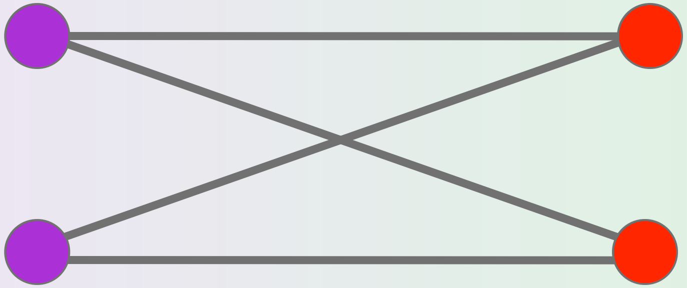
Model of Kinetics

The Collision Theory of Chemical Kinetics

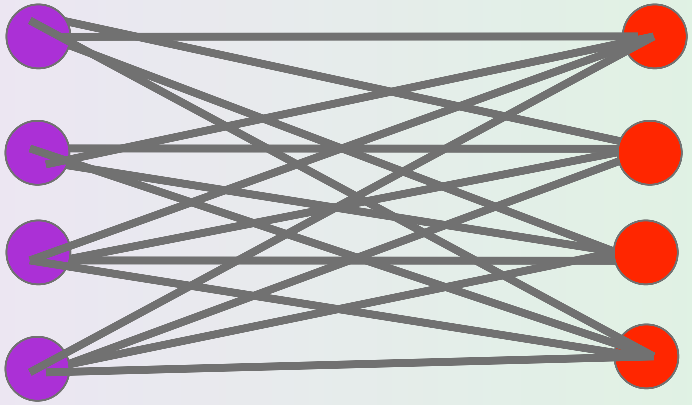
The dependence of number of collisions on concentration



doubling the concentration of both reactants

quadrupled the number of collisions

The dependence of number of collisions on concentration



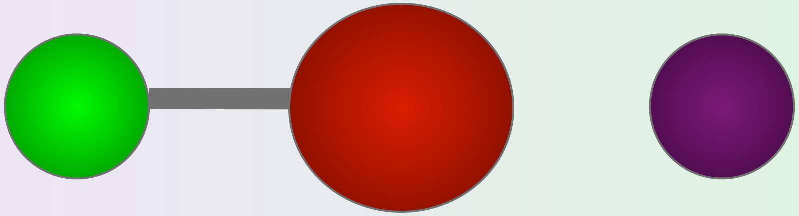
higher the concentration of reactants

the higher the number of collisions

faster the reaction rate

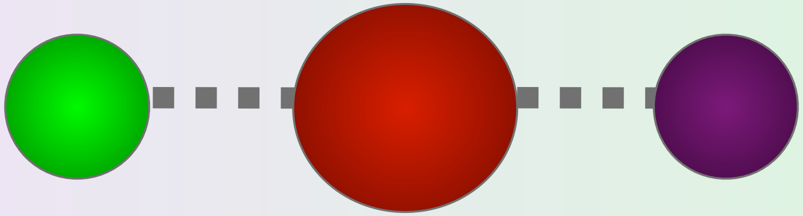
Collision Theory

in order to react two molecules must encounter one another (collide)



Collision Theory

in order to react two molecules must encounter one another (collide)

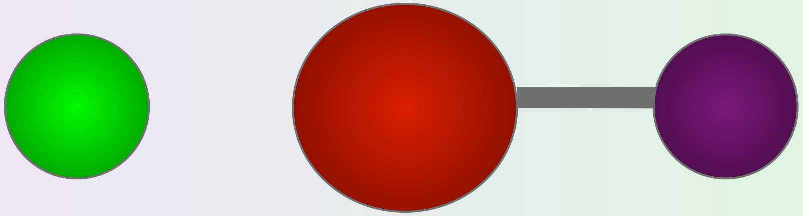


Activated complex

A short lived transient species

Collision Theory

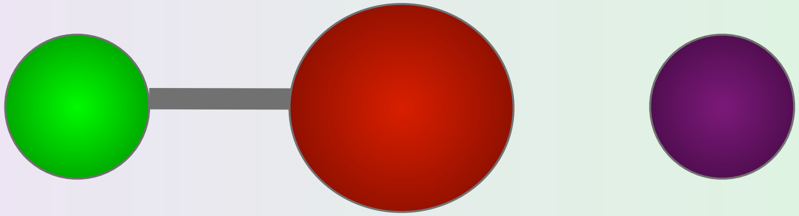
in order to react two molecules must encounter one another (collide)



