

Lecture 35 CH102 A1 (MWF 9:05 am) Spring 2018 Copyright © 2017 Dan Dill dan@bu.edu

[TP] When T is increased, the **rate of every** chemical reaction **must...**

25% 1. increase
25% 2. stay the same
25% 3. decrease
25% 4. More information needed

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Response Counter

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Wednesday, April 25, 2018

- Complete: Making sense of rate constants: The Arrhenius relation
- Rate versus temperature: E_a and A .

Next lecture: Catalysis. Half-life.

Maxwell-Boltzmann kinetic energy distribution
<http://quantum.bu.edu/CDF/102/MaxwellBoltzmannEnergyDistribution.cdf>

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Making sense of rate constants

To understand what determines the relative size of rate constants, let's begin by imagining how **enthalpy changes** as an **exothermic reaction**, such as

$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

evolves as reactants, R, are transformed into products, P.

Sketch a diagram showing how enthalpy changes (vertical axis) as time passes (horizontal axis), starting with all reactants, R, and ending with all products, P.

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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

Because reactions involve both **bond breaking** in reactants and **bond making** in products, **energy must be supplied** for both $\text{R} \rightarrow \text{P}$ and $\text{P} \rightarrow \text{R}$.

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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

Where does the energy come from for $R \rightarrow P$?

It comes from **the kinetic energy** of reactant molecules.

Maxwell-Boltzmann kinetic energy distribution
<http://quantum.bu.edu/CDF/102/MaxwellBoltzmannEnergyDistribution.cdf>

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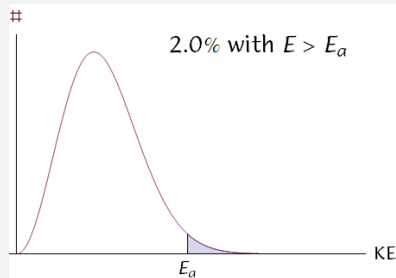
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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

Where does the energy come from for $R \rightarrow P$?

Kinetic energy of reactant molecules.



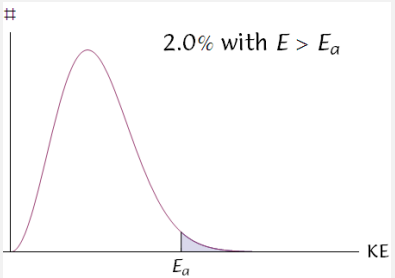
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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

Only molecules with kinetic energy greater than the activation energy, E_a , can react.



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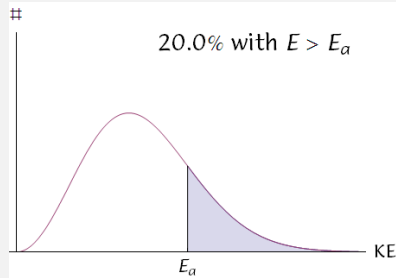
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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

Only molecules with kinetic energy greater than E_a can react

Raising temperature increases the number with at least kinetic energy E_a



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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

Only molecules with kinetic energy greater than the activation energy E_a can react.

A $\exp\left[-\frac{E_a}{RT}\right] = \dots$

Fraction of molecules with minimum kinetic energy E_a required for the reaction to take place (always less than 1)

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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

What is fraction $\exp\left[-\frac{E_a}{RT}\right]$ for $E_a = 100 \text{ kJ/mol}$ and $T = 300 \text{ K}$?

Answer: 4×10^{-18} !

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$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

What is fraction $\exp\left[-\frac{E_a}{RT}\right]$ for $E_a = 100 \text{ kJ/mol}$ and $T = 5000 \text{ K}$?

Answer: 0.09!

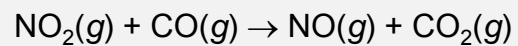
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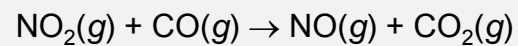
What role does the relative orientation of the colliding molecules (**collision geometry**) play?



