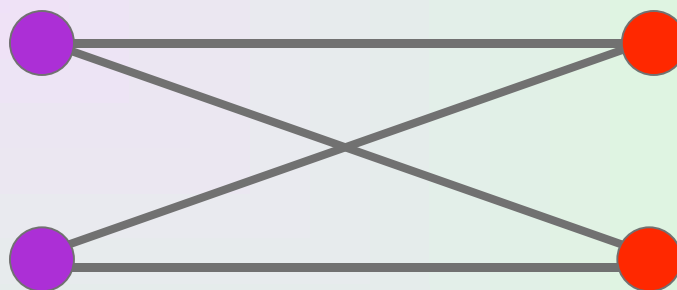


Model of Kinetics

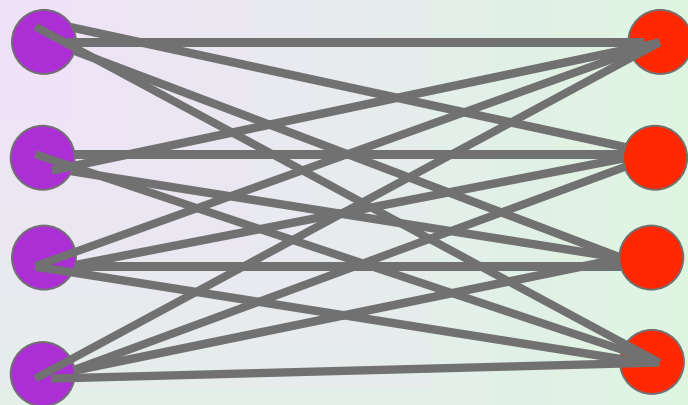
The Collision Theory of Chemical Kinetics

The dependence of number of collisions on concentration



**doubling the concentration of both reactants
quadrupled the number of collisions**

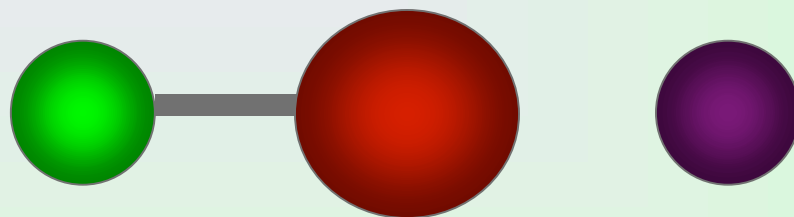
The dependence of number of collisions on concentration



**higher the concentration of reactants
the higher the number of collisions
faster the reaction rate**

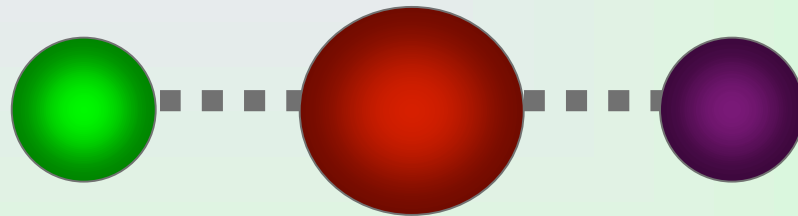
Collision Theory

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



Collision Theory

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

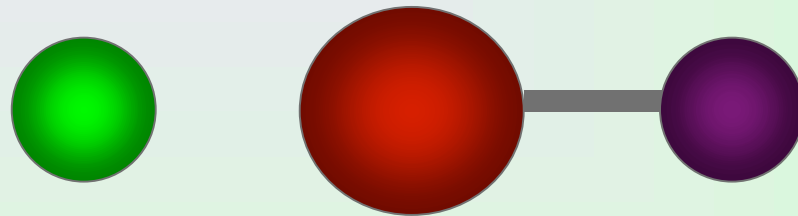


Activated complex

A short lived transient species

Collision Theory

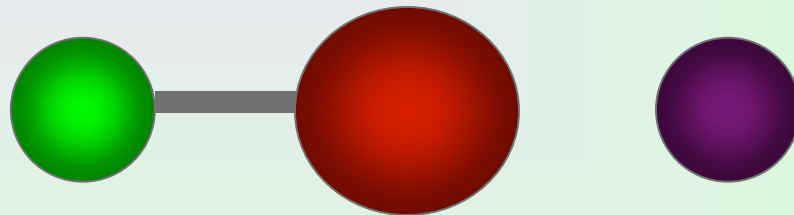
in order to react two molecules must encounter one another (collide)



products

Collision Theory

But not all collisions result in reaction



reaction rate is much smaller than the calculated collision frequency ?