products

Collision Theory

But not all collisions result in reaction



reaction rate is much smaller than the calculated collision frequency ?

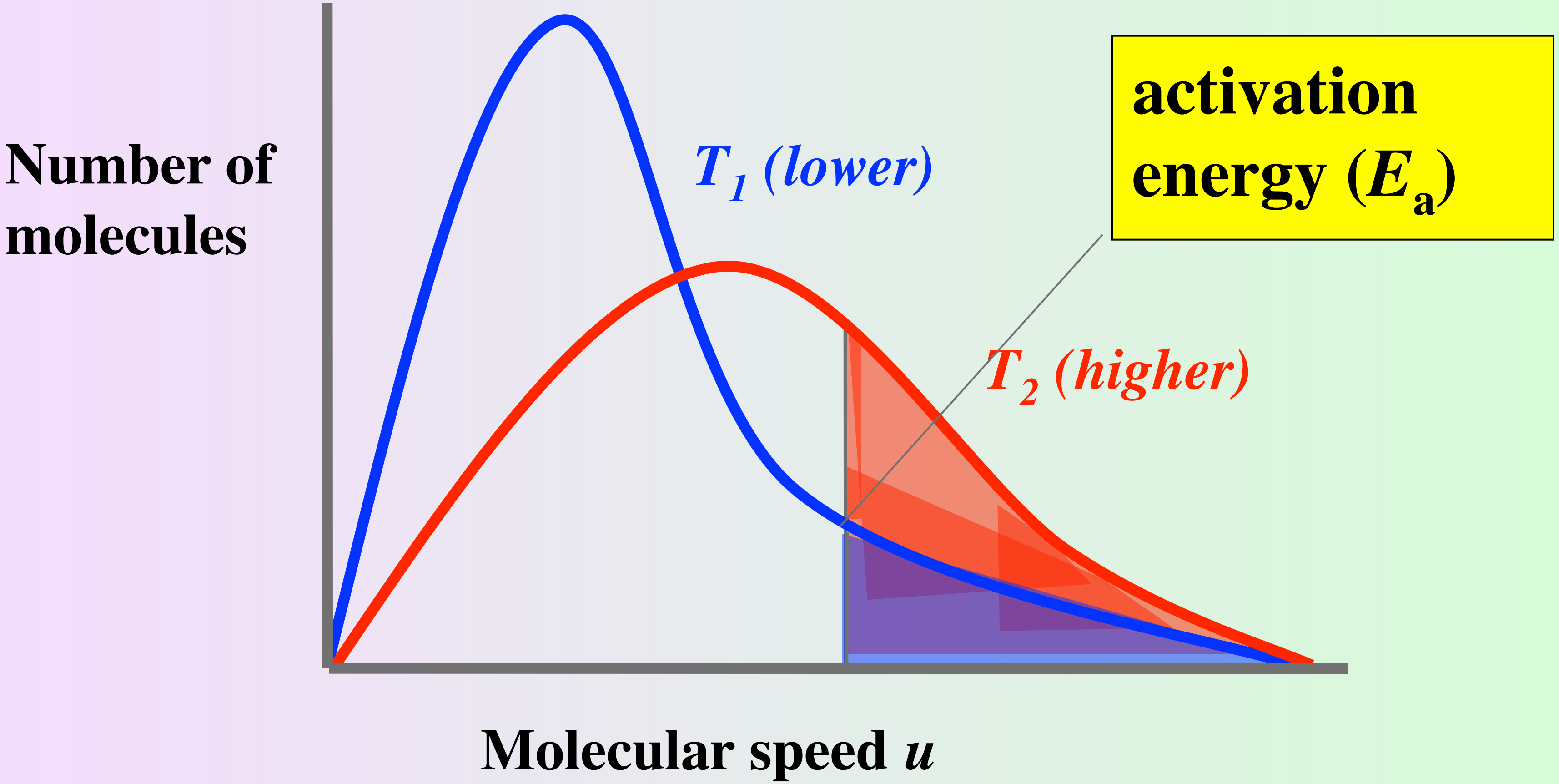
Svante Arrhenius

in order to react, the colliding molecules must possess enough kinetic energy to overcome the repulsive and bonding forces of the reactants

