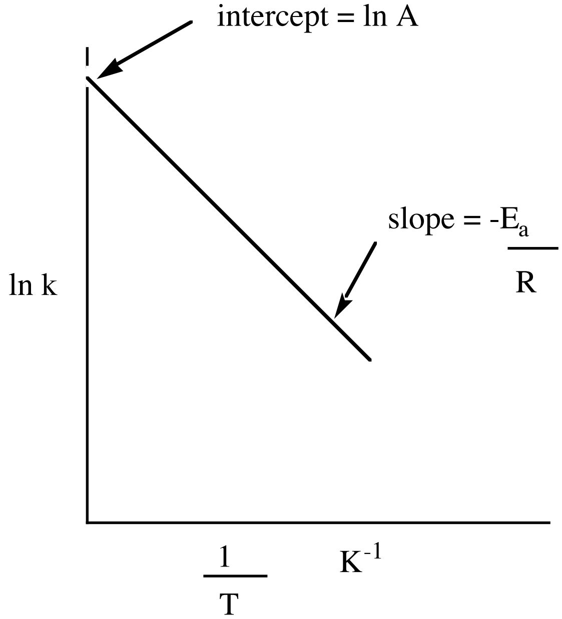
5.111 Lecture 34
Kinetics Topics: Effect of Temperature, Collision Theory, Activated Complex Theory.
Chapter 13.11-13.13

Effect of Temperature on Reaction Rates

Gas-Phase

A qualitative observation is that reaction rates tend to increase with increased temperature. Now we will consider the quantitative effect.

In 1889, Svante Arrhenius plotted rate constants (k) versus temperature. He found that plotting ln k versus inverse temperature gave a straight line.



k = rate constant

T = temperature

A = factor A or pre-exponential factor (same units as k)

E_a = activation energy

R = gas constant

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$y \quad = \quad mx \quad + b$$

Rate constants vary ____________________ with inverse temperature

A and E_a depend on the reaction being studied.

Is factor A temperature dependent?

Is E_a temperature dependent?

$\ln k = \frac{-E_a}{RT} + \ln A$ can also be written

$$\ln k = \ln A - \frac{E_a}{RT}$$ Arrhenius equation

or

$$k = Ae^{-E_a/RT}$$

What is E_a, activation energy?

Consider $CH_3\,(g) + CH_3\,(g) \rightarrow C_2H_6\,(g)$

2 molecules collide to form product (bimolecular) but every two molecules that collide won't form product. Why?

Only those collisions for which the collision energy exceeds some critical energy

(_________________ energy) result in a reaction.

At low temperatures, a small fraction will have this much energy.

At higher temperatures, a larger fraction will have this much energy.

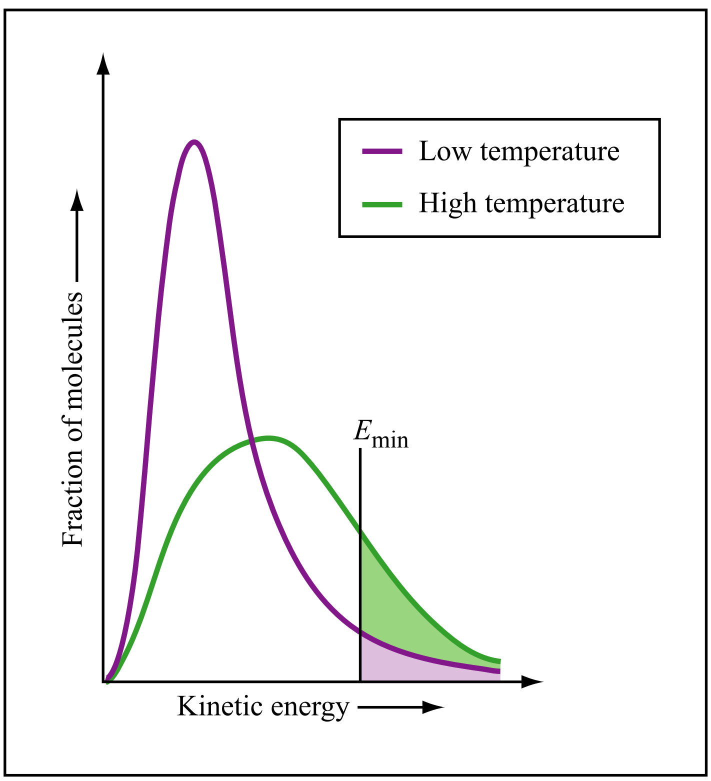


Figure by MIT OpenCourseWare.

