

2/25/2019

The effect of temp upon rxn rate

rate \uparrow as $T \uparrow$ (for every $\sim 10^\circ\text{C}$ increase in temp, rxn rate doubles)

rate law: $\text{rate} = k[A]^m$

rate const:

has a strong T -dependence!

$k \uparrow$ as $T \uparrow$

slight decrease as we increase T .
(why? $V \uparrow T \uparrow$)

1889, Swedish Chemist: Svante Arrhenius

Arrhenius Equation

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

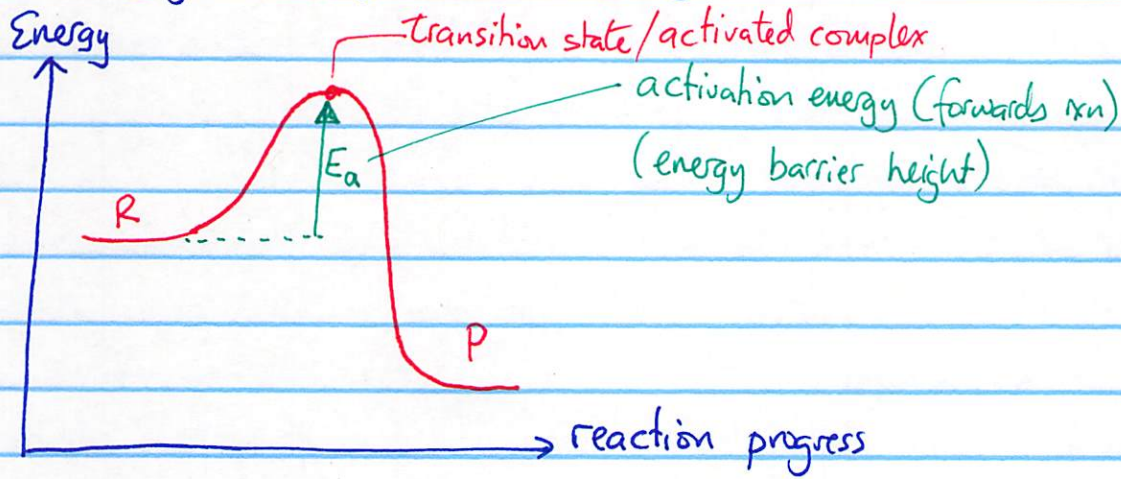
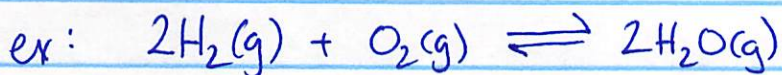
E_a — activation energy (J/mol, kJ/mol)
absolute temp (K)
gas constant = $8.3145 \text{ J/mol}\cdot\text{K}$

pre-exponential factor

exponential factor (strong T -dependence)

(OR) frequency factor

- related to # reactant collisions/s



note: exothermic rxn.
 $\Delta H = -ve$
 $\Delta H < 0$

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

1. $A \sim$ pre-exponential factor / Frequency factor

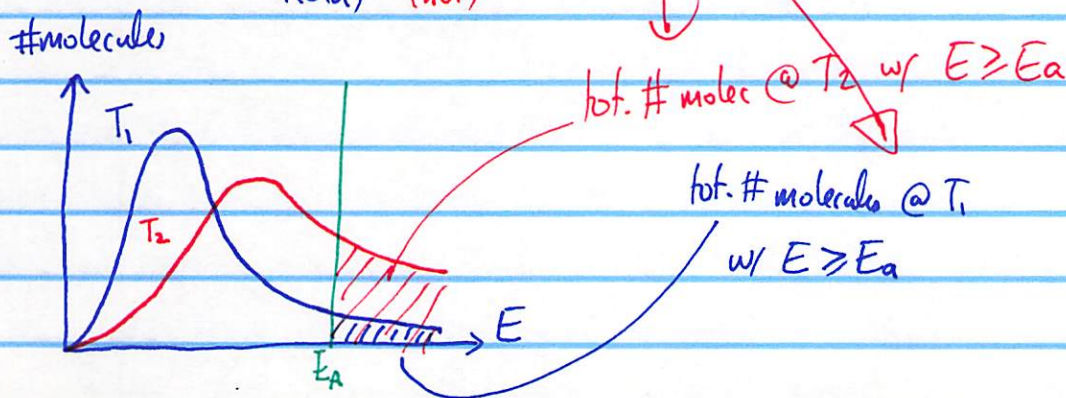
$$A = p \cdot Z$$

\swarrow collision frequency
 (# collisions/s)
 \swarrow orientation factor
 (prob. that molecules collide w/ proper orientation)