activation energy (E_a) the minimum energy required for a chemical reaction to occur

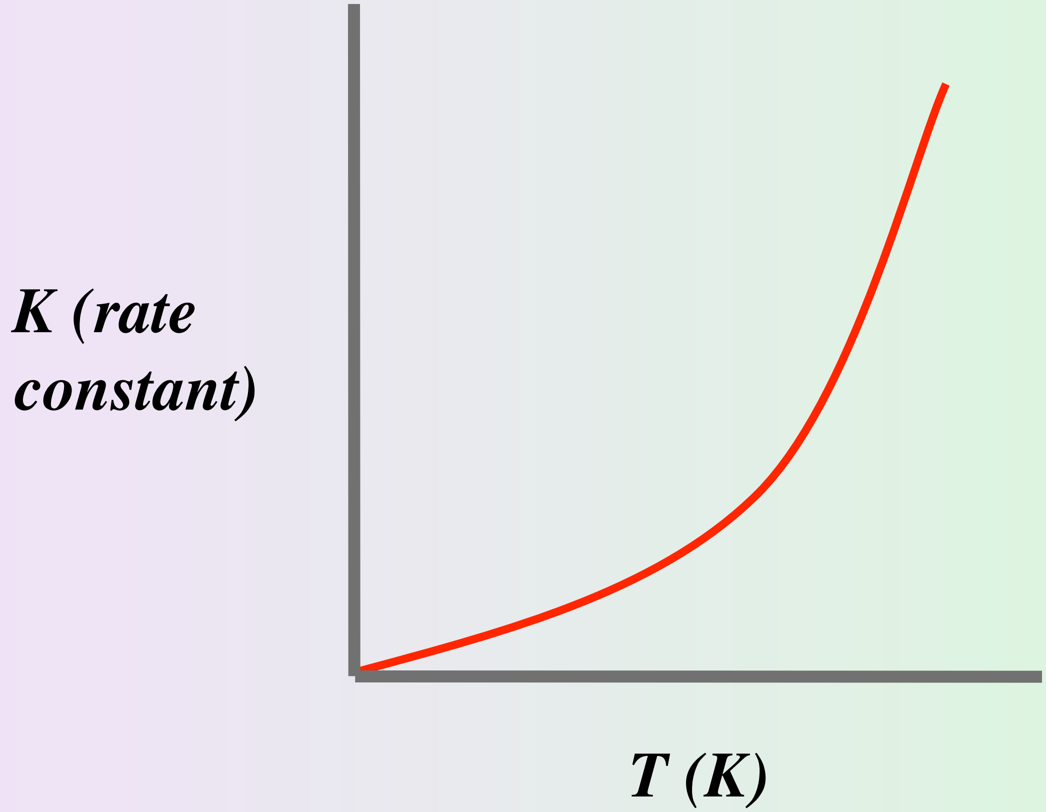
Temperature and Rate of Reaction

At a certain temperature only a certain fraction of the molecules possess enough energy to create effective collisions.