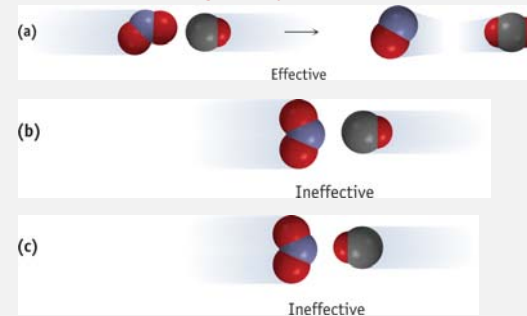
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Collisions must have the **correct geometry: A**



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Putting geometry and temperature together

$$k = A \exp\left[-\frac{E_a}{RT}\right]$$

$A = \dots$

frequency of collisions $\times \dots$

probability that collisions have an appropriate **collision geometry**

$$\exp\left[-\frac{E_a}{RT}\right] = \dots$$

Fraction of molecules with **minimum kinetic energy E_a** for reaction (always less than 1)



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Rate versus temperature: E_a and A



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- 25% 1. increase
 25% 2. stay the same
 25% 3. decrease
 25% 4. More information needed



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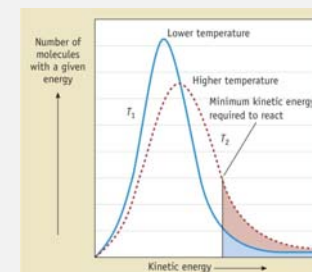
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[TP] Rate constants depend on T as $k = A \exp[-E_a/(RT)]$.The value of k at $T = 0$ is ...

- 25% 1. 0
 25% 2. A
 25% 3. $E_a/(RT)$
 25% 4. ∞



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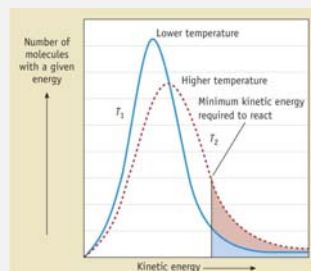
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[Quiz] Rate constants depend on T as $k = A \exp[-E_a/(RT)]$.The value of k at $T = \infty$ is ...

- 25% 1. 0
 25% 2. A
 25% 3. $E_a/(RT)$
 25% 4. ∞



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Rate versus temperature

Arrhenius relation: $k = A \exp[-E_a/(RT)]$ E_a is activation energy A is frequency factorHow could we use data for k versus T to get E_a and A ?

$$\ln(k) = -\frac{E_a}{R} \frac{1}{T} + \ln(A)$$



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

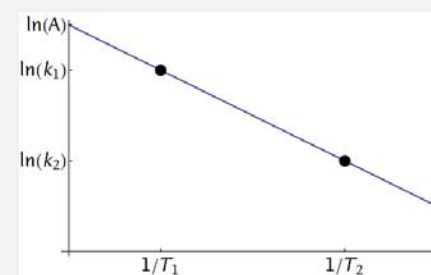
Sketch $\ln(k)$ versus $1/T$ for an arbitrary reaction.

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

Sketch $\ln(k)$ versus $1/T$ for an arbitrary reaction.Slope = $-E_a/R$ Intercept (at $T = \infty$) = $\ln(A)$ 

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[TP] For $A \rightarrow B$, k_{for} is 0.003/min at 25 °C and 0.025/min at 35 °C.
 For $C \rightarrow D$, k_{for} is 0.003/min at 25 °C and 0.035/min at 35 °C.
 Compared to the activation energy of $A \rightarrow B$, the activation energy of $C \rightarrow D$ is ...

- 25% 1. smaller
 25% 2. the same
 25% 3. larger
 25% 4. More information needed



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

For $A \rightarrow B$, k_{for} is 0.003/min at 25 °C and 0.025/min at 35 °C.

$$\text{slope} = -E_a/R = (\ln(k_{A,2}) - \ln(k_{A,1})) / (1/T_2 - 1/T_1) = -19000$$

For $C \rightarrow D$, k_{for} is 0.003/min at 25 °C and 0.035/min at 35 °C.

$$\text{slope} = -E_a/R = (\ln(k_{C,2}) - \ln(k_{C,1})) / (1/T_2 - 1/T_1) = -23000$$



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