Example: Using the activation energy to predict a rate constant

The hydrolysis of sucrose to form a molecule of glucose and a molecule of fructose is part of the digestive process.

$E_a = 108$ kJ/mol
$k_{obs} = 1.0 \times 10^{-3}\ M^{-1}s^{-1}$ at 37°C (normal body temperature)

What is k_{obs} at 35°C?

$$\ln k_1 = \ln A - \frac{E_a}{RT_1} \qquad \ln k_2 = \ln A - \frac{E_a}{RT_2}$$

$$\ln k_2 - \ln k_1 = \ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{1.0 \times 10^{-3}\ M^{-1}\ s^{-1}}\right) = \frac{-108 \times 10^3\ J\ mol^{-1}}{8.315\ JK^{-1}\ mol^{-1}}\left(\frac{1}{308K} - \frac{1}{310\ K}\right)$$

$$k_2 = 7.6 \times 10^{-4}\ M^{-1}\ s^{-1}$$

A large activation energy means that the rate constant is ________ sensitive to changes in temperature.

What do you think happens to the rate of an enzymatic reaction at liquid N_2 temperatures?

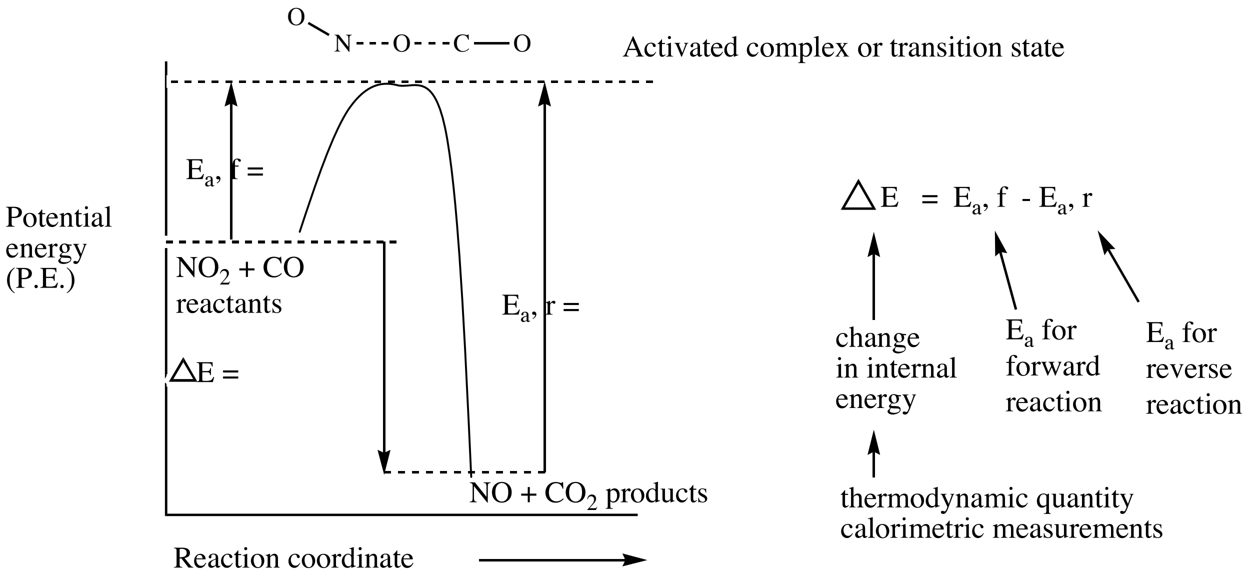
<u>The Reaction Coordinate and the Activation Complex</u>

Why is there a critical collision energy, E_a, for the reaction between two molecules?

As two reactant molecules approach each other along a reaction path, their potential energy increases as the bonds within them distort. The encounter results in the formation of an activated complex or transition state, a combination of molecules that can either go on to form products or fall apart again into unchanged reactants.

Only molecules with sufficient energy can overcome the activation energy barrier.

Example $NO_2\,(g) + CO\,(g) \rightleftharpoons NO\,(g) + CO_2\,(g)$



Recall from Lecture #17, $\Delta H = \Delta E + \Delta(PV)$

For gases, these quantities differ by 1-2% and for liquids and solids, there is a negligible difference.

For elementary reactions, the activation energy barrier is always positive (some barrier to overcome).

Therefore increasing the temperature ___________________the rate of an elementary reaction.