Temperature and Rate of Reaction

effective collisions increase exponentially with an increase in temperature



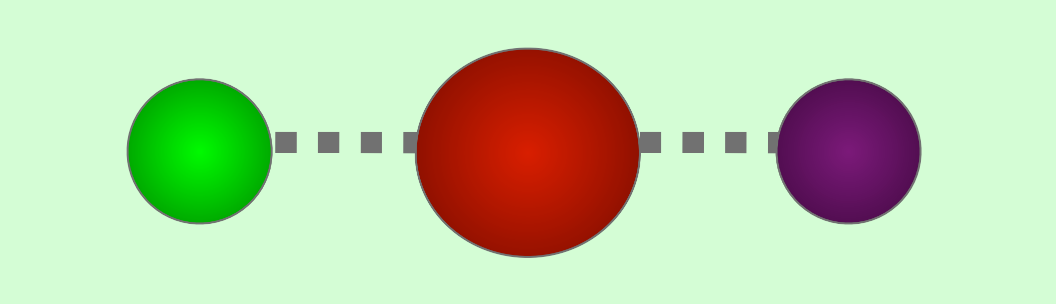
Temperature and Rate of Reaction

An increase in temperature increases the rate of almost all chemical reactions.

Faster moving particles collide more often and with greater kinetic energy.

