

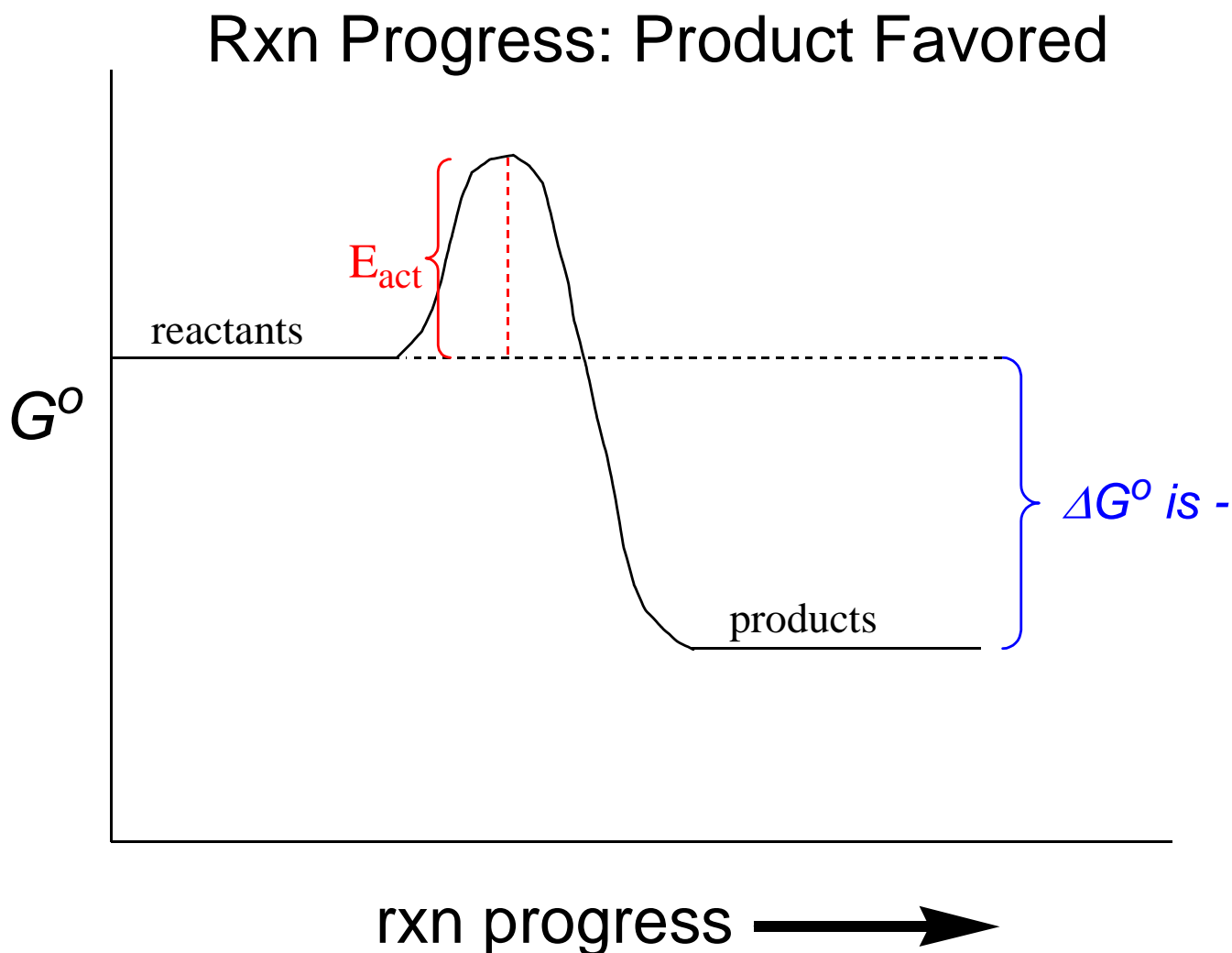
Chemical Equilibrium

You may have gotten the impression that when you mix two reactants together, the ensuing reaction goes to completion. In other words, the reactants are converted completely to products. In this chapter we will learn that is frequently not the case, at least not in a rigorous quantitative sense.

