

CHAPTER 12 KINETICS



Rates and Mechanisms of Chemical Reactions

CHM152

GCC

Chemistry: OpenStax OER text

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Kinetics

- Some chemical reactions occur almost instantaneously, while others are very slow.
- **Chemical Kinetics** - study of factors that affect how fast a reaction occurs and the step-by-step processes involved in chemical reactions.

Factors That Affect Reaction Rate

- Concentration - higher concentration of reactants increases rate*
- Temperature - higher T increases rate*
- Catalysts - accelerate reaction rate*
- Surface area of solid - smaller particles increase rate*

Rate of Reaction

- the change in the amount of a reactant or product per unit time

$$\text{Rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}} = \frac{\Delta[A]}{\Delta \text{time}}$$

◆ [] means concentration

◆ Typical Rate Units: M/time or mol/(L×time)

➤ Recall: M = moles solute/L of solution

➤ M = mol/L = mol·L⁻¹

Calculating Rates of Substances

- For the reaction: A → B, we can measure rate of disappearance of reactants:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

[A] decreases (include - sign so rate is +)

and appearance of products:

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



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Rates of Substances

- Reaction: $A \rightarrow B$

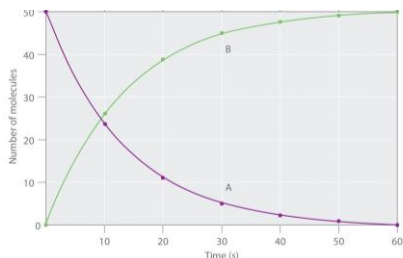


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Rate Characteristics

- **Rate is a measure of the speed of a reaction.**
- **Rate can be expressed as rate of formation of products or rate of disappearance of reactants.**
- **Reaction rate is always positive: (-) sign used for reactants since they decrease with time (this gives rate a + sign.)**
- **Reaction rates decrease with time as reactants are used up.**

Rate of Reaction Calculation

- $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$
- What is the rate of disappearance of H_2O_2 for each time interval?

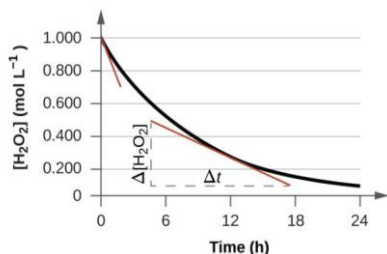
$$\text{rate} = \frac{-\Delta[\text{H}_2\text{O}_2]}{\Delta t} = \frac{-(M_f - M_i)}{t_f - t_i}$$

Time (hr)	$[\text{H}_2\text{O}_2]$, M	$\Delta[\text{H}_2\text{O}_2]$, M	Δt (hr)	Rate of H_2O_2 , M/hr
0	1.000			
6.00	0.500	-0.500	6.00	0.0833
12.00	0.250			
18.00	0.125			
24.00	0.0625			

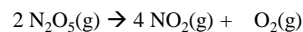
Different ways to measure rate

- **Initial rate** is measured by the slope of the tangent line when initial reactant concentrations are measured (find the slope of the tangent line at time $(t) = 0$).
- **Instantaneous rate** is measured at a specific point in time (find the slope of a tangent line at a specified time).
- **Average rate** is measured as the average between two times. Use rate formula to calculate average rate.

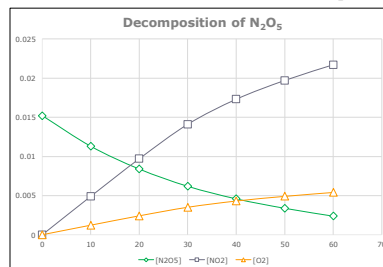
Different Rates for H_2O_2 decomposition



Rates of Substances



Rates are related by coefficients. Which curve is the reactant? How can you tell the difference between the curves of the products?



Rate Expressions



The rate of disappearance of N_2O_5 is twice the rate of formation of O_2

- To make rates equal, divide rates by their stoichiometric coefficients:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

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E.g. For $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$,

Write the rate expressions in terms of the disappearance of the reactants and the appearance of the products:

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Example. For the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, if the rate of decomposition of N_2O_5 is $4.2 \times 10^{-7} \text{ mol/(L}\cdot\text{s)}$, what is the rate of appearance of (a) NO_2 ; (b) O_2 ? (c) What is the rate of reaction?

a)

b)

c)

* Always express Rate as a + value

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RATE LAW

Rate law: relationship between the reaction rate and the concentration of each reactant.