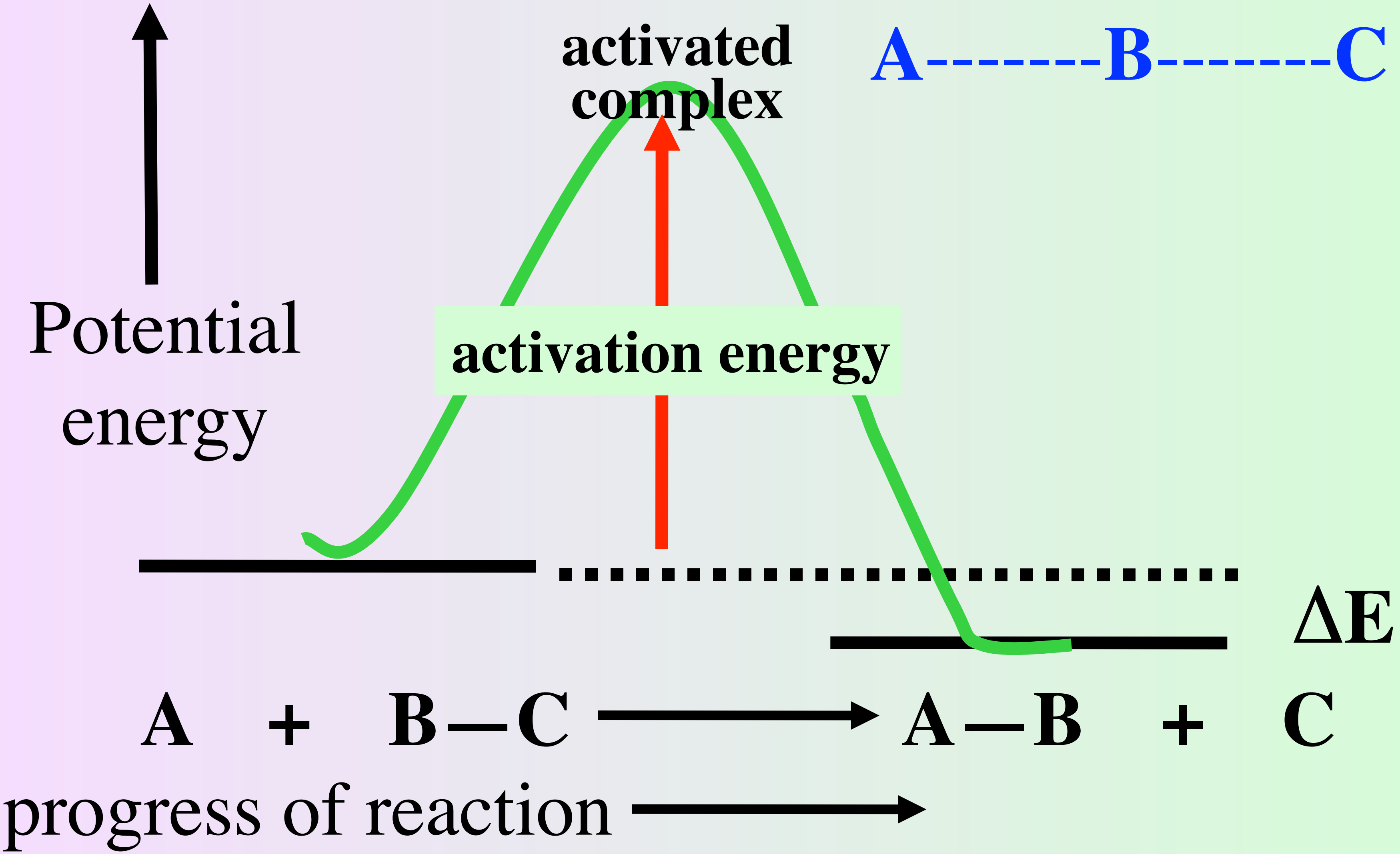
Activated complex

the species temporarily formed by the reactant molecules as a result of the collision before they form product