We will now learn:

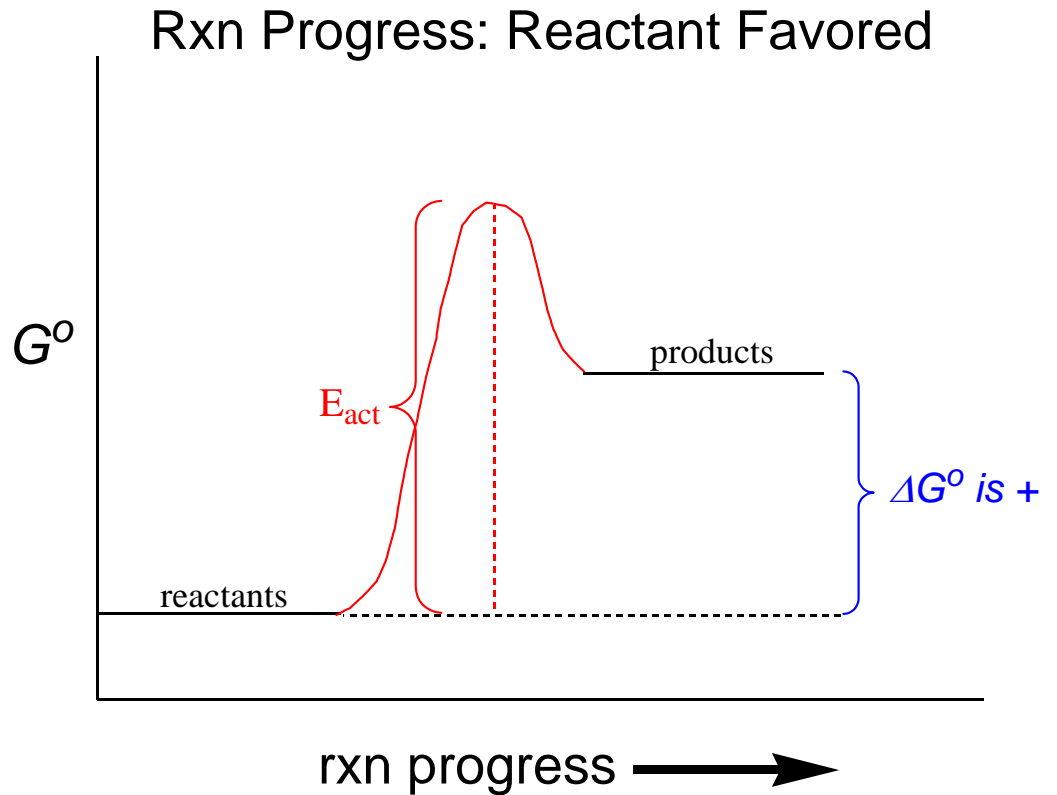
1. how to give quantitative descriptions of how far toward completion a given reaction proceeds.
2. how altering conditions can shift equilibrium concentrations in a reaction vessel.

Most of the rxns. we have looked at so far (Chemistry of Cu, rxn of H_2 with O_2 [Hindenberg], rxn of alkali [Group IA] metals with water) go essentially completely to products. Their rxn coordinate diagrams would look qualitatively like this:

