

Lecture 19

Tuesday, November 19, 2024 10:08

Topic 17C: Reactions Approaching Equilibrium

First-order:

Net rate of change in $[A]$:

$$\frac{d[A]}{dt} = -k_f [A] + k_r [B]$$

If the initial concentration of $[A]$ is $[A]_0$ and there is no $[B]$ initially, then

$$[A] + [B] = [A]_0$$

at all times.

$$\frac{d[A]}{dt} = -k_f [A] + k_r ([A]_0 - [A])$$

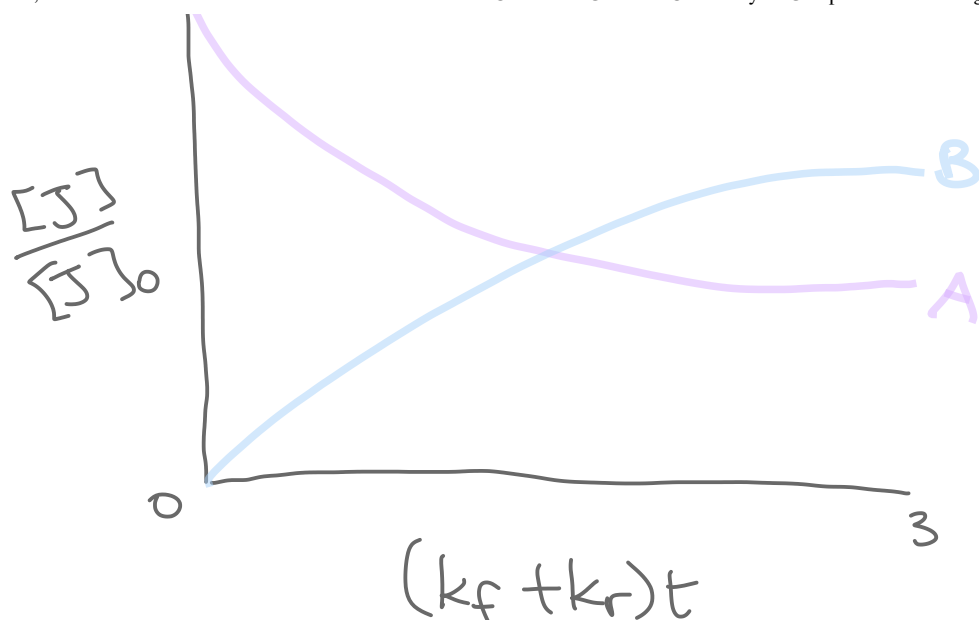
$$\frac{d[A]}{dt} = -(k_f + k_r) [A] + k_r [A]_0$$

Solution :

$$[A] = \frac{k_r + k_f e^{-(k_f + k_r)t}}{k_f + k_r} [A]_0$$

$$[B] = [A]_0 - [A]$$

N.B. the text book uses " k_r ", where the r stands for rate, for a general rate constant. I prefer using " k " for rate constant, and k_B for Boltzmann's constant.



At $t = \infty$,

$$\frac{k_r + k_f e^{-(k_f + k_r)t}}{k_f + k_r} [A]_0 \rightarrow \boxed{\frac{k_r [A]_0}{k_f + k_r} =}$$

$$[B]_{eq} = [A]_0 - \frac{k_r [A]_0}{k_f + k_r}$$

$$= \frac{k_f [A]_0 + k_r [A]_0 - k_r [A]_0}{k_f + k_r}$$

$$\boxed{[B]_{eq} = \frac{k_f [A]_0}{k_f + k_r}}$$

How about the equilibrium constant?

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f [A]_0 / (k_f + k_r)}{k_r [A]_0 / (k_f + k_r)}$$

$$K = \frac{k_f}{k_r}$$

Another way we could have found the equation for the equilibrium constant is by noting that the forward and reverse rates must be the same at equilibrium.