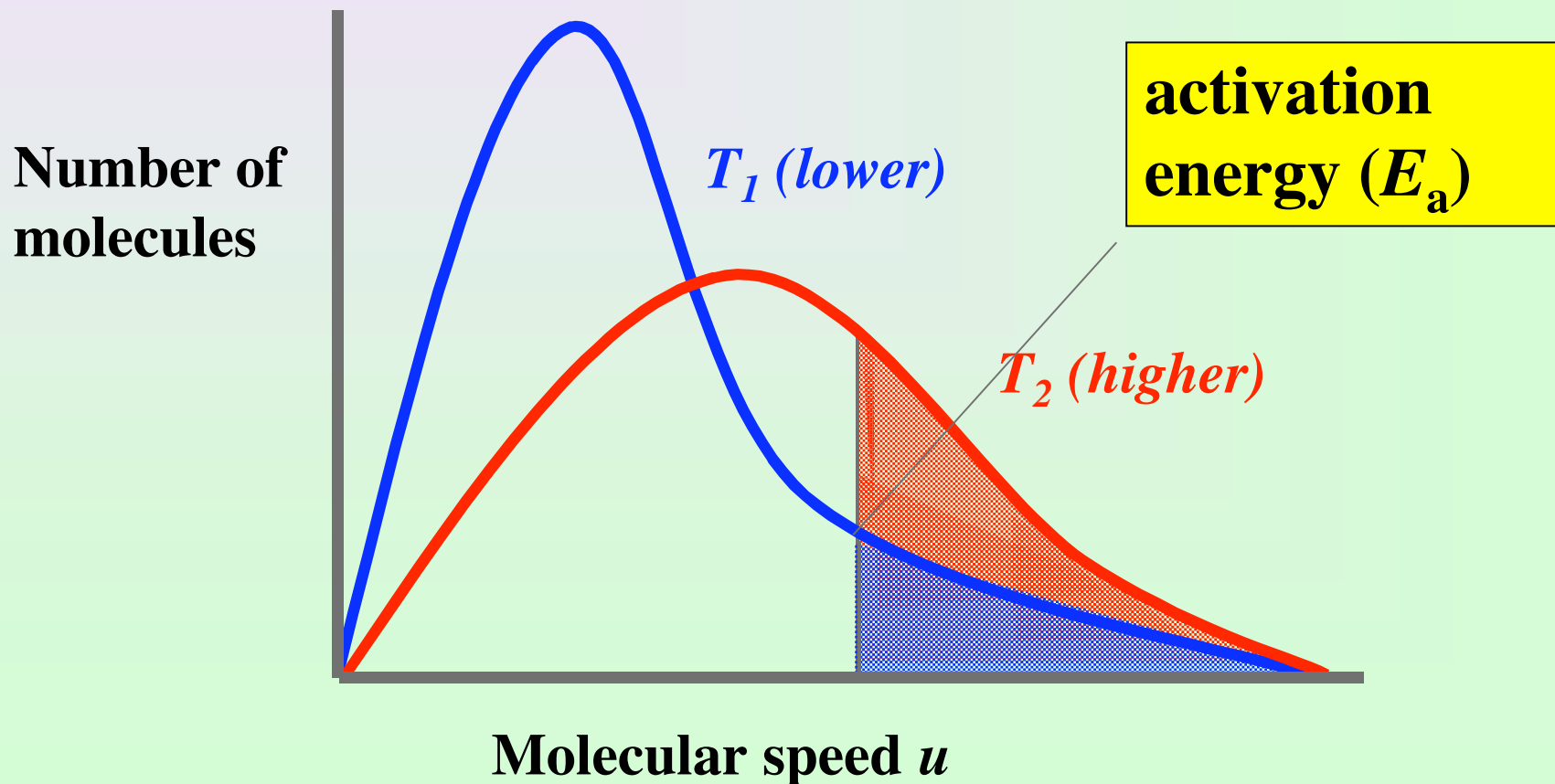
Svante Arrhenius

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

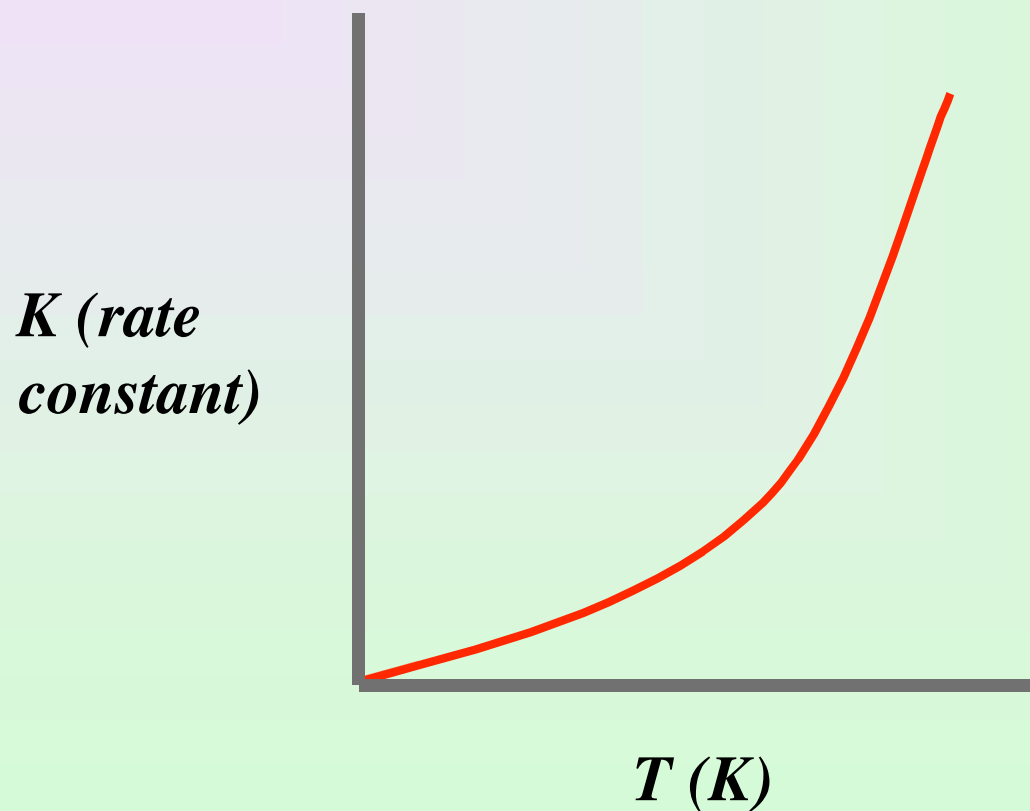
Temperature and Rate of Reaction

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



