Equilibrium

A Simple Energetic Model

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Equilibrium

Equilibrium is a dynamic process in which the net concentrations of reactants and products remains constant.

This does ***not*** mean that the reaction “stops”. It means that the forward and reverse reactions are happening at the same rate.

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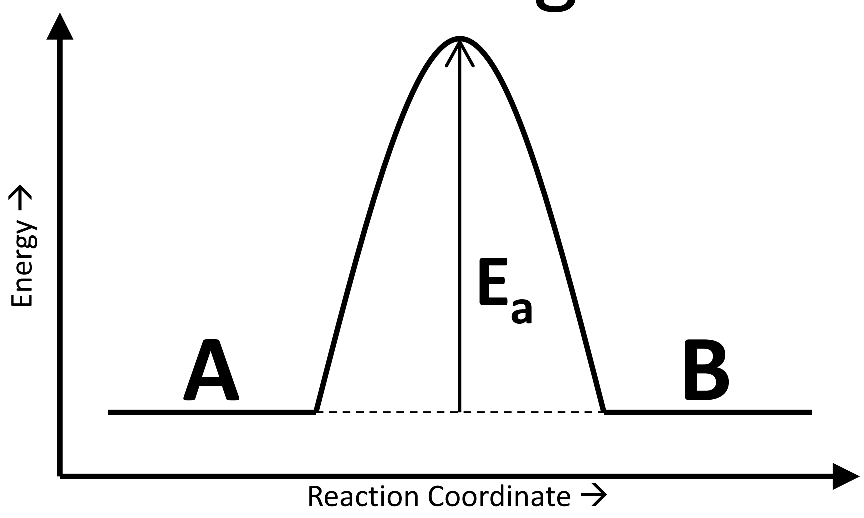
A Simple Example

To start, let's consider a very simple reaction:

$$A \leftrightarrow B$$

And to make it as simple as possible, let's further assume that the energy of "A" is the same as the energy of "B". This gives us a reaction coordinate diagram that looks like this:



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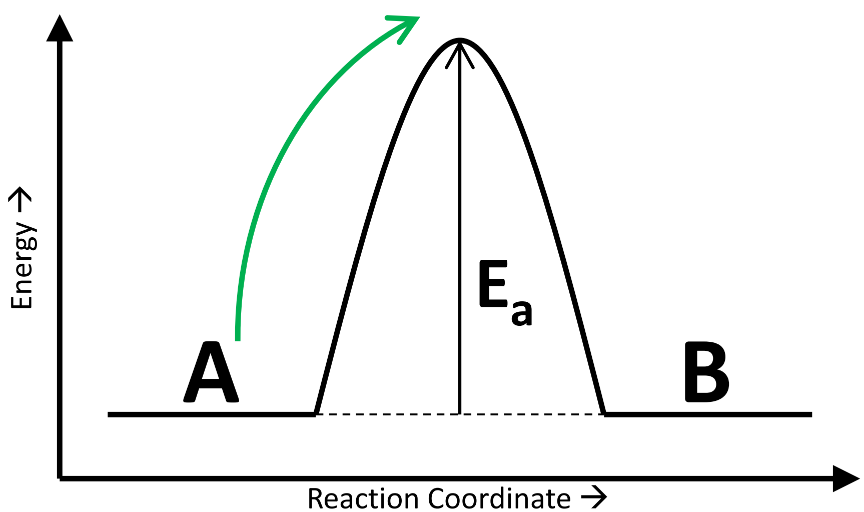
The Forward Reaction

To keep things *really* simple, let's also assume that the reaction is 1st order w.r.t. A so the rate law expression is:

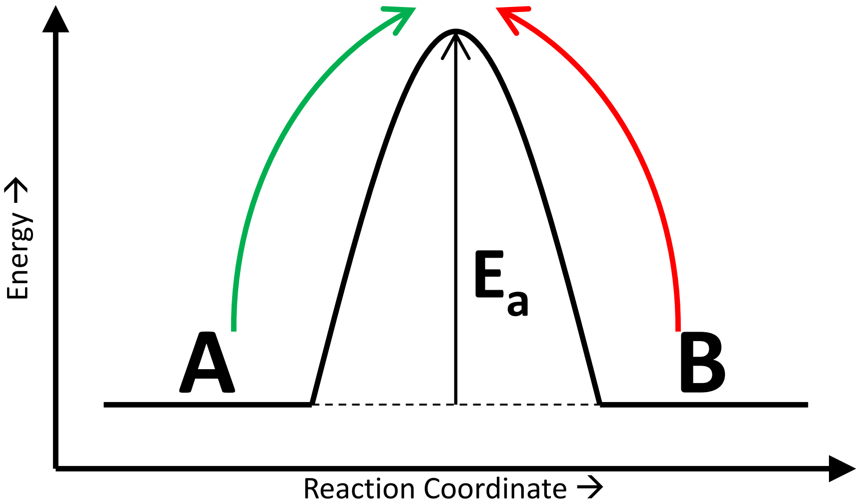
$$Rate_0 = k\,[A]_0$$

When the reaction starts, we have a relatively high concentration of "A" so the rate is "high".



The Reverse Reaction

As the reaction occurs, [B] increases. The E_a to go from B→A is the same as the E_a from A→B. If there is enough energy to go *forward*, there's also enough energy to go *backward*.