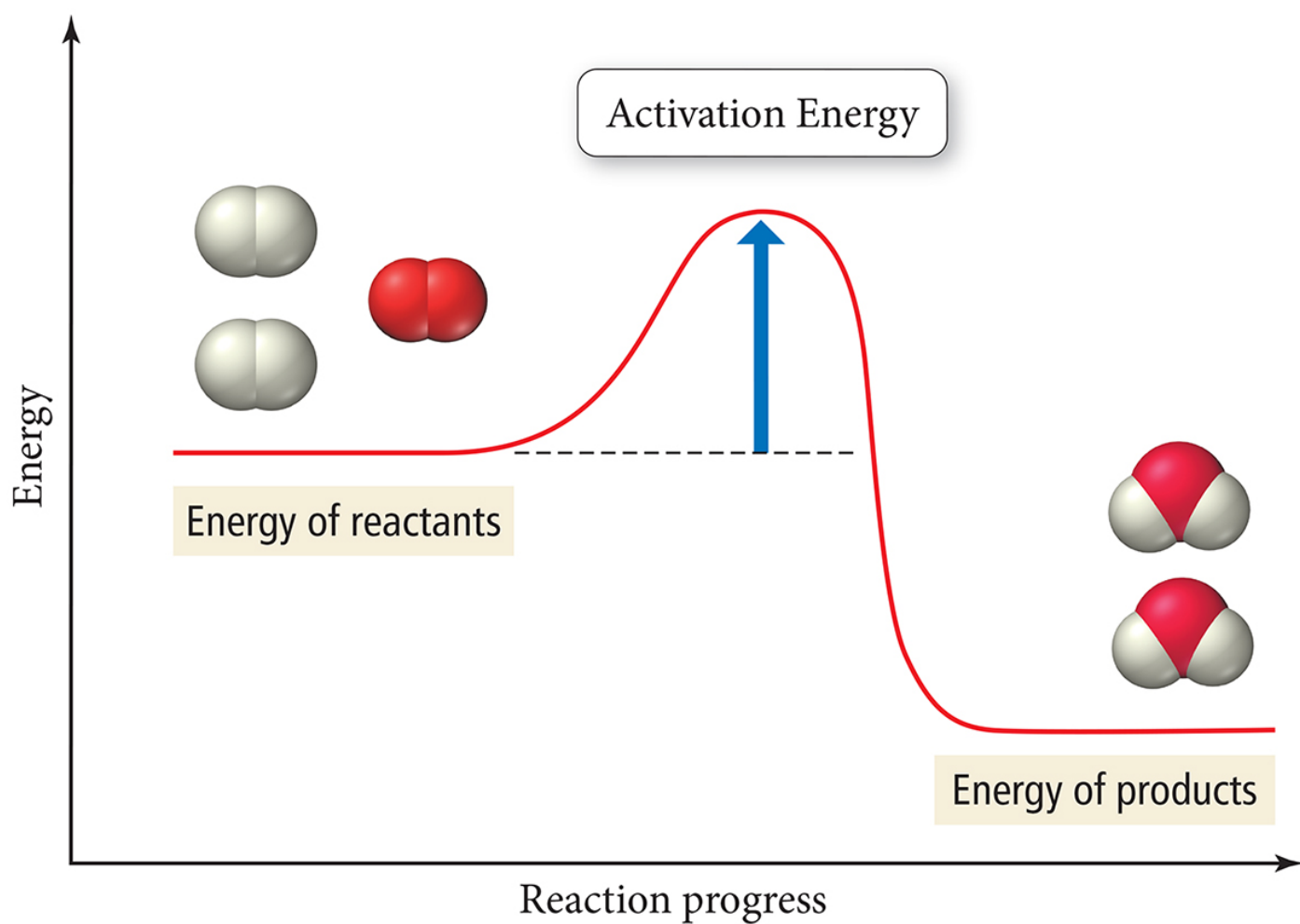
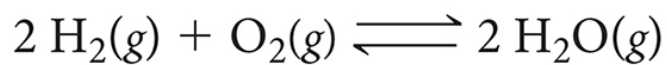
2. Exponential factor, $e^{-E_a/RT}$

- represents prob. molecules collide w/ $E \geq E_a$

Graph: T_1, T_2 $T_1 < T_2$
 (cold) (hot)