For a reaction $a\text{A} + b\text{B} \rightarrow \text{Products}$

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

k = Rate Constant: it is a numerical constant for a reaction at a given temperature.

$[\text{A}]$, $[\text{B}]$ are concentrations of reactants

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Rate Law continued

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

- x & y = **order of reactants** = exponent of reactant in rate law
- Overall Reaction Order** = sum of all exponents in rate law
- Exponents cannot be obtained by looking at the equation; they are experimentally determined values.**
- exponents are usually **0, 1 or 2**

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Reaction Order Example



Given its experimental Rate law:

$$\text{Rate} = k[\text{ClO}_2][\text{F}_2]$$

order of ClO_2 =

order of F_2 =

Overall order =

- You cannot determine the reactant orders by looking at the coefficients in a chemical equation!

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Determination of Rate Law from Initial Rates Data

To determine the rate law, we observe the effect of changing initial concentrations of reactants on the initial rate of reaction.

Exp. Data: Initial rates ($\Delta[\text{Products}]/\Delta t$ after 1-2% of limiting reactant has been consumed) are usually given; there is less chance of error from competing side reactions & reversible reactions.

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Inspection Method

➤ A reactant is 1st order if doubling [A] causes rate to double; rate is directly proportional to [A].

➤ A reactant is 2nd Order if doubling [A] causes rate to quadruple (or tripling [A] causes 3² increase in rate).

➤ A reactant is Zero order if changing [A] does not affect the rate.

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Reaction Orders may also be found mathematically

To find the order for a specific reactant, examine what happens to the rate as the concentration of only that reactant changes (note: the rate constant k and other concentration terms cancel out, since they don't change!):

$$\left(\frac{\text{concentration 2}}{\text{concentration 1}}\right)^x = \frac{\text{Rate 2}}{\text{Rate 1}}$$

➤ Repeat this process for each reactant. 21

e.g. Finding Rate Law using Initial Rates

Experiment	[A] M	[B] M	Rate M/s
1	0.020	0.010	1.0
2	0.040	0.010	2.0
3	0.040	0.020	8.0

Order A = ?

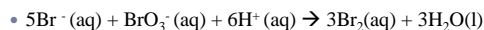
Order B = ?

Rate = ?

k = ?

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12.3 Determining a Rate Law



Experiment	[Br ⁻](M)	[BrO ₃ ⁻](M)	[H ⁺](M)	Initial Rate (M/s)
1	0.10	0.010	0.15	1.2×10^{-3}
2	0.10	0.020	0.15	4.8×10^{-3}
3	0.30	0.010	0.15	3.6×10^{-3}
4	0.10	0.020	0.30	4.8×10^{-3}

- Need two trials where only one reactant concentration changes (all others are constant).
- Compare changes in rate to changes in concentration to determine the order of the reactant (the exponent in the rate law).

Integrated Rate laws

1st order Reaction

• For a reaction, $A \rightarrow B$ Rate = $k[A]$

• Rate also expressed: Rate = $-\frac{\Delta[A]}{\Delta t}$

• Setting these equal: $-\frac{\Delta[A]}{\Delta t} = k[A]$

• Integrate to get 1st order IRL (calculus ☺)

1st order IRL: $\ln \frac{[A]_t}{[A]_0} = -kt$

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IRL variables

t = time

k = rate constant

$[A]_0$ = initial concentration

$[A]_t$ = concentration at time t

➤ Units for A can be g, moles, M, torr, etc.

➤ A_t is always less than A_0

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1st order problems

1. The rate law for the decomposition of N_2O_5 is $\text{Rate} = k[N_2O_5]$, where $k = 5.0 \times 10^{-4} \text{ s}^{-1}$. What is the concentration of N_2O_5 after 1900 s, if the initial concentration is 0.56 M?
2. The first order reaction, $SO_2Cl_2 \rightarrow SO_2 + Cl_2$, has a rate constant of 0.17 h^{-1} . If the initial concentration of SO_2Cl_2 is $1.25 \times 10^{-3} \text{ M}$, how many seconds does it take for the concentration to drop to $0.31 \times 10^{-3} \text{ M}$?

