will also always stay constant. Let's rename the right hand side of the equation as  $K$  and rewrite the equation.

$$K = \frac{k_1}{k_2} \tag{1}$$

Let's apply the Arrhenius equation to look at the problem in more detail.

Recall that for the forward reaction:

$$k_1 = A_1 e^{\frac{E_{a1}}{RT}}$$

For the backward reaction:

$$k_2 = A_2 e^{\frac{E_{a2}}{RT}}$$

Where:

$A_1$  and  $A_2$  - Arrhenius Constants responsible for the geometry of particle collisions for forward and backward reactions respectively.

$E_{a1}$  and  $E_{a2}$  - activation energies for forward reaction and backward reactions respectively.

$T$  - temperature at which equilibrium takes places.

$R$  - universal gas constant.

Substitute this into equation (1) to get:

$$K = \frac{A_1 e^{-\frac{E_{a1}}{RT}}}{A_2 e^{-\frac{E_{a2}}{RT}}} \quad K = \frac{A_1}{A_2} e^{\frac{(E_{a2}-E_{a1})}{RT}} \quad (2)$$

### 0.1.2 Gibbs Free Energy

**Definition 1** *The Gibbs Free Energy is the maximum amount of non-expansion work that can be extracted from a closed system (citation here).*

To understand what this definition means, we have to first understand what non-expansion work is.

**Definition 2** *Work: In thermodynamics, work performed by a closed system is the energy transferred to another system that is measured by the external generalized mechanical constraints on the system (please pretend this is also cited).*

We now see that work is the energy transferred outside of some system, but what does non-expansion mean?

Expansion work, is the energy that can be taken out of a system from some change in pressure or volume. Non-expansion work is everything else.

This means, that the change in Gibbs Free Energy ( $\Delta G$ ) for a chemical reaction, is all the energy that isn't used in changing the volume/pressure of reactants.

We can assume that first all of the energy given off as part of a reaction is in the form of heat (enthalpy,  $\Delta H$ ). To get Gibbs Free Energy, we would need to subtract all of the energy used to change around the volume and pressure of the system. This has to do with the order of the particles in the system, which is entropy! To get units of energy, multiply entropy by temperature and subtract it from enthalpy to get.

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

Now, we have given the change in Gibbs Free Energy formula some intuitive physical motivation.

### 0.1.3 Gibbs Free Energy for an Equilibrium System

Let's go back to equation (2) and derive the formula for the Gibbs Free Energy of a system in an equilibrium.

Rewrite equation (2), take natural logarithm of both sides and simplify to get:

$$K = \frac{A_1}{A_2} e^{\frac{(Ea_2 - Ea_1)}{RT}}$$

$$\ln K = \ln \left( \frac{A_1}{A_2} e^{\frac{(Ea_2 - Ea_1)}{RT}} \right)$$

$$\ln K = \ln \frac{A_1}{A_2} + \ln e^{\frac{(Ea_2 - Ea_1)}{RT}}$$

$$\ln K = \ln \frac{A_1}{A_2} + \frac{Ea_2 - Ea_1}{RT}$$

$$RT \ln K = RT \ln \frac{A_1}{A_2} + (Ea_2 - Ea_1)$$

Using Figure one determine that  $\Delta H = Ea_1 - Ea_2 \Rightarrow Ea_2 - Ea_1 = -\Delta H$ .

Substitute this into equation above:

$$RT \ln K = RT \ln \frac{A_1}{A_2} - \Delta H$$

$$-RT \ln K = \Delta H - T \cdot R \ln \frac{A_1}{A_2}$$

The formula above looks very much like the equation (3). We can notice that  $R$  has the same units as entropy  $\frac{J}{K}$ . It can also be noted that  $A_1$  and  $A_2$  deal with the geometry of the reaction (and entropy is a measure of the geometrical disorder). We are therefore justified in assuming that  $\Delta S = R \ln \frac{A_1}{A_2}$ .

Therefore, for a reaction in equilibrium the following is true:

$$\Delta G = -RT \ln K \quad (4)$$

Where:

$R$  - universal gas constant.

$T$  - temperature at which equilibrium takes place

$K$  - equilibrium constant for reactions.

As a side note, recall that in our definition of Gibbs Free Energy, we said it was all energy changes unrelated to changes in volume or pressure, (which is why we subtract entropy multiplied by temperature, from total energy released in reaction).

We can recall, that for gasses  $PV = nRT$ . This means that energy changes due to changes in pressure and volume are proportional to  $RT$  times some unit less scaling factor. This only supports our assumption above that:  $\Delta S = R \ln \frac{A_1}{A_2}$ .

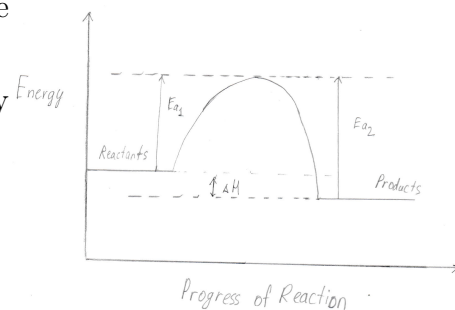


Figure 1: Poorly drawn, slightly tilted diagram, using which you can determine that:

$$\Delta H = Ea_1 - Ea_2$$