

# Dougherty Valley HS • AP Chemistry

## Kinetics: Rates of Reaction

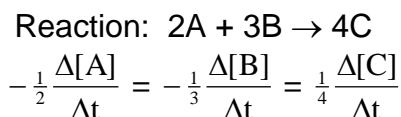
Inspired by Paul Groves

## A BLUFFER'S GUIDE

### 1. How to talk about Reaction Rate

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

- Common Units:  $\text{M/s}$ ,  $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}$
- Rate of **disappearance** of reactant or Rate of **appearance** of product
- Use **coefficients** to change one rate to another



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

### 2. From a graph of [R] vs time

**Average rate** is the **slope** of a **segment**.  
**Instantaneous rate** is **slope** of the **tangent**.  
 Initial rate is often used.

### 3. How to **Speed Up** a Reaction

Use Collision Theory and Kinetic Molecular Theory

increase the **concentration** of reactants

- increase **molarity** of solutions
- increase partial **pressure** of gases

collision model  $\rightarrow$  more collisions

more **surface area** between unlike phases

collision model  $\rightarrow$  more collisions

increase the **temperature**

collision model  $\rightarrow$  more & harder collisions

add a **catalyst**

- homogeneous catalyst (used & reformed)
- heterogeneous catalyst (surface catalyst)

collision model  $\rightarrow$  alternate mechanism/

pathway that needs lower energy

collision and/or helps correct orientation

### 4. Because Rate depends on Concentration...

we use Rate Laws

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

### 5. General Form:



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

k is the "specific rate constant"

Use experimental data to determine the values of x, y, and k.

### 6. 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."

### 7. Rate law can be determined from initial rates. *See your notes and worksheets!*

- Hold [ ] of all chemicals except one constant.
- Change [ ] of one chemical and see how it changes the rate.
- Determine what the exponent order must be to result in that change.
- If [A] doubles, and rate quadruples, then [A] must be raised to the 2<sup>nd</sup> power.  $[\text{A}]^2$ , it is second order with respect to A

### 8. Rate Law matches Molecularity of the Rate Determining Step in the Mechanism

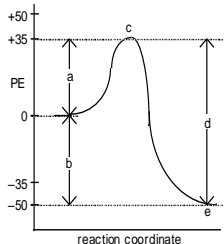
Examples for:  $2\text{A} + 3\text{B} \rightarrow \text{C}$

Rate Law	Rate Determining Step in the mechanism
$\text{Rate} = k [\text{A}][\text{B}]$	$\text{A} + \text{B} \rightarrow \text{X}$ (slow)
$\text{Rate} = k [\text{A}]^2$	$\text{A} + \text{A} \rightarrow \text{X}$ (slow)
$\text{Rate} = k [\text{A}]^2[\text{B}]$	$\text{A} + \text{A} \rightleftharpoons \text{X}$ (fast) $\text{B} + \text{X} \rightarrow \text{Y}$ (slow) Each step is usually bimolecular. A 3 <sup>rd</sup> order overall rxn often comes from a fast equilibrium before a slow step.
$\text{Rate} = k$	This could be a mechanism that depends on a catalyst only. The concentrations would not matter.

9. Determining the order by graphing

	order	straight-line plot	slope
<b>C</b> Concentration	0	$[A]_t$ vs. $t$	$-k$
<b>N</b> Natural Log	1	$\ln[A]_t$ vs. $t$	$-k$
<b>R</b> Reciprocal	2	$1/[A]_t$ vs. $t$	$k$

10. PE energy profile of a reaction

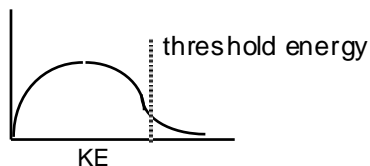


$\Delta H$  of the reaction relates reactant and product PE's / exo- or endothermic/ downhill,  $-\Delta H$ , or uphill,  $+\Delta H$

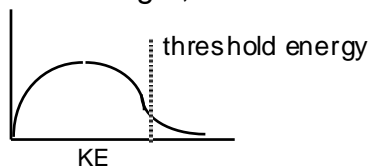
11. Activation energy ( $E_a$ ) = energy barrier

- Activated complex (transition state) is at the peak of the graph.
- Whether a rxn 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  $E_a$

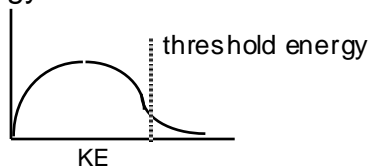
12. The KE distribution of a substance



- Temperature is the **average** KE
- Increasing temperature spreads out curve to the right, increases average KE

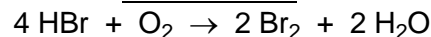


- Adding a catalyst moves the threshold energy to the left.

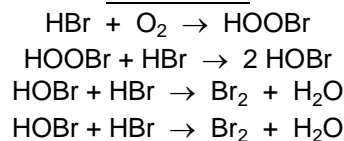


13. Reaction mechanisms how the reaction happens step by step

Overall reaction:



Mechanism:



**NOTE:** HOBr and HOBr are not in the overall rxn because they are not reactants or products, they are "intermediates." We don't like putting intermediates into our rate laws, we often will substitute things to make them not show up.

- Overall reaction is sum of steps
- Slowest step is **rate-determining step**

14. Half-Life

- relationship to radioactivity (a first order reaction)

Order	Half-Life
0	$\frac{[A]_0}{2k}$
1*	$\frac{0.693}{k}$
2	$\frac{1}{k[A]_0}$

\*This is the one that typically shows up on the AP exam.

15. Arrhenius Equation

$$k = Ae^{\frac{-E_a}{RT}}$$

Graphing to find  $E_a$

Graph:  $\ln(k)$  vs  $1/T$

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

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

$\ln(A)$  = y-intercept