Answers:

<http://web.gccaz.edu/~ldiebolt/00152note/work/13kineticsproblemskey.pdf>

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1st Order IRL linear format

- Can rearrange first-order IRL to get linear form:

$$\ln [A]_t = -kt + \ln [A]_0$$

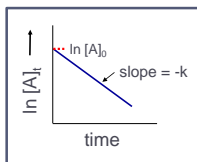
$$y = mx + b$$

$$y = \ln [A]_t$$

$$m = -k ; \text{ thus } k = -\text{slope}$$

$$x = t$$

$$b = \ln [A]_0 = y \text{ intercept}$$

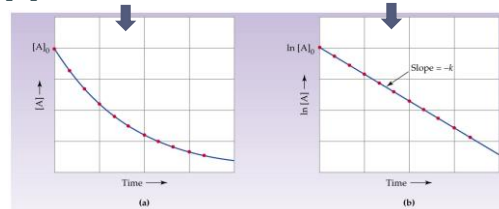


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1st order reaction

$[A]$ vs t is not linear

$\ln [A]$ vs t is linear



Only 1st order reactions will give you a straight line when plotting $\ln [A]_t$ vs. time!

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Half Life of First Order Reactions

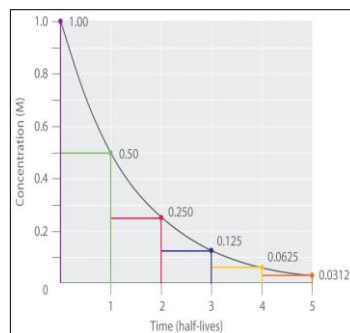
Half-life ($t_{1/2}$): time it takes for half (50%) of a reactant to be consumed.

➤ 50% of the reactant also remains unreacted.

❖ How much of a sample remains after 3 half-lives?

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Half-Life 1st order Reactions



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Derivation of 1st order Half life

$$\text{At } t = t_{1/2} \Rightarrow [A]_t = \frac{1}{2} [A]_0$$

Plug into IRL: $\ln \frac{\frac{1}{2} [A]_0}{[A]_0} = -kt_{1/2}$

$$\ln 0.5 = -kt_{1/2}$$

$$kt_{1/2} = 0.693$$

$t_{1/2}$ does not depend on $[A]$, only for 1st order reactions!

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1st order half life problems

- Cobalt-60 is a radioisotope that decays by first-order kinetics and has a half-life of 5.26 years. The Co-60 in a radiotherapy unit must be replaced when the concentration of Co decreases to 75% of its initial value. When does this occur?
- The first order reaction, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$, has a rate constant of $6.3 \times 10^{-4} \text{ s}^{-1}$ at 230°C .
 - What is the half-life of the reaction?
 - How much of a 10.0 g sample of CH_3NC will remain after 5 half-lives?
 - How many seconds would be required for 75% of a CH_3NC sample to decompose?

Answers:

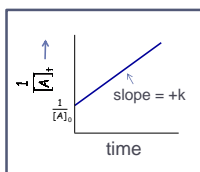
<http://web.gccaz.edu/~ldiebolt/00152note/work/13kineticsproblemskey.pdf>

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Second Order Plot and IRL

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

2nd order IRL: $\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$



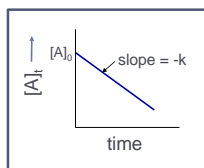
Only 2nd order reactions will give you a straight line when plotting $\frac{1}{[A]}$ vs. time.

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Zero Order Plot and IRL

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^0 = k$$

0 order IRL: $[A]_t = -kt + [A]_0$



Only 0 order reactions will give you a straight line when plotting $[A]$ vs. time.

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Comparison Table for Typical Reaction Orders

Order	Rate Law	Integrated Law	Linear graph	slope	Half-life
0	Rate = k	$[A]_t = -kt + [A]_0$	$[A]$ vs. t	-k	$t_{1/2} = \frac{[A]_0}{2k}$
1	Rate = k[A]	$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt$	$\ln [A]$ vs. t	-k	$t_{1/2} = \frac{0.693}{k}$
2	Rate = k[A] ²	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs. t	+k	$t_{1/2} = \frac{1}{k[A]_0}$

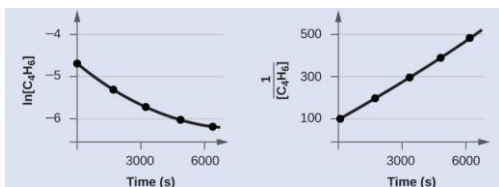
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Graphical Method of Determining Rate Law

- Make 3 plots: $[A]$ vs time; $\ln [A]$ vs. time; and $1/[A]$ vs. time.
- The most linear plot gives the correct order for A; the other 2 graphs should be curves.

