

16 • Chemical Kinetics: Rates of Reaction

A BLUFFER'S GUIDE

- How to talk about Rate

$$\text{rate} = \Delta[\text{chemical}]/\Delta\text{time}$$

rate of **disappearance** of reactant or

rate of **appearance** of product

use **coefficients** to change one rate to another

watch your **signs** ($\Delta[\text{React.}] = -\Delta[\text{Prod.}]$)

instantaneous rate is **slope** of [R] vs. time graph. Initial rate is often used.

- How to Speed Up a Reaction

[Use Collision Theory, Kinetic Molecular Theory]

increase the **concentration** of reactants

- increase **molarity** of solutions

- increase partial **pressure** of gases

[collision model: more collisions]

more **surface area** between unlike phases

[collision model: more collisions]

increase the **temperature**

[collision model: more & harder collisions]

add a **catalyst**

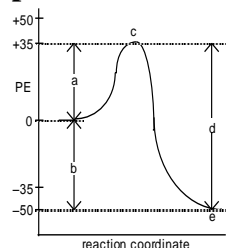
- homogeneous catalyst (used & reformed)

- heterogeneous catalyst (surface catalyst)

[collision model: alternate mechanism that requires lower energy collision or ensures that correct particles collide]

- **Two Important Diagrams**

PE energy profile of a reaction

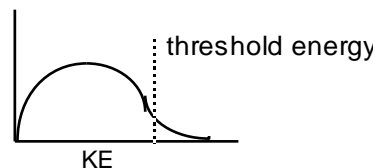


ΔH of the reaction relates reactant and product PE's / exo- or endothermic/ downhill, $-\Delta H$, or uphill, $+\Delta H$

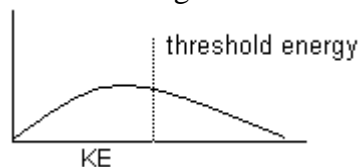
Activation energy (E_a) = energy barrier

- activated complex (at the peak)
- whether a reaction is fast or slow depends on the activation energy in the PE profile
- PE profile does not change with change in temperature of the reactants?
- adding a catalyst lowers the E_a

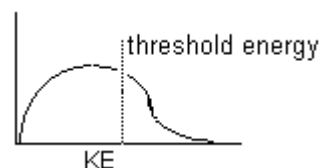
The **KE distribution** of a substance



- **temperature** is a measure of the **average KE**
- increasing temperature spreads out curve to the right, increases average KE



- adding a **catalyst** moves the threshold energy (E_a) to the left.

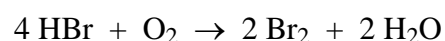


How do these two picture **relate** to each other (turn the KE on its side... the particles use their KE to provide the needed PE to react)

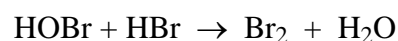
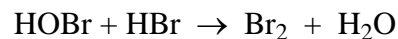
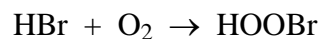
- **Reaction mechanisms**

- step-by-step...two particles at a time
- example

overall:



mechanism:



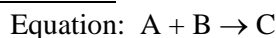
[note: HOBr and HOBr are not in the overall reaction because they are neither reactants nor products, they are "reactive intermediates"]

- overall reaction is sum of steps
- slowest step is **rate-determining step**

Rate Laws

- what they mean
- how to determine them
- how they relate to the rate determining step
- how they help you choose a mechanism

General Form:



$$\text{Rate} = k [A]^x [B]^y$$

k is the "specific rate constant"

Use experimental data to determine x, y, and k.

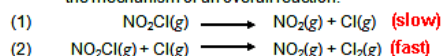
The Rate Law CANNOT be determined from the overall reaction. It MUST be determined experimentally because the rate law reflects only the "rate determining step."

Rate law can be determined from the initial rates.

See *Sample Problems 16.2 and 16.3* in *Silberberg*

Rate Law matches the Reaction Mechanism

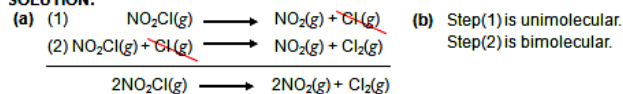
PROBLEM: The following two reactions are proposed as elementary steps in the mechanism of an overall reaction:



- (a) Write the overall balanced equation.
(b) Determine the molecularity of each step.
(c) Write the rate law for the overall reaction.

PLAN: (a) The overall equation is the sum of the steps.
(b) The molecularity is the sum of the reactant particles in the step.
(c) The rate law of the reaction is the rate law of the slow (rate determining) step. Intermediates must be eliminated from the rate law. See problem 5 of ALE 5 as an example of how to do this.

SOLUTION:



(c) The rate law for the overall reaction is the rate law of the slow (rate determining) step.
 $\text{rate}_1 = k_1[\text{NO}_2\text{Cl}]$

Half-life

- relationship to radioactivity (a first order reaction)
- the equation
$$\ln \frac{[A]_o}{[A]_t} = kt$$
- the special case of half-life
$$\ln(2) = 0.693 = kt_{1/2}$$

Order of rxn

- first and second order reactions
- what these look like graphically
- how you can graphically tell the order of a reaction

order	straight-line plot	Slope
0	$[\text{Reactant}]_t$ vs. t	-k
1	$\ln[\text{Reactant}]_t$ vs. t	-k
2	$1/[\text{Reactant}]_t$ vs. t	k

- how this relates to the integrated rate laws:

$$\text{rate} = - \frac{\Delta[A]}{\Delta t} = k [A] \quad \text{first order rate equation}$$

$$\ln \frac{[A]_o}{[A]_t} = -kt \quad \ln [A]_o = -kt + \ln [A]_t$$

$$\text{rate} = - \frac{\Delta[A]}{\Delta t} = k [A]^2 \quad \text{second order rate equation}$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt \quad \frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

$$\text{rate} = - \frac{\Delta[A]}{\Delta t} = k [A]^0 \quad \text{zero order rate equation}$$

$$[A]_t - [A]_o = -kt$$

Determining E_a from calculations using the Arrhenius Equation

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

where k is the kinetic rate constant at

E_a is the activation energy

R is the energy gas constant

T is the Kelvin temperature

A is the collision frequency factor

$$\ln k = \ln A - E_a / RT$$

$$y = b + mx$$

$$m = \text{slope} = \frac{-E_a}{R}$$

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

Acknowledgement: This document is adapted from a similar document from South Pasadena • AP Chemistry