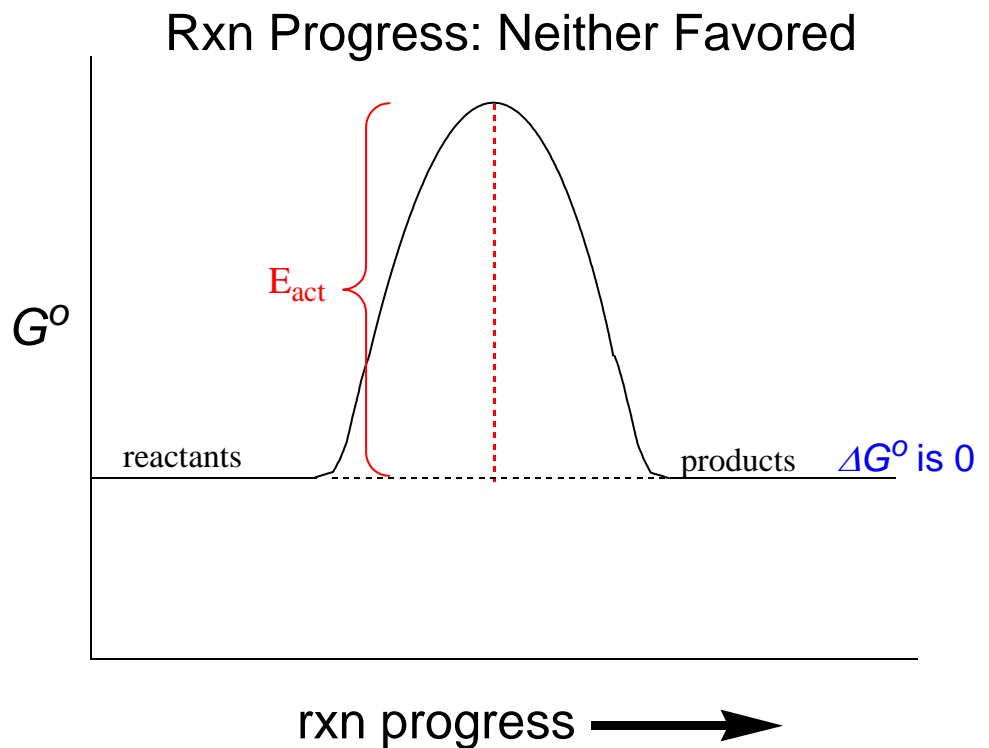


There are two other qualitative possibilities:

1. Rxns that are reactant favored (i.e., There is relatively little change when the reactants are mixed together.):

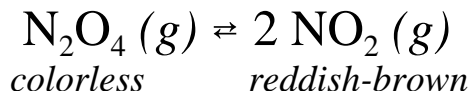


2. Rxns where product and reactant have equal Gibbs Free energy values. Is product or reactant favored here?



I. What is equilibrium?

A. We will start by looking at a rxn. that clearly does not go to completion:



Aside on terms:

The “stuff” on the left is *reactant*, on the right is *product*.

The rxn. toward the right (forming NO₂) is the *forward* rxn. The leftward (forming N₂O₄) is the *backward* rxn.

We can study this reaction by introducing a pure sample of either N₂O₄ or NO₂ into a reaction vessel.

1. Starting with a pure sample of N₂O₄, what would occur?

If this rxn proceeds by a single elementary step, what is the rate law?

2. Starting with a pure sample of NO₂, what would occur?

What is the rate law? (Comment on “energy pathways” of rxns.)

View the animation: [Chemical_Equilibrium.swf](#)

3. What happens at the leveled off point?

a) Is the system frozen in place? _____

b) Are the reactions (forward and backward) still occurring, but at equal rates?

B. At equilibrium, the forward and backward rates of the reaction are equal.

1. Based on your work in Kinetics, why is the rate of the forward rxn. decreasing as the rxn. proceeds?

2. Likewise, why is the rate of the reverse rxn. increasing as the rxn. proceeds?

C. We can develop an interesting and useful mathematical tool by looking a little more deeply:
forward rate law: _____

reverse rate law: _____

If these are equal, we can write: _____

which can be rearranged to give: _____

We can now define a new constant, $K_{eq} = k_f/k_r$. Substitute to obtain:

D. What would happen if you started with different initial $[N_2O_4]$ or $[NO_2]$

1. $[N_2O_4]$ & $[NO_2]$ at equil. depend on $[N_2O_4]_0$ & $[NO_2]_0$
2. The ratio $[NO_2]^2/[N_2O_4]$ is a constant!!!