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What order is this reaction?



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2nd order IRL example

The rate constant for a 2nd order reaction is $0.54 \text{ M}^{-1}\text{s}^{-1}$ at 300°C . If the initial concentration is 0.62 M , what will be the final concentration after 145 seconds?

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Reaction Mechanisms

- Many chemical reactions occur by a sequence of 2 or more steps.
- Each individual event in the overall reaction is called an elementary step.
- Molecularity: the number of molecules that react in an elementary step.

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Molecularity – based on # of reactant molecules!

Unimolecular: 1 molecule
 $A \rightarrow \text{products}$

Bimolecular: 2 molecules
 $2A \rightarrow \text{products}$ or
 $A + B \rightarrow \text{products}$

Termolecular (uncommon):
 $3A \rightarrow \text{products}$ or
 $2A + B \rightarrow \text{Products}$ or
 $A + B + C \rightarrow \text{Products}$

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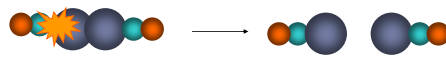
Mechanism example

E.g. A 2 step Overall rxn:
 $\text{Br}_2 + 2\text{NO} \rightarrow 2\text{BrNO}$

Step 1: $\text{Br}_2 + \text{NO} \rightarrow \text{Br}_2\text{NO}$
 (Bimolecular step)

Step 2: $\text{Br}_2\text{NO} + \text{NO} \rightarrow 2\text{BrNO}$
 (Bimolecular step)

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Net Reaction:



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Intermediates

Intermediates are short lived species that are formed during the reaction, then are subsequently consumed
 ⇒ Its 1st a product, then a reactant

• Br₂NO in last example is intermediate

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Rate Law for Elementary Step

For an elementary step, the rate law can be written using stoichiometric coefficients of the reactants. (molecularity = order).

E.g. Step 1: Rate = k[Br₂][NO]

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Rate Determining Step

The slowest step in the reaction is the rate determining step; this step limits how fast products can form.

Analogy: freeway during rush hour

➤ The rate law for the overall rxn is determined by the rate of this slow step.

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2-Step Reaction Mechanism

- Step 1: NO₂(g) + NO₂(g) → NO(g) + NO₃(g)
- Step 2: NO₃(g) + CO(g) → NO₂(g) + CO₂(g)

- What is the overall equation? (Hint: Think Hess's Law - adding equations)

❖ NO₃ and one NO₂ cancels so net rxn is:



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2 Step Reaction Mechanisms

- Rate laws for these elementary steps:
- **Step 1:** NO₂(g) + NO₂(g) → NO(g) + NO₃(g)
- **Step 1:** rate = k[NO₂][NO₂] (bimolecular)
- **Step 2:** NO₃(g) + CO(g) → NO₂(g) + CO₂(g)
- **Step 2:** rate = k[NO₃][CO] (bimolecular)
- **Intermediates:** product in one step and consumed in a later step
- **Catalyst:** reactant in one step and product in later step
- Note: Intermediates and catalyst cannot be part of overall reaction!

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Rate Laws/Reaction Mechanisms

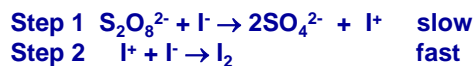
- **Step 1 (slow):** NO₂(g) + NO₂(g) → NO(g) + NO₃(g)
- **Step 2 (fast):** NO₃(g) + CO(g) → NO₂(g) + CO₂(g)
- **Overall:** NO₂(g) + CO(g) → NO(g) + CO₂(g)

- a) What is the rate law for this 2-step reaction?
- b) What is the intermediate? Catalyst?

a)

b)

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Example

- Which step is rate determining?
- What is the intermediate?
- What is the rate law for the slow step?
- What is the overall rate law?

