# Chemistry 331

Lecture 25

Collision Theory

**NC State** University

# Kinetics

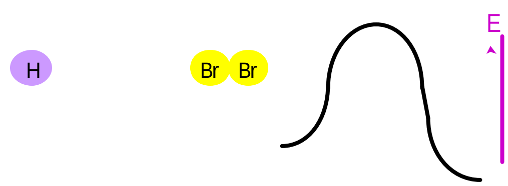
Gas Phase Kinetics
Elementary Reactions
Collision Theory
Experimental Rate Law
Application to Formation of $NO_2$

## Elementary Reactions

Reactions usually occur in a series of steps involving one or two molecules.
The molecularity of an elementary reaction is equal to the number of molecules that come together in an elementary step.
The reaction order is an empirical quantity that does not have to equal the molecularity.

## Collision theory

In order to react molecules must collide with enough energy to surmount the energy barrier.

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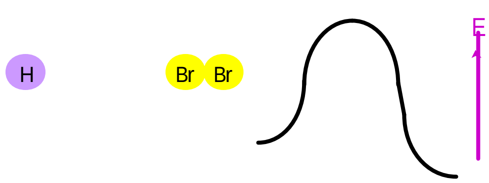


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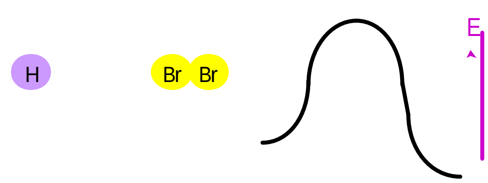

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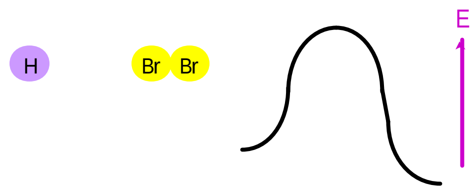


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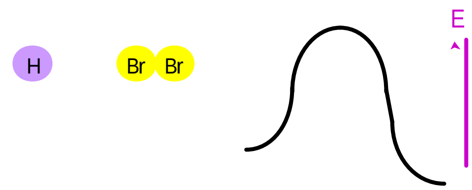


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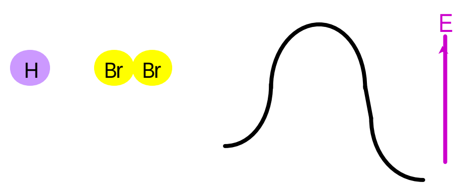


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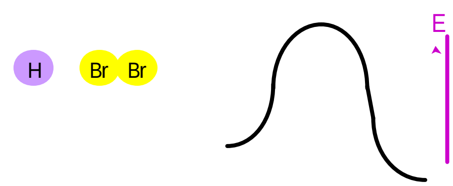


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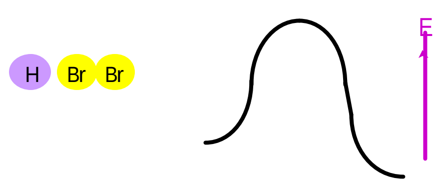


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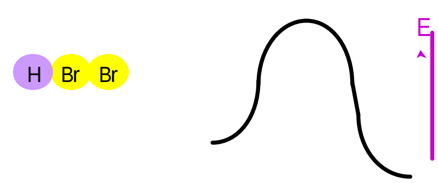

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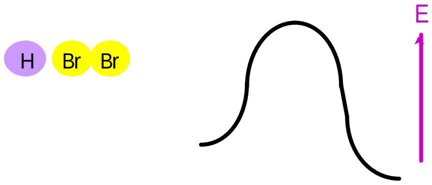


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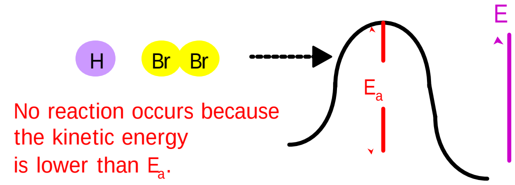


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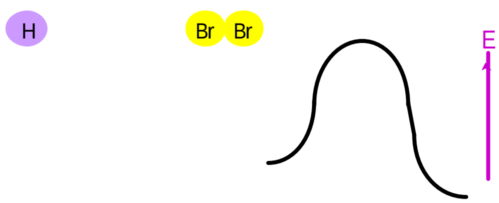


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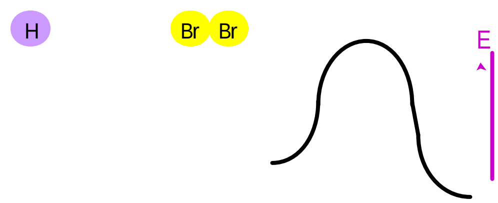


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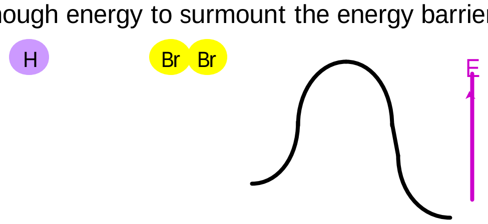


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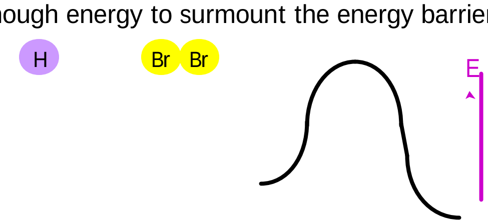

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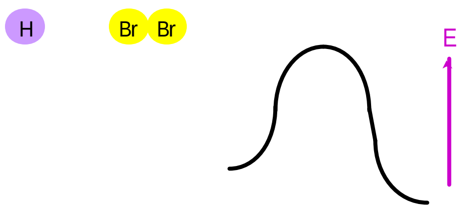