II. The Equilibrium Constant K_{eq} (Note: upper case K)

A. For any rxn. of the type: $a A + b B \rightleftharpoons c C + d D$
you can write an equilibrium constant expression (*circa* 1860's, Norway):

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

Note: $K_{eq} = \frac{[\text{product terms}]}{[\text{reactant terms}]}$

Important: Because a pure liquid or solid can have only one concentration, reactants and products in these states $\{(l) \text{ and } (s)\}$ are **not included** in K_{eq} .

1. K_{eq} is constant for a specific rxn. at a specific temp.
2. For our rxn. with N_2O_4 :

At 25°C
$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 4.64 \times 10^{-3}$$

B. Units of K_{eq}

1. If K_{eq} is sometimes shown with units, they are determined by the concentration units and the number of terms in the K_{eq} expression. From above:

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(M)^2}{(M)} = M$$

2. In some areas of chemistry it is the custom to omit units when using equilibrium constants. I will warn you if you need to worry about units.

C. Equilibrium constant for the reverse rxn.

What is K_{eq} for: $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$?

(The reverse rxn. equilibrium constant is called K_{eq}' .)

Problem: Write K_{eq} expressions for the following:



D. It is also possible to write K_{eq} expression using units of partial pressure instead of molar concentrations.

1. If you have an interest in respiratory physiology, you might use these constants. O_2 levels (regarding hemoglobin binding, *etc.*) are usually expressed as partial pressures. (Recovery room?)

2. Hemoglobin is half-saturated with O_2 at 26 mm Hg. (More on this later.)

III. Calculating and Using Equilibrium Constant Values

A. Judging the extent of a reaction. *How far (qualitatively) does it go?*

The numerical value of K_{eq} tells us whether we will have mostly products or mostly reactants at equilibrium. Usually, you can't predict the value of K_{eq} from first principles. You must go into the lab and measure it.

The Haber Process (\$\$\$!!!) $\text{N}_{2(g)} + 3 \text{H}_{2(g)} \rightleftharpoons 2 \text{NH}_{3(g)}$

$K_{eq} =$ (You fill it in!)

At equilibrium, if $[\text{N}_2] = 0.0784 \text{ M}$, $[\text{H}_2] = 2.01 \text{ M}$, and $[\text{NH}_3] = 0.248 \text{ M}$, what is K_{eq} equal to?

What does this mean in terms of the relative $[\text{NH}_3]$, $[\text{H}_2]$, and $[\text{N}_2]$ values at equilibrium?

B. If you are given some of the concentrations and the K_{eq} , you should be able to calculate the concentration of the remaining concentration term(s).

1. In the reaction above, if $[\text{H}_2] = 0.10 \text{ M}$, and $[\text{NH}_3] = 1.50 \text{ M}$, what is $[\text{N}_2]$

2. If $[\text{NH}_3] = 8.5 \text{ M}$ and $[\text{N}_2] = 0.46 \text{ M}$, what is $[\text{H}_2]$?

IV. Link Thermodynamics to Kinetics & Equilibrium, Quantitatively

A. We have previously discussed a qualitative relationship between the activation energy (E_{act}) and the value of the rate constant, k .

What was that relationship? _____

There is also a quantitative relationship called the Arrhenius Equation:

$$k = A e^{-E_{act}/RT}$$

A: frequency factor, related to #collisions with appropriate orientation

R: *the* gas constant, but different units (below)

T: _____

k : the rate constant

You don't have to memorize this equation.

Important: The Arrhenius Equation shows there is a link between k & E_{act} , and that k is temperature dependent (except nuclear rxns).

B. Previous discussion of relationship between Gibbs' Free Energy change and equilibrium?

$$K_{eq} = e^{-\Delta G^0/RT}$$

ΔG^0 : _____ R:

8.3145 J/(K•mol) Comment?

T: _____

K_{eq} : _____

*You don't have to
memorize this equation.*

Note: Superscript to the right (as in G^0) means under *standard conditions*. Standard conditions here are: 25° C (298.15 K), all concentrations = 1 M, and all gases are present at 1 atm partial pressure.