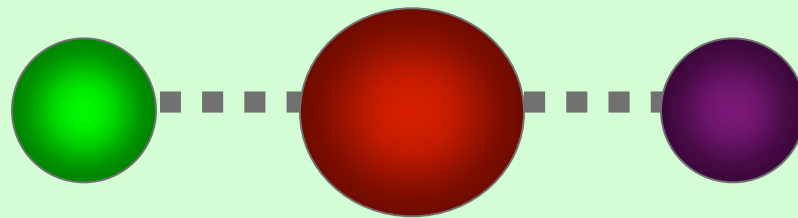
Temperature and Rate of Reaction

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

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

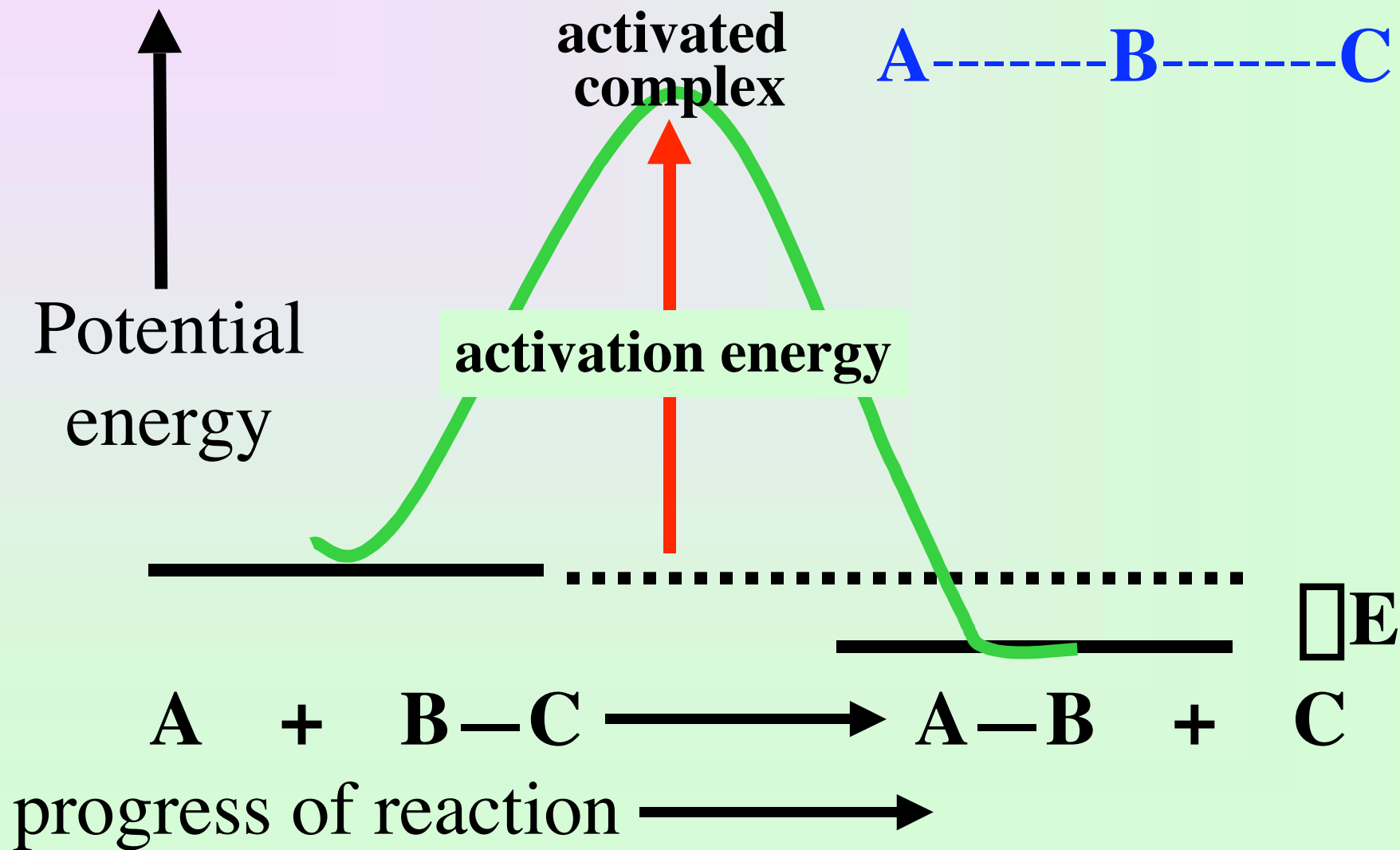
Activated complex