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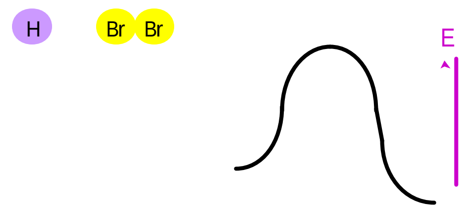


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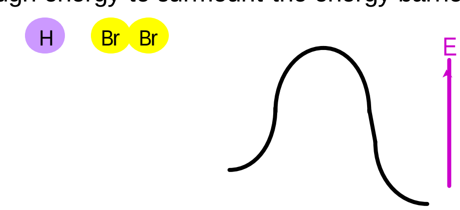


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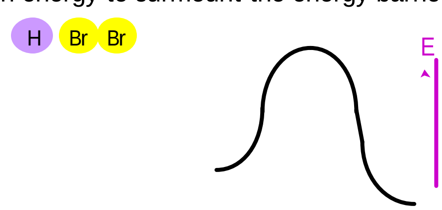


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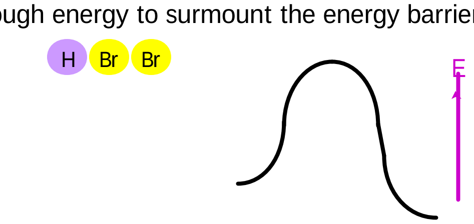


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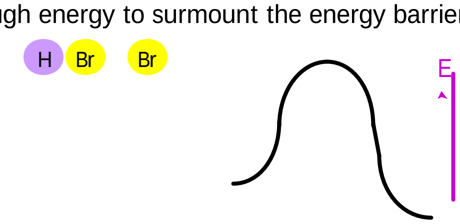

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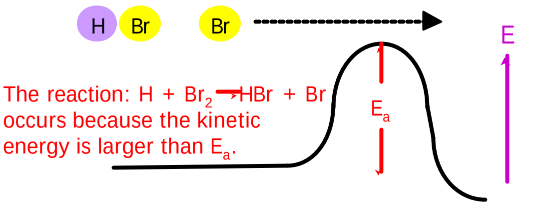


## Relationship to Arrhenius theory

For the preceeding reaction the molecularity is two. It is a bimolecular reaction. Thus,

rate of collision $\propto$ [H][$Br_2$]

But, as we saw the collisions must occur with an energy of $E_a$ or greater for a reaction to occur. The kinetic theory of gases tells us that there is a connection between the kinetic energy and the temperature.

## The rate law and the probability

The probability that a given reaction will occur at given temperature is

$$f = e^{-E_a/RT}$$

Thus, the rate of reaction $\propto$ [H][$Br_2$]$e^{-E_a/RT}$

If we compare to the second order rate law

rate of reaction = k[H][$Br_2$]

If follows that $k \propto e^{-E_a/RT}$.

## The pre-exponential factor

The value of A can be calculated from the kinetic theory of gases

$$A = \sigma\left(\frac{8k_BT}{\pi\mu}\right)^{1/2} N_A^2$$

$\mu = m_1m_2/(m_1 + m_2)$ is the reduced mass

$\sigma$ is the collision cross section

There is also an orientational factor P.

If not all orientations lead to products then P < 1.

## The formulation of rate laws

The empirical rate law for the reaction

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

is:

Rate of formation of $NO_2$ = k[NO]$^2$[$O_2$]

Does this rate law mean that $NO_2$ is formed in a termolecular process? Such collisions have very low probability.

A combination of bimolecular processes is much more likely.

The following reaction mechanism has been proposed.

## Elementary steps in the formation of $NO_2$

Step 1. Two NO molecular collide to form a dimer

$$NO + NO \underset{k_{a'}}{\overset{k_a}{\rightleftharpoons}} N_2O_2$$

Step 2. The $O_2$ molecule collides with the dimer to form $NO_2$

$$O_2 + N_2O_2 \xrightarrow{k_b} NO_2 + NO_2$$

For step 2 the rate of consumption of $N_2O_2$ is $k_b$[$N_2O_2$][$O_2$] and the rate of formation of $NO_2$ is $2k_b$[$N_2O_2$][$O_2$].

## Applying the steady state approximation to intermediate $N_2O_2$

The rate of formation of $NO_2 = 2k_b[N_2O_2][O_2]$ is not acceptable as a rate law since it contains the concentration of the intermediate $N_2O_2$.

$$\frac{d[N_2O_2]}{dt} = k_a[NO]^2 - k_{a'}[N_2O_2] - k_b[N_2O_2][O_2]$$

Now we use the steady state approximation:

$$0 = k_a[NO]^2 - k_{a'}[N_2O_2] - k_b[N_2O_2][O_2]$$

## How to deal with the intermediate $N_2O_2$

Solving the steady state equation we find:

$$[N_2O_2] = \frac{k_a[NO]^2}{k_a' + k_b[O_2]}$$

so that the rate of formation of $NO_2$ can be written:

$$v = 2k_b[N_2O_2][O_2] = \frac{2k_ak_b[NO]^2[O_2]}{k_a' + k_b[O_2]}$$

Note that this agrees with the empirical rate law provided $k_{a'} >> k_b[O_2]$. Thus,

Rate of formation of $[NO_2] = (2k_ak_b/k_{a'})[NO]^2[O_2]$.

## Rate limiting step

If the concentration of $O_2$ is increased to a very high level then the second step is very rapid compared to the first. The first step becomes the rate limiting step. Under these conditions the rate law becomes:

$$k = 2k_a[NO]^2$$

Such conditions are used experimentally to determine the order of NO in the reaction.