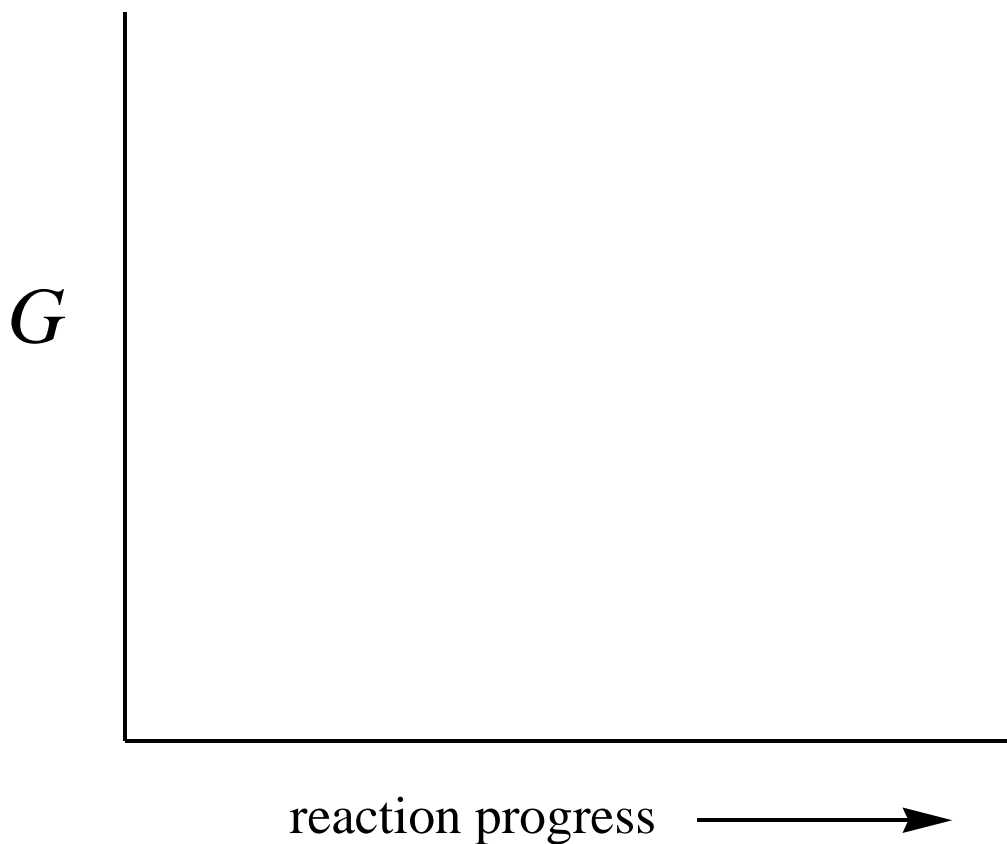
Soon we will get to ΔG^0 , referred to as "G zero prime." This is standard conditions except, $[H_3O^+] = 1 \times 10^{-7} \text{ M}$ (pH = 7).

Important: This equation shows there is a link between K_{eq} & ΔG^0 (temp dependence)

C. Finally, we need to express this in a rxn coordinate diagram. Let's do one for:



- How do we decide the relative Y-axis positions of reactants and products? *Note: There are only 3 different qualitative options here.*
- Do you need more information to decide how high to draw the hill that connects the reactants & products? (If yes, what do you need? _____)



Can you draw diagrams for the other two options?

Closing comments:

- 1. Even though **you** aren't **at** equilibrium, your reactions are always headed that way. (Some of your rxns. are close to equilibrium.)*
- 2. Once you are familiar with K_{eq} values, they provide nice reference points for making predictions. (Pharmacology, respiratory physiology, others.)*