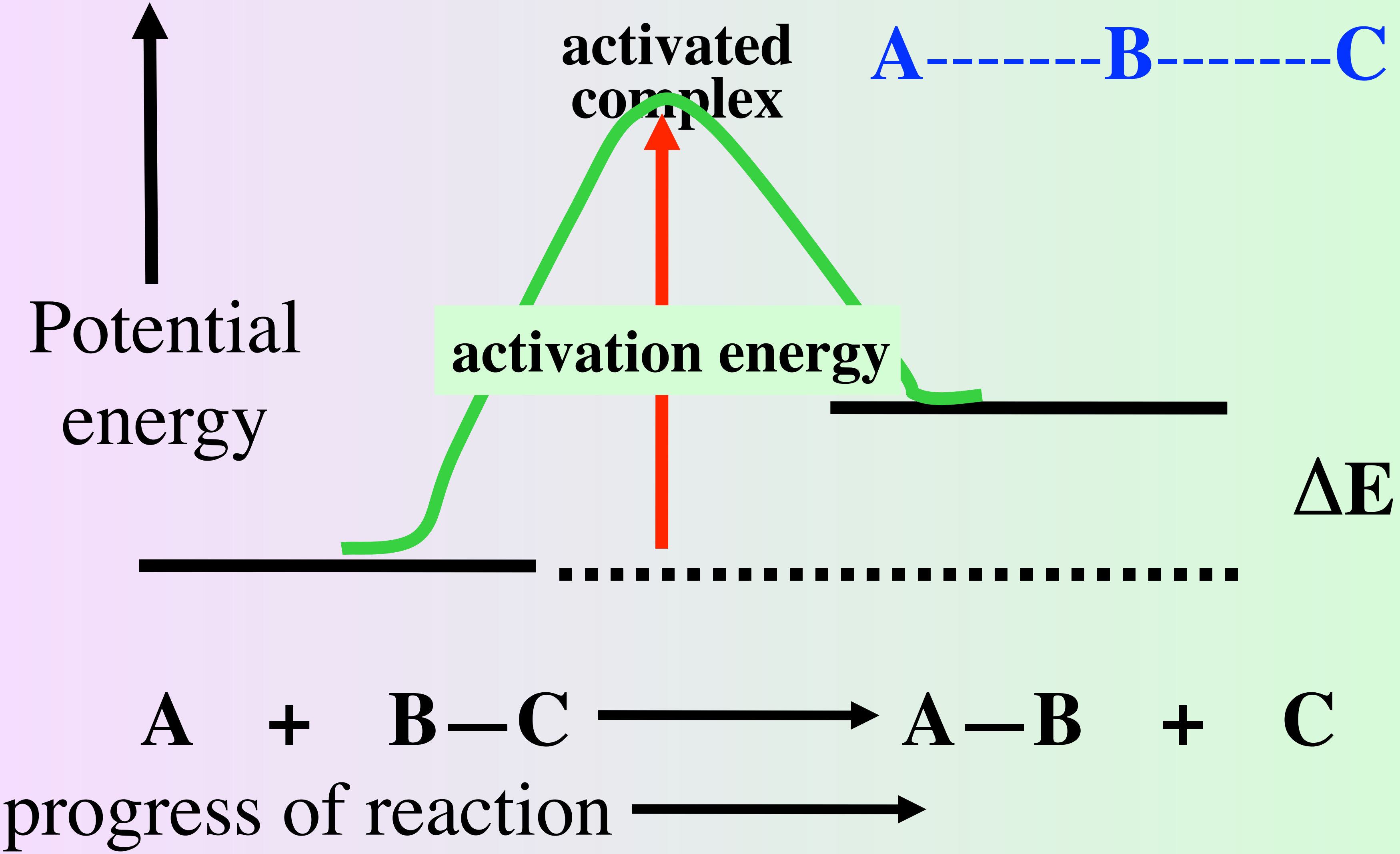


Activated complex

Consider a hypothetical one-step reaction (exothermic)


activated complex
A--------B--------C
Potential energy
activation energy
ΔE
A + B—C ⟶ A—B + C
progress of reaction

Consider a hypothetical one-step reaction (endothermic)



Potential energy

activated complex

A--------B--------C

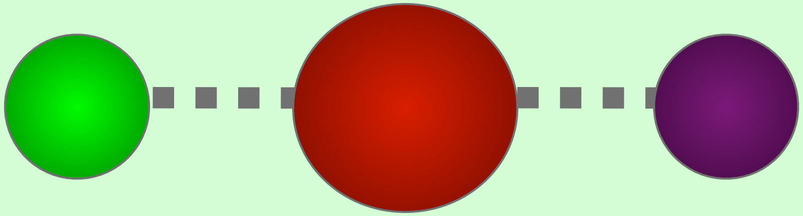
activation energy

ΔE

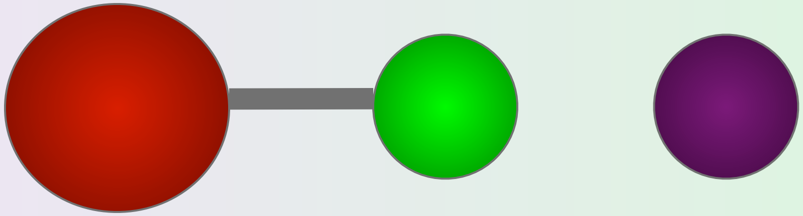
$A + B{-}C \longrightarrow A{-}B + C$

progress of reaction →

Molecules must collide with proper geometry



Activated complex



No reaction

Reaction rate is directly proportional to:

- **the number of collisions per second**

  with the proper orientation

- **the fraction of collisions that possess sufficient energy for reaction**

Arrhenius equation

rate constant (*k*)

the frequency of collisions with correct geometry

$$k \propto \mathbf{A}$$

Arrhenius equation

rate constant (k)

the frequency of collisions with correct geometry

x

the fraction of molecules with enough energy to react

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

(R = .008314 kJ /mol K)

Determining activation energy graphically

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

$$\ln k = \ln A - (E_a/RT)$$

$$\ln k = -(E_a/R)(1/T) + \ln A$$

a plot of ln k versus 1/T gives a straight line with slope = $-(E_a/R)$

Example

$$N_2O \longrightarrow N_2 + O$$

Calculate the activation energy for the reaction shown.

Rate constant *k* **$M^{-1}\ s^{-1}$**	**T** **°C**
0.00187	**600**
0.0113	**650**
0.0569	**700**
0.244	**750**

Plot *ln* k versus 1/T

(don’t forget to convert to kelvins)

Example

$$N_2O \longrightarrow N_2 + O$$

Calculate the activation energy for the reaction shown.