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

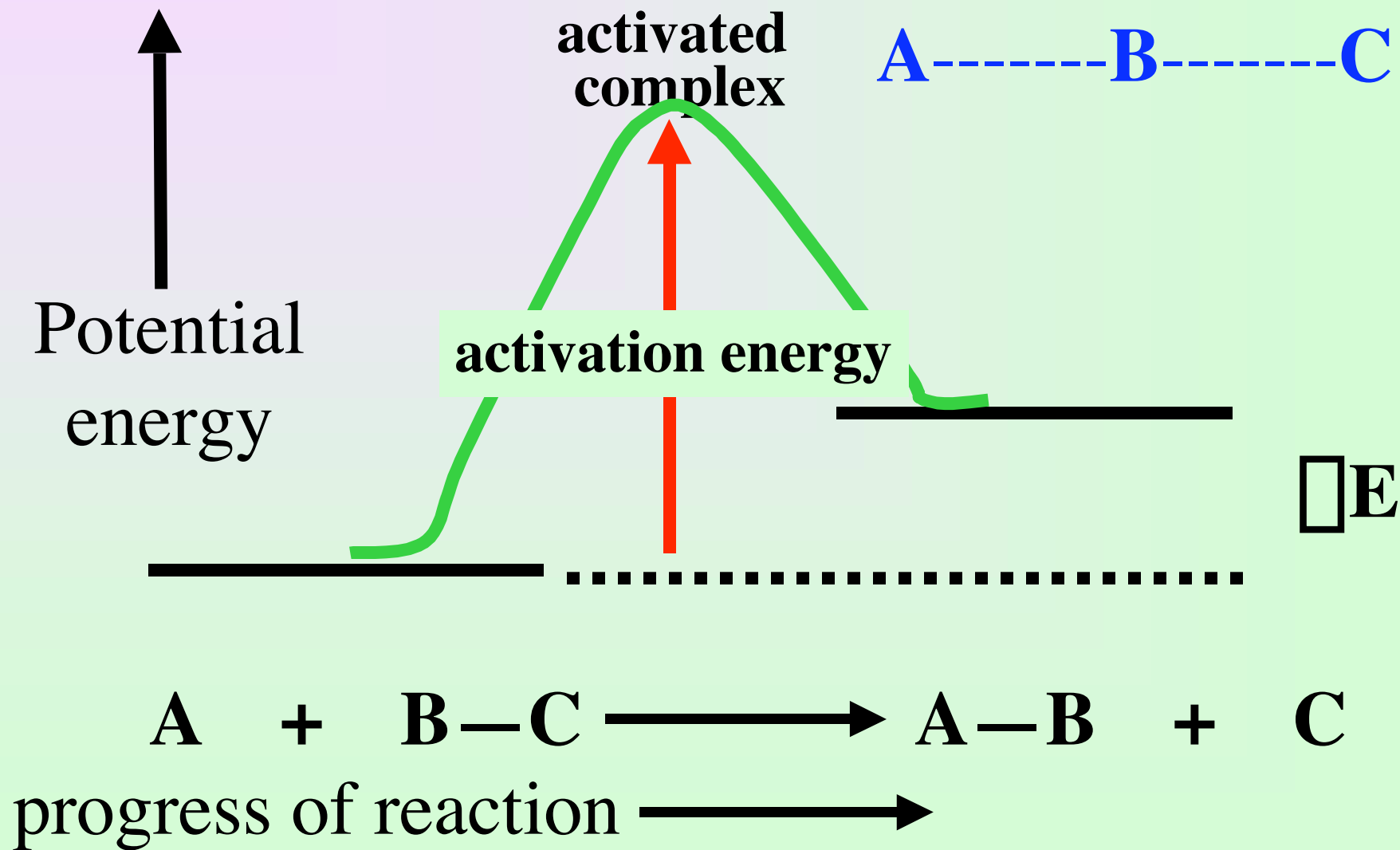


Activated complex

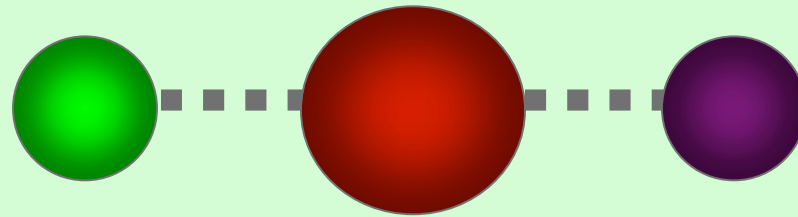
Consider a hypothetical one-step reaction (exothermic)



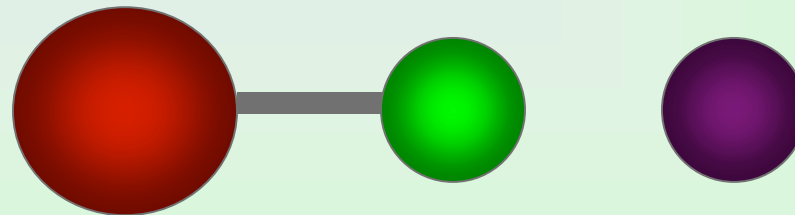
Consider a hypothetical one-step reaction (endothermic)



**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

$$k \propto A$$

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



Calculate the activation energy for the reaction shown.

