[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

BOSTON UNIVERSITY

Response Counter

10

1

Lecture 35 CH102 A1 (MWF 9:05 am)

Monday, April 29, 2019

- Complete: Rate vs concentration from experiment
- Making sense of rate vs concentration: Reaction mechanism
- Making sense of rate constants: The Arrhenius relation
- Rate versus temperature: E_a and A.

Next lecture: Complete: Rate versus temperature: E_a and A. First law, second law, equilibrium, and kinetics.

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

BOSTON UNIVERSITY

[TP] For $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$
what is the order in ${}^-OCH_3$?

1. 1
2. 2
3. Neither of the above
4. More info needed

$[(CH_3)_3CBr]$	$[{}^-OCH_3]$	Rate (M/s)
0.0001	0.0001	2.8×10^{-5}
0.0002	0.0001	5.6×10^{-5}
0.0001	0.0002	2.8×10^{-5}

BOSTON UNIVERSITY

Response Counter

10

11

[TP] For $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$
what is the full differential rate law?

1. rate $= k_{for}\,[(CH_3)_3CBr]\,[{}^-OCH_3]$
2. rate $= k_{for}\,[(CH_3)_3CBr]$
3. rate $= k_{for}\,[{}^-OCH_3]$
4. Neither of the above

$[(CH_3)_3CBr]$	$[{}^-OCH_3]$	Rate (M/s)
0.0001	0.0001	2.8×10^{-5}
0.0002	0.0001	5.6×10^{-5}
0.0001	0.0002	2.8×10^{-5}

BOSTON UNIVERSITY

Response Counter

12

[Quiz] For $(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$ what is the value of k_{for}?

1. 2.8×10^{-5} M s^{-1}
2. 2.8×10^{-1} s^{-1}
3. 2.8×10^{-1} M s^{-1}
4. None of the above

$[(CH_3)_3CBr]$	$[{}^-OCH_3]$	Rate (M/s)
0.0001	0.0001	2.8×10^{-5}
0.0002	0.0001	5.6×10^{-5}
0.0001	0.0002	2.8×10^{-5}

Making sense of rate vs concentration

From data, we have found that the differential rate law for

$(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

is

$\text{rate} = k_{for}[(CH_3)_3CBr]$

Shouldn't the rate depend on $[{}^-OCH_3]$ too?

$(CH_3)_3CBr + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3 + Br^-$

A possible mechanism that accounts for rate not depending on $[{}^-OCH_3]$ is ...

Step 1: $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$, slow

Step 2: $(CH_3)_3C^+ + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3$, fast

Show that this accounts for the observed rate law.

Making sense of rate constants

The mechanism is

Step 1: $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$, slow

Step 2: $(CH_3)_3C^+ + {}^-OCH_3 \rightarrow (CH_3)_3COCH_3$, fast

Step 1 is much slower than step 2 because ...

$k_{1,for}$ is much smaller than $k_{2,for}$

What determines the relative size of $k_{1,for}$ and $k_{2,for}$?

Making sense of rate constants

To understand what determines the relative size of rate constants, let's consider a different, gas-phase exothermic reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

BOSTON UNIVERSITY

Making sense of rate constants

Sketch a two-dimensional diagram showing how enthalpy changes (vertical axis) as time passes (horizontal axis), starting with all reactants, R, on the eft, and ending with all products, P, on the right.

Take into account that sinxw the reaction involves both bond breaking in reactants and bond making in products, energy must be supplied for both R → P and P → R.

BOSTON UNIVERSITY

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Where does the energy come from for R → P?

Kinetic energy of reactant molecules.

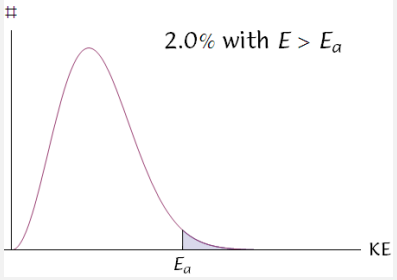
Maxwell-Boltzmann kinetic energy distribution
http://quantum.bu.edu/CDF/102/MaxwellBoltzmannEnergyDistribution.cdf

BOSTON UNIVERSITY

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Where does the energy come from for R → P?

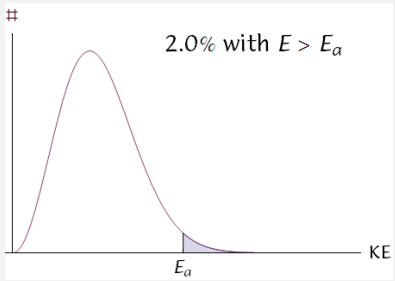
Kinetic energy of reactant molecules.



BOSTON UNIVERSITY

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

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



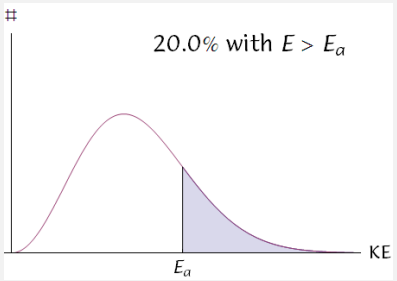
BOSTON UNIVERSITY

32

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Only molecules with kinetic energy greater than E_a can react

Raising temperature increases the number with at least kinetic energy E_a



BOSTON UNIVERSITY

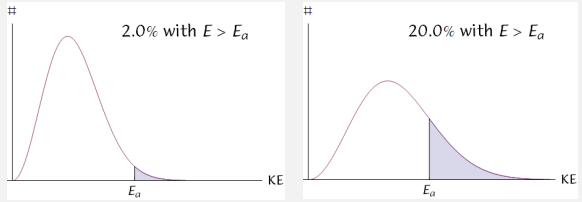
33

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

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

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

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



BOSTON UNIVERSITY

34

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

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

Answer: 4×10^{-18} (really small!)

BOSTON UNIVERSITY

35

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

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

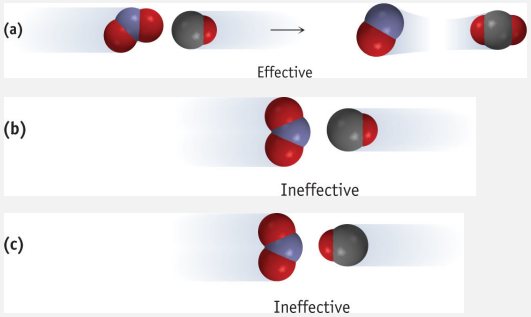
Answer: 0.09 (much bigger!)

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

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

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Collisions must have the correct geometry:



Putting geometry and temperature together

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

A =...

frequency of collisions × ...

probability that collisions have an appropriate collision geometry

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

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

Rate versus temperature: E_a and A

BOSTON UNIVERSITY

41

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

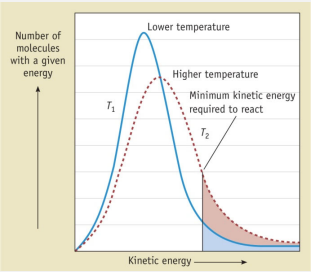
0% 1. increase
0% 2. stay the same
0% 3. decrease
0% 4. More information needed

BOSTON UNIVERSITY

42

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

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

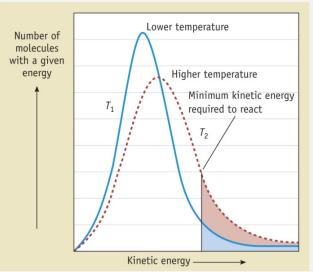


BOSTON UNIVERSITY

44

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

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



BOSTON UNIVERSITY

Response Counter

10

45