Plot *ln* k versus 1/T

ln k	**T** **K**
-6.28	873
-4.48	923
-2.87	973
-1.50	1023

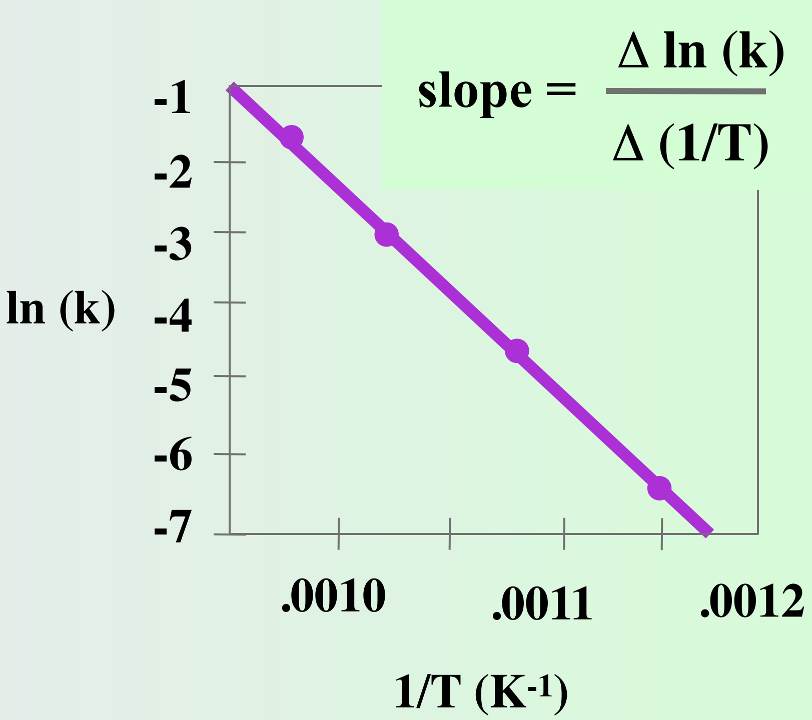
Example

$$N_2O \longrightarrow N_2 + O$$

Calculate the activation energy for the reaction shown.

Plot *ln* k versus 1/T

ln k	**1/T K^{-1}**
-6.28	**0.00115**
-4.48	**0.00108**
-2.87	**0.00103**
-1.50	**0.000978**



$$\text{slope} = \frac{\Delta \ln (k)}{\Delta (1/T)}$$

$$\text{slope} = -(E_a/R)$$

$$E_a = -R \text{ (slope)}$$

$$\text{slope} = -28{,}113 \text{ K}$$

$$E_a = -8.314 \text{ J/mol K } (-28{,}113 \text{ K})$$

$$E_a = 230 \text{ kJ/mol}$$

Alternative for Determining activation energy

We can also calculate E_a from values of rate constant (*k*) at two temperatures using a derivative formula

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

$$= \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1\ T_2}\right)$$

Example

The first-order rate constant for the reaction of methanol (CH_3OH) and hydrochloric acid (HCl) is $3.32\text{x}10^{-10}\ s^{-1}$ at 25°C. Calculate the rate constant at 40°C if the activation energy is 116kJ/mol.