<u>For overall reactions, increasing temperature can decrease or increase the overall rate.</u>

<u>Example</u> $2NO + O_2 \rightarrow 2NO_2$ with proposed mechanism:

1st step (Fast, reversible) $NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$

2nd step slow $N_2O_2 + O_2 \xrightarrow{k_2} 2NO_2$

rate of product formation = $2k_2\,[N_2O_2]\,[O_2]$

↑ intermediate

Since first step is fast and reversible and the second step is slow, we can solve for $[N_2O_2]$ by setting up an equilibrium expression:

$K_1 =$ $[N_2O_2] =$

Substituting:
rate of product formation $= 2k_2\,[N_2O_2]\,[O_2] =$

$$\text{rate} = 2k_2K_1\,[NO]^2\,[O_2]$$

elementary rate constant	equilibrium constant
rate increases with temperature	effect of temperature on an equilibrium constant depends on whether the reaction is endothermic or exothermic

Here the reaction is exothermic, so increasing temperature ___________the equilibrium constant

$k_{obs} = 2k_2K_1$ with increased temperature / the rate constant increases
and the equilibrium constant decreases

(Magnitude of change depends on E_a (for rate constant) and ΔH (for equilibrium constant.)

For $2NO + O_2 \rightleftharpoons 2NO_2$, E_a is a small number and ΔH is a big number

Since E_a is small, the rate constant increases only a little

Since ΔH is big, the equilibrium constant decreases a lot with temperature

Thus, increasing the temperature actually decreases k_{obs}.

$$\ln\left[\frac{k_{Temp2}}{k_{Temp1}}\right] = \frac{-E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \ln\left[\frac{K_{Temp2}}{K_{Temp1}}\right] = \frac{-\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

A large E_a means that k is very sensitive to changes in temperature.

A large ΔH means that K is very sensitive to changes in temperature.

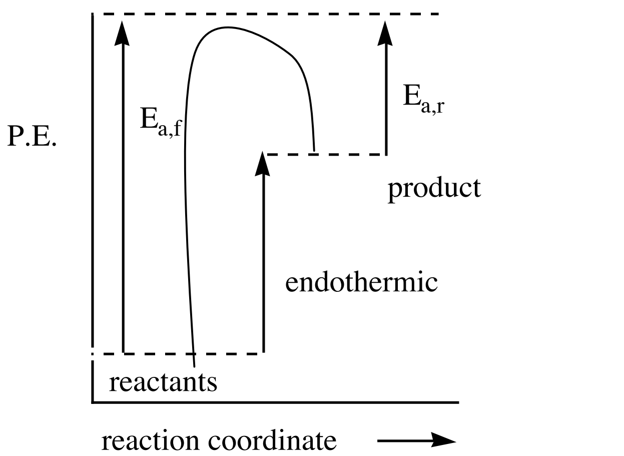
Rate constants always increase with temperature, since E_a is always ______________.

Equilibrium constants can increase or decrease with temperature, since ΔH can be (-) or (+).

The magnitude of ΔH indicates the magnitude of the change, and the sign of ΔH indicates the direction of the change.

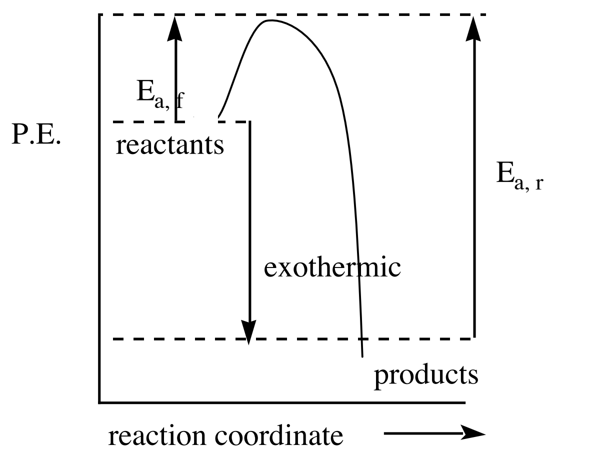
Le Chatelier's Principle - when a stress is applied to a system in equilibrium, the equilibrium tends to adjust to _____________the effect of the stress.

Increasing the temperature...



$\Delta E = E_{a,f} - E_{a,r}$
+ (endo) = big number - small number

increase temperature, easier to overcome $E_{a,f}$. Equilibrium shifts toward products for endothermic reaction.



$\Delta E = E_{a,f} - E_{a,r}$
- (exo) = small number - large number

increase temperature, easier to overcome $E_{a,r}$. Equilibrium shifts toward reactants in the exothermic reaction.

most molecules have enough energy to overcome small barriers
increasing temperature allows more molecules to overcome larger barriers

Recall, a large E_a means that the rate constant is very sensitive to changes in temperature.

Big E_a - increasing the temperature makes a ________ difference

Small E_a - increasing the temperature does not make much of a difference.