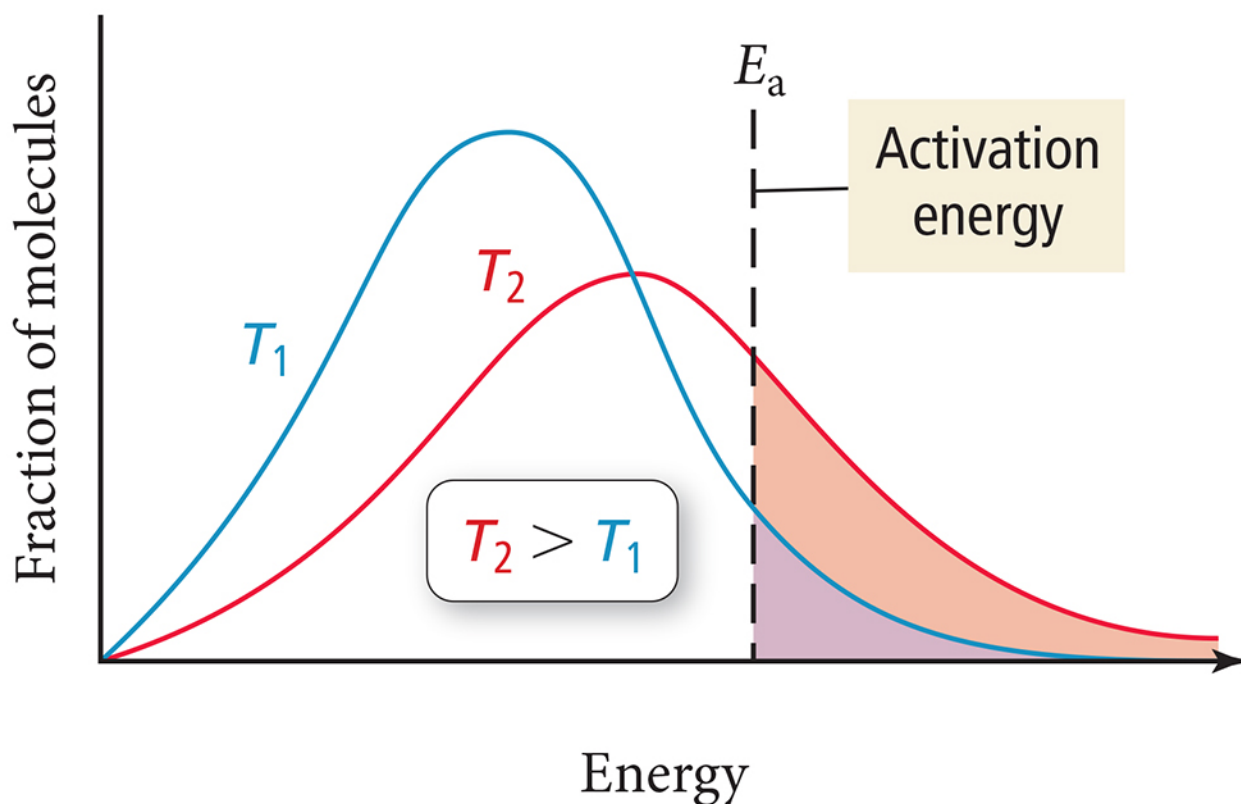


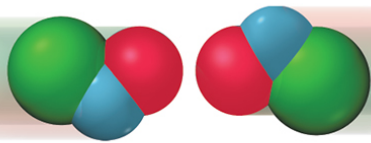
Activation Energy



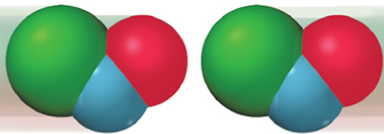
Thermal Energy Distribution

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.

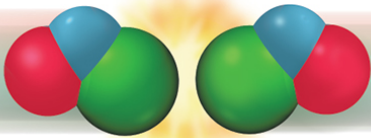




Ineffective collision



Ineffective collision



Effective collision

$$e^{-E_a/RT} \quad \text{as } T \rightarrow \infty \quad // \quad \text{as } T \rightarrow 0$$

$$(\text{prob } E \geq E_a) \cdot e^{-E_a/RT} \rightarrow 1 \quad e^{-E_a/RT} \rightarrow 0$$

$$\text{as } E_a \rightarrow \infty \quad // \quad \text{as } E_a \rightarrow 0$$
$$e^{-E_a/RT} \rightarrow 0 \quad e^{-E_a/RT} \rightarrow 1$$

Arrhenius plots

graphical methods of finding A , and E_a

$$\ln() \hookrightarrow k = A \cdot e^{-E_a/RT}$$
$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\text{OR: } \ln k = -\frac{E_a}{R} \cdot \left(\frac{1}{T}\right) + \ln A$$
$$\updownarrow \quad \updownarrow \quad \updownarrow \quad \updownarrow$$
$$y = m \cdot x + b$$