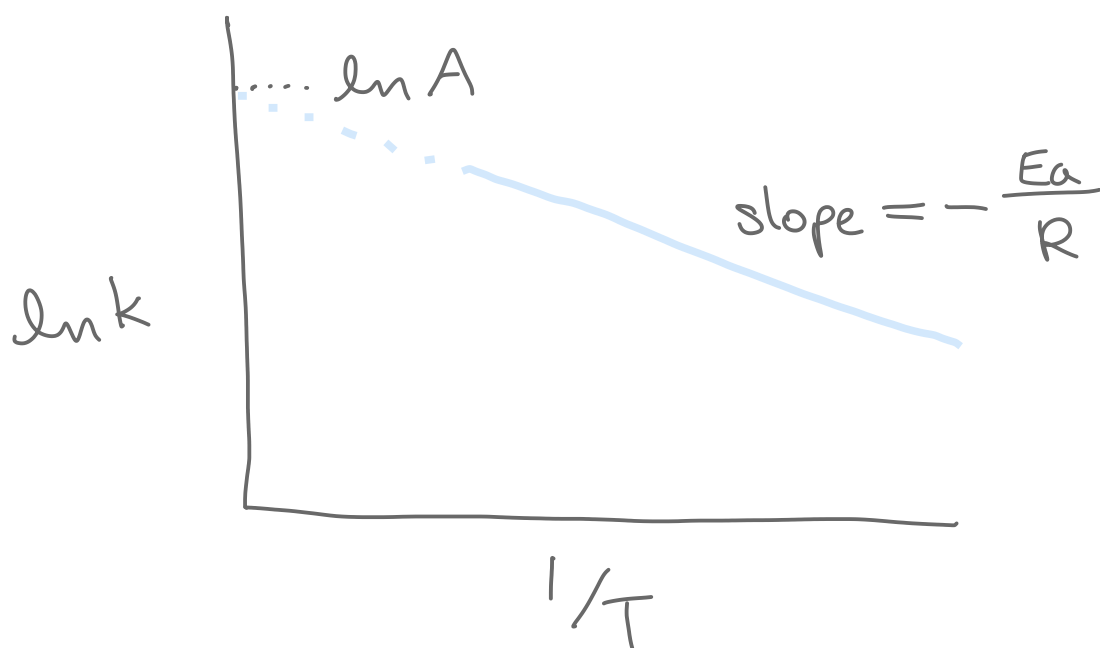
$$k_f [A]_{eq} = k_r [B]_{eq}$$

$$\frac{[B]_{eq}}{[A]_{eq}} = K = \frac{k_f}{k_r}$$

Overall equilibrium constant for a series of reaction steps:

$$K = \left(\frac{k_{1f}}{k_{1r}} \right) \left(\frac{k_{2f}}{k_{2r}} \right) \dots$$

Topic 17D: The Arrhenius Equation



The temperature dependence of reaction rates

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

equation

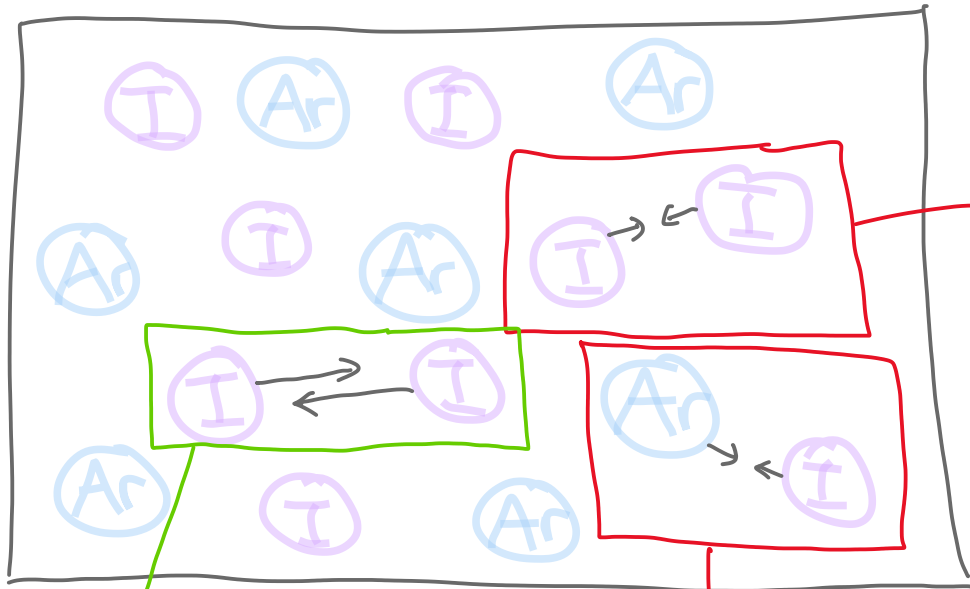
$$k = A e^{-E_a/RT}$$

alternate form

A : frequency factor

E_a : activation energy

Arrhenius parameters



collision, but not enough kinetic energy to overcome barrier

collision, but not the right reactants

collision with enough kinetic energy to form product

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

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

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

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

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

predict k_2
from k_1 ,
given E_a

- a high activation energy signifies that the rate constant depends strongly on temperature
- if a reaction has zero activation energy, its rate is independent of temperature
- a negative activation energy indicates that the rate decreases as the temperature is raised

For "non-Arrhenius" reactions, we can still define an activation energy

by writing:

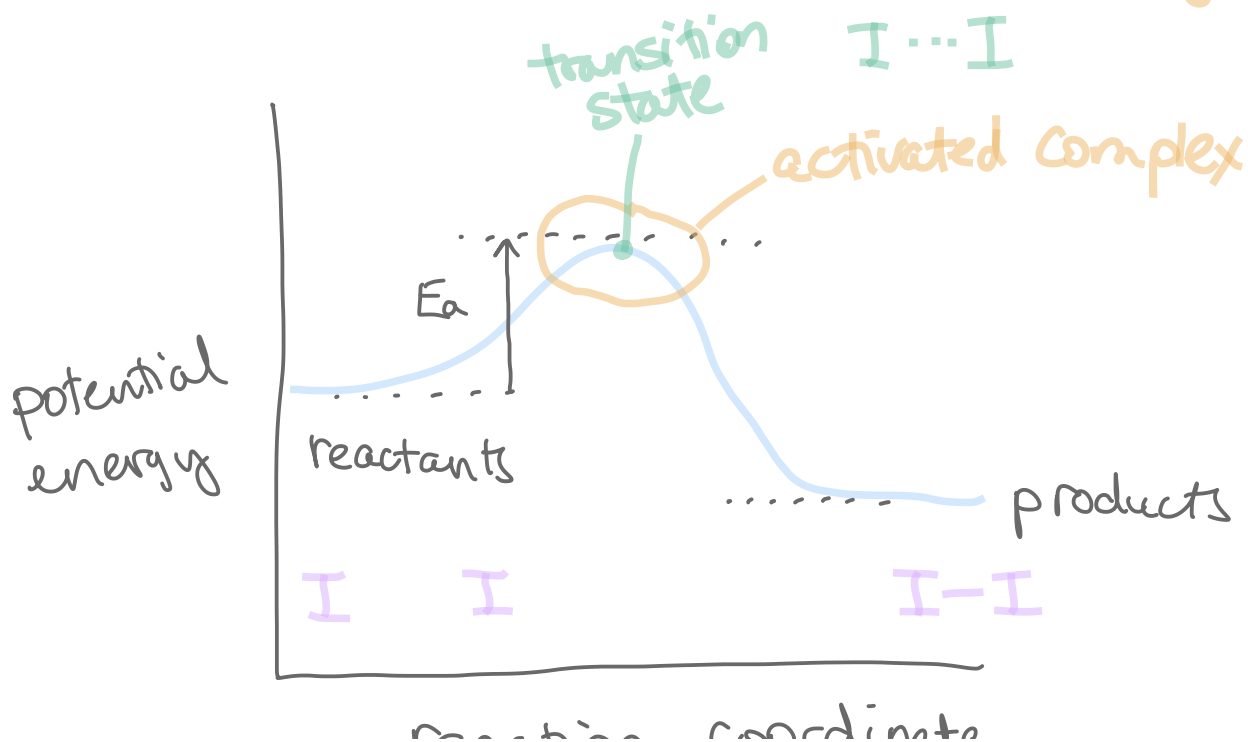
$$-\frac{E_a}{R} = \frac{d \ln k}{d(1/T)} = -T^2 \frac{d \ln k}{dT}$$