Rate constant k

$\text{M}^{-1} \text{s}^{-1}$

0.00187

0.0113

0.0569

0.244

T

$^{\circ}\text{C}$

600

650

700

750

Plot $\ln k$ versus $1/T$

**(don't forget to
convert to kelvins)**

Example



Calculate the activation energy for the reaction shown.

<i>ln k</i>	T K	Plot <i>ln k</i> versus 1/T
-6.28	873	
-4.48	923	
-2.87	973	
-1.50	1023	

Example



Calculate the activation energy for the reaction shown.

<i>ln k</i>	$1/T$ K^{-1}	Plot <i>ln k</i> versus $1/T$
-6.28	0.00115	
-4.48	0.00108	
-2.87	0.00103	
-1.50	0.000978	

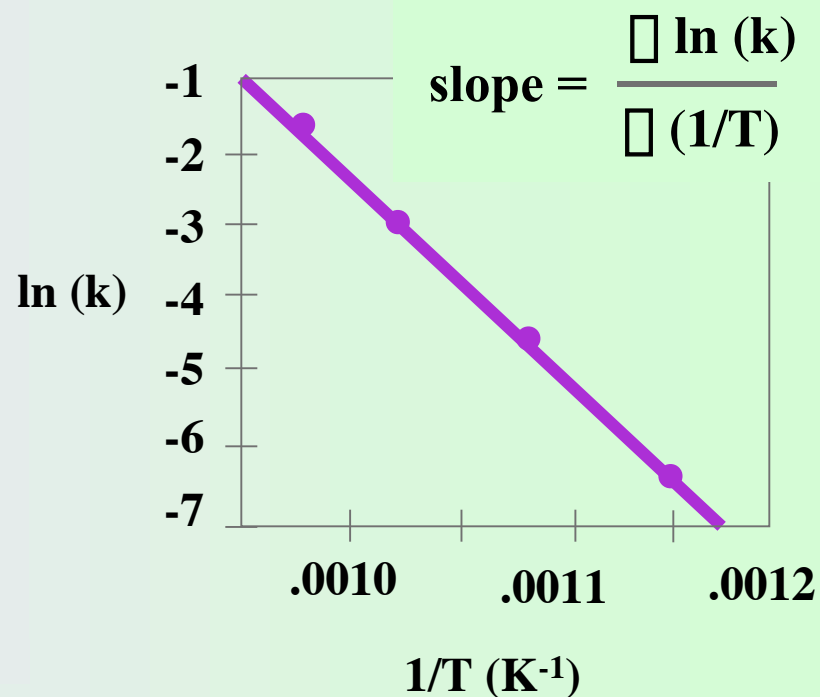
$$\text{slope} = -(E_a/R)$$

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

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

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

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



Alternative for Determining activation energy

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

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

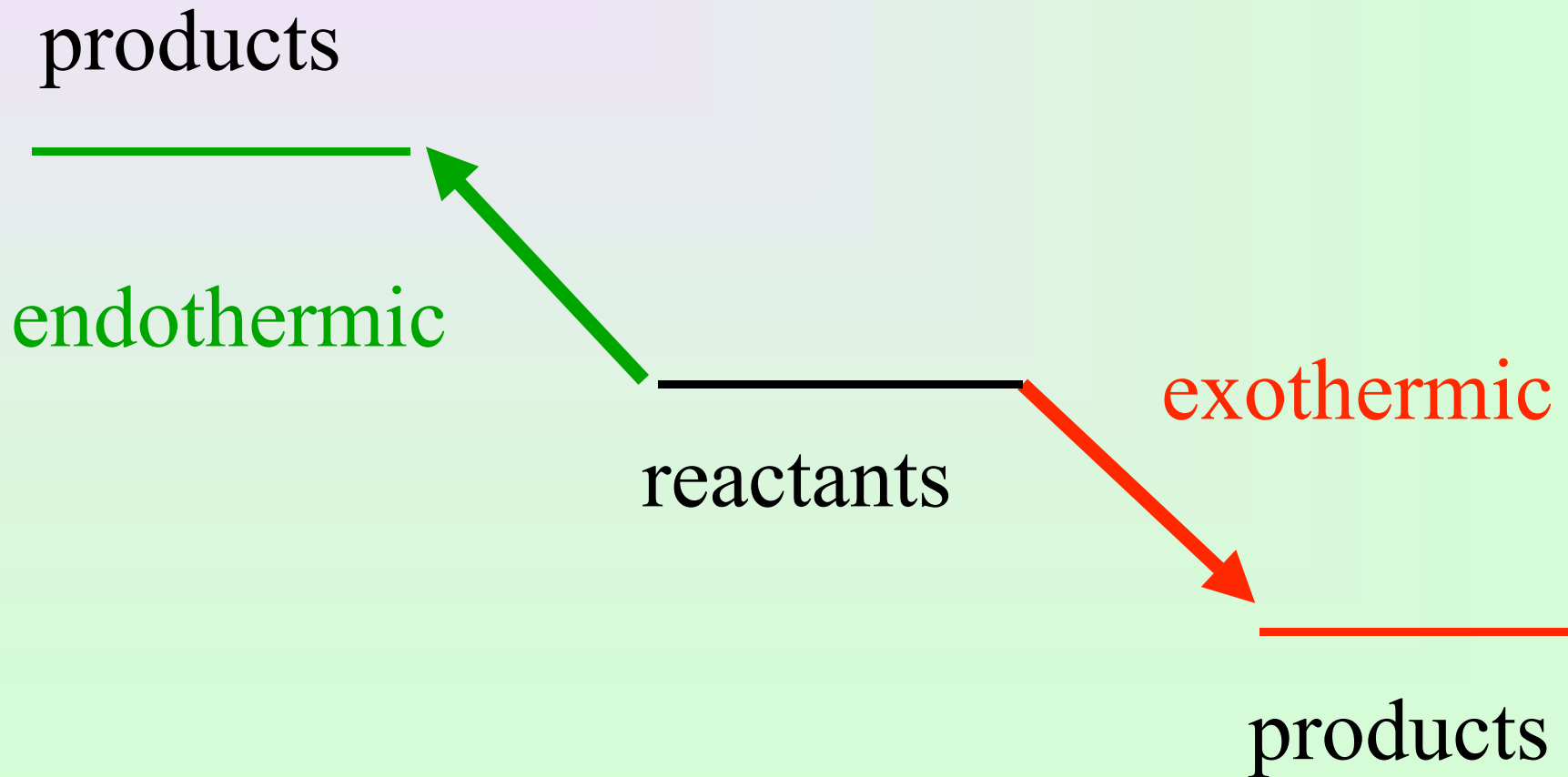
Example