$$K_1 = 3.32\text{x}10^{-10}\ s^{-1}$$

$$T_1 = 298\ K$$

$$T_2 = 313\ K$$

$$E_a = 116\text{kJ/mol}$$

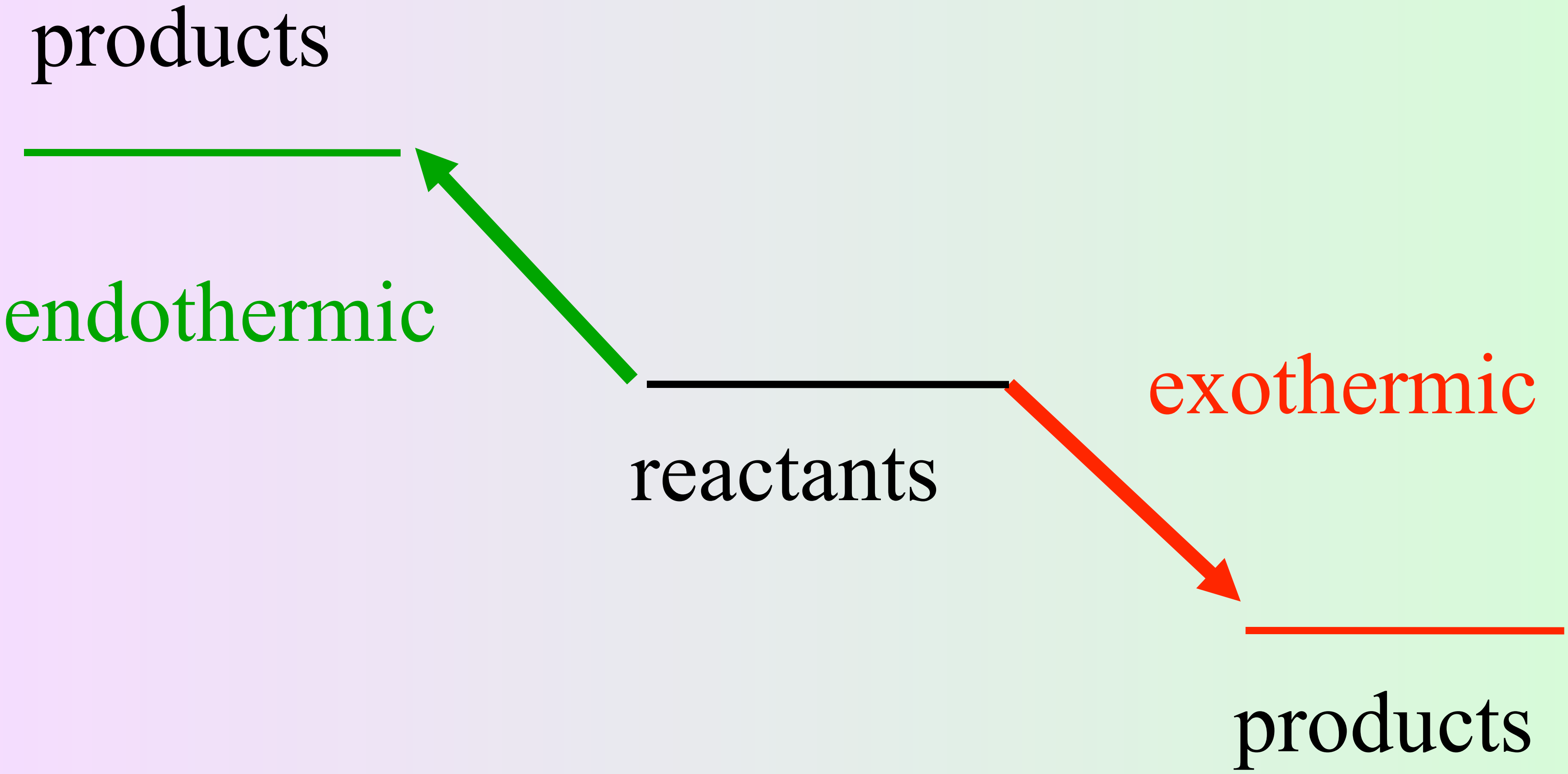
$$ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1\ T_2}\right)$$

$$ln\ \frac{3.32\text{x}10^{-10}\ s^{-1}}{k_2} = \frac{E_a}{8.314\ \text{J/K.mol}}\left(\frac{298\ K - 313\ K}{(313\ K)\ (298\ K)}\right)$$

$$K_2 = 3.13\ \text{x}\ 10^{-9}\ s^{-1}$$

Thermodynamics

Deals with energy relationships between reactants and products at equilibrium



products

endothermic

reactants

exothermic

products

Concentration effect on reaction rate can only be established by experiment

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{Rate} = -\frac{1/2\,\Delta\,[N_2O_5]}{\Delta\,t} = \frac{1/4\,\Delta\,[N_2O]}{\Delta\,t} = \frac{\Delta\,[O_2]}{\Delta\,t}$$

Since all three terms are proportional to $[N_2O_5]$, the reaction rate equation: where k is the rate constant for the reaction.

$$= -\frac{1/2\Delta\,[N_2O_5]}{\Delta\,t} = k\,[N_2O_5]$$

Rate constant