$$d\left(\frac{1}{T}\right)/dT = -\frac{1}{T^2}$$

$$d\left(\frac{1}{T}\right) = -\frac{1}{T^2} dT$$

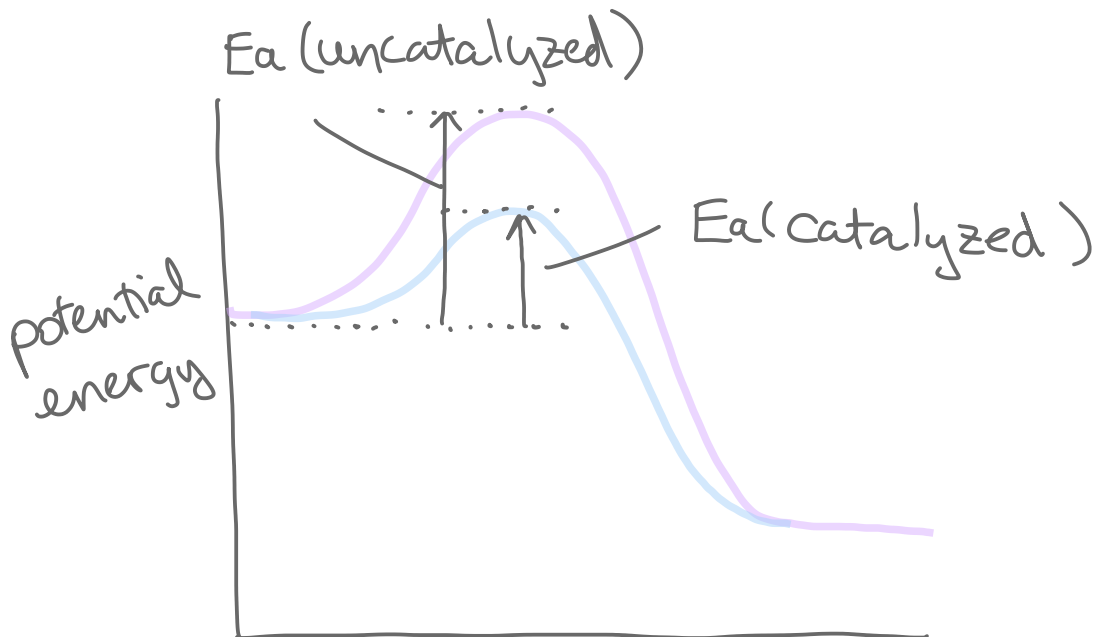
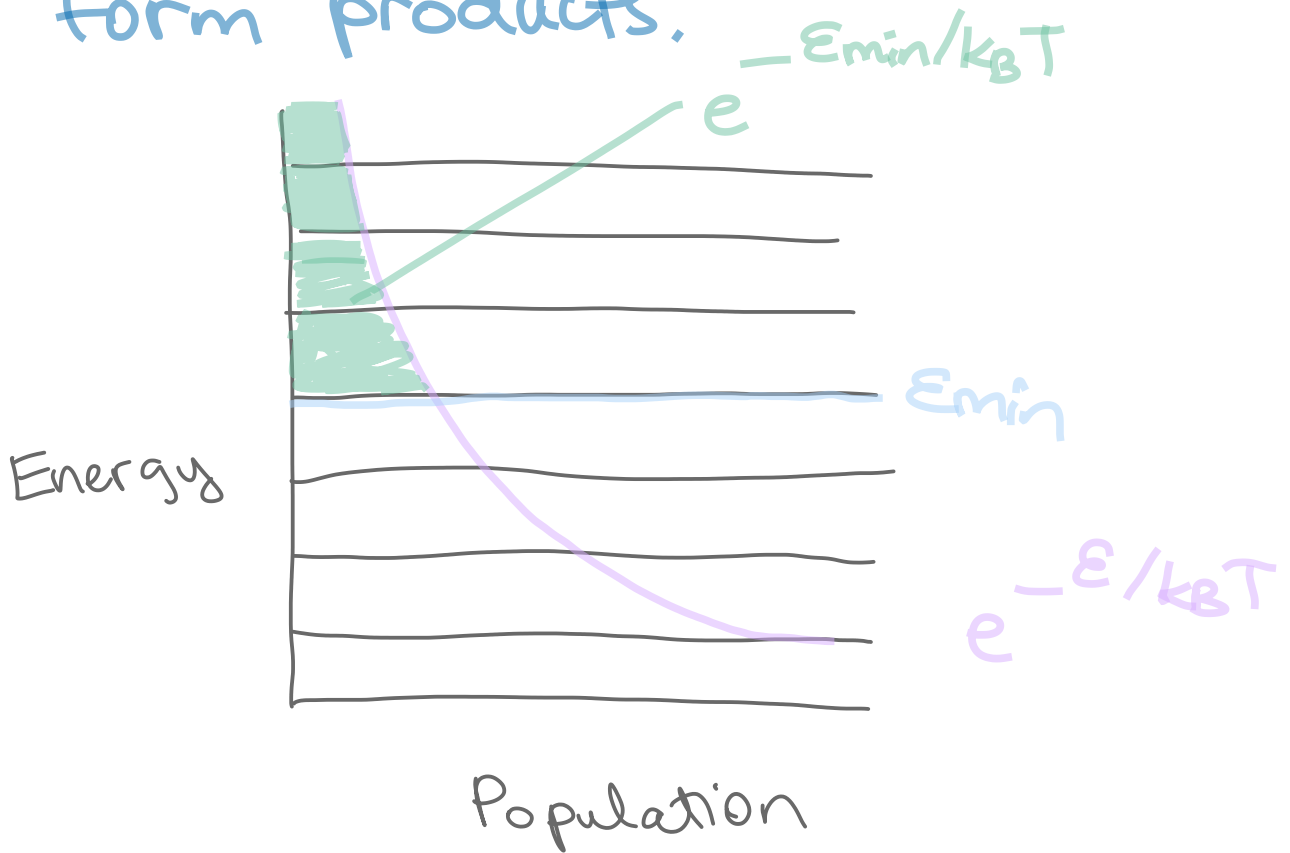
$$E_a = RT^2 \frac{d \ln k}{dT}$$

formal definition
of activation
energy



REACTION COORDINATE

The activation energy is the minimum energy reactants must have in order to form products.



reaction coordinate