The first-order rate constant for the reaction of methanol (CH₃OH) and hydrochloric acid (HCl) is $3.32 \times 10^{-10} \text{ s}^{-1}$ at 25°C. Calculate the rate constant at 40°C if the activation energy is 116 kJ/mol.

$$k_1 = 3.32 \times 10^{-10} \text{ s}^{-1} \quad \ln \left(\frac{k_1}{k_2} \right) = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$
$$T_1 = 298 \text{ K}$$
$$T_2 = 313 \text{ K} \quad \ln \frac{3.32 \times 10^{-10} \text{ s}^{-1}}{k_2} = \frac{E_a}{8.314 \text{ J/K.mol}} \left(\frac{298 \text{ K} - 313 \text{ K}}{(313 \text{ K})(298 \text{ K})} \right)$$
$$E_a = 116 \text{ kJ/mol} \quad K_2 = 3.13 \times 10^{-9} \text{ s}^{-1}$$

Thermodynamics

Deals with energy relationships between reactants and products at equilibrium



Concentration effect on reaction rate can only be established by experiment



$$\text{Rate} = -\frac{1/2 \Delta [\text{N}_2\text{O}_5]}{\Delta t} = \frac{1/4 \Delta [\text{N}_2\text{O}]}{\Delta t} = \frac{\Delta [\text{O}_2]}{\Delta t}$$

Since all three terms are proportional to $[\text{N}_2\text{O}_5]$, the reaction rate equation: where k is the rate constant for the reaction.

$$= -\frac{1/2 \Delta [\text{N}_2\text{O}_5]}{\Delta t} = k [\text{N}_2\text{O}_5]$$

Rate constant