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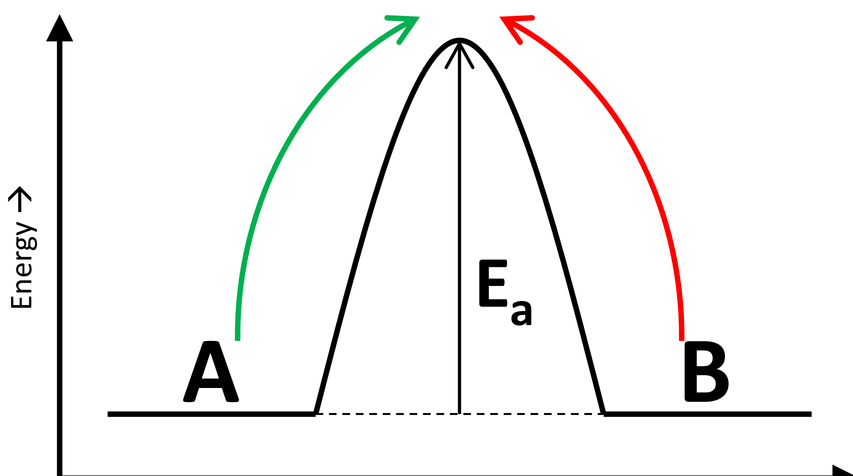
Equal Rates, No Net Change

As [A] decreases, the forward rate decreases.
As [B] increases, the reverse rate increases.
At some point, the concentrations and the rates will balance each other so that there is no net change in [A] or [B]
That's equilibrium!



Equilibrium Constant

The rate laws in this process are:

$$\text{Rate}_{\text{forward}} = \text{k}_{\text{forward}}\,[\text{A}]_{\text{eq}}$$

$$\text{Rate}_{\text{reverse}} = \text{k}_{\text{reverse}}\,[\text{B}]_{\text{eq}}$$

At equilibrium, $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$ so:

$$\text{k}_{\text{forward}}\,[\text{A}]_{\text{eq}} = \text{k}_{\text{reverse}}\,[\text{B}]_{\text{eq}}$$

Rearranging to put similar terms together:

$$\frac{k_{forward}}{k_{reverse}} = \frac{[B]_{eq}}{[A]_{eq}}$$

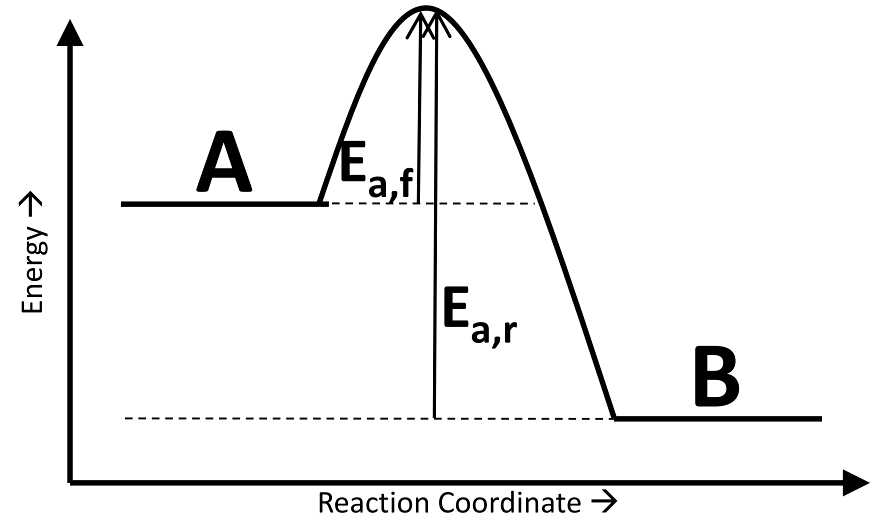
A ratio of constants is a constant, so:

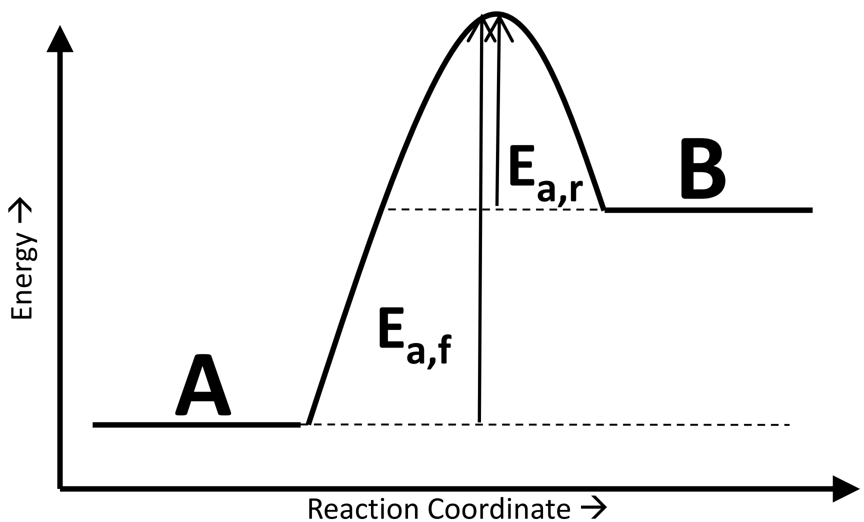
$$K_{eq} = \frac{[B]_{eq}}{[A]_{eq}}$$

Less “Simple” Systems

What if the energies of A & B are *not* equal?

If B is lower than A, then at equilibrium $[B]_{eq}$ will be *higher* than $[A]_{eq}$ so K_{eq} will be *greater than* 1.





If A is lower than B, then at equilibrium $[A]_{eq}$ will be *higher* than $[B]_{eq}$ so K_{eq} will be *less than* 1.

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Equilibrium Constants

Equilibrium constant expressions can be similarly derived for more complex systems, but the final result is that for *any* chemical equation, we can write an equilibrium constant expression based solely upon the balanced chemical equation:

$$a\,A + b\,B \leftrightarrow c\,C + d\,D$$

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