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Collision Theory**Molecules must collide to react!**

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Collision Theory
Collision Frequency affects Reaction Rate

- \uparrow concentrations of reactants result in more collisions, thus the reaction rate \uparrow .
- \uparrow **Temperatures cause molecules to move faster and collide more often, increasing the rate.**

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Most collisions don't cause a reaction because

- 1) **molecules must have enough Kinetic Energy to:**
 - \triangleright **overcome electron cloud repulsions between atoms/molecules**
 - \triangleright **weaken/break reactant bonds**
- 2) **molecules must have the proper orientation to have an effective collision**

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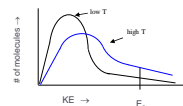
Activation Energy, E_a

- energy barrier that molecules have to surmount in order to react. Energy is needed to break reactant bonds (endothermic process).

analogies:

- **pushing a boulder up a hill**
- **getting started on an unpleasant task**

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Comments on E_a 

- Only a small fraction of molecules have enough KE to initiate reaction.
- E_a is different for each reaction.
- Reactions with low E_a are faster & k is larger because more molecules can overcome E_a .
- At higher T , a larger fraction of molecules have enough KE to overcome E_a . (This is the main reason why the rxn rate increases dramatically as $T \uparrow$)

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Orientation of molecules matters!

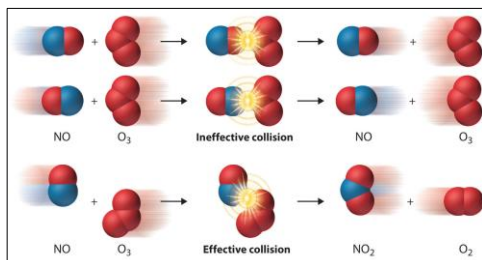
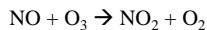


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Arrhenius Equation relates k and T

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

R = gas constant = 8.314 J/K-mol

T = temperature in K

$e^{-E_a/RT}$ = fraction of molecules that have enough KE to react

A = frequency factor (depends on # of collisions that are properly oriented)

➤ Linear form: $\ln k = -E_a/RT + \ln A$

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Arrhenius equation

E_a can be found graphically:

- plot of $\ln k$ (y axis) vs $1/T$ (x axis) yields a straight line.
- slope = $-E_a/R$; y intercept = $\ln A$
- Thus $E_a = -R \cdot \text{slope}$

If you have 2 sets of conditions, solve for k_1 , k_2 , T_1 , T_2 or E_a using:

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

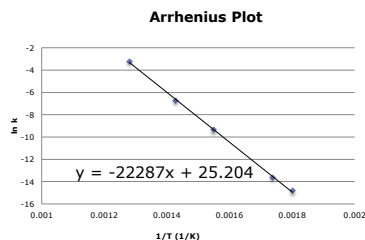
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Arrhenius Equation

- Worked Example 12.11:** Rate constants for the reaction $2\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$ were measured at five different temperatures. The data are shown in the table below. Determine the activation energy for this reaction. (This will be done in Kinetics lab!)

T (K)	k ($\text{M}^{-1}\cdot\text{s}^{-1}$)	$1/T$ (1/K)	$\ln k$
555	3.52×10^{-7}	0.00180	-14.86
575	1.22×10^{-6}	0.00174	-13.62
645	8.59×10^{-5}	0.00155	-9.362
700	1.16×10^{-3}	0.00143	-6.759
781	3.95×10^{-2}	0.00128	-3.231

Arrhenius Equation: Example 12.11



$$m = -E_a/R \rightarrow E_a = -m \cdot R =$$

$E_a =$

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Arrhenius Eq – 2 point formula example

$E_a = 185 \text{ kJ/mol}$ for $2\text{HI}(g) \rightarrow 2\text{H}_2(g) + \text{I}_2(g)$, find the rate constant at 325°C if $k = 3.52 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}$ at 282°C

- $E_a = 185 \frac{\text{kJ}}{\text{mol}}$ so convert R to kJ/K-mol (or E_a to J/mol)
- $R = 8.314 \frac{\text{J}}{\text{K-mol}} \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) =$
- Convert T to Kelvin
- $k_1 = 3.52 \times 10^{-7} \text{ M}^{-1}\text{s}^{-1}$, $T_1 = 282^\circ\text{C} + 273 = 555 \text{ K}$
- $k_2 = ?$ $T_2 = 325^\circ\text{C} =$

$k_2 =$

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Potential Energy Curves/ Energy profiles

transition state – a highly unstable species formed by the collision of the reactant molecules; arrangement of atoms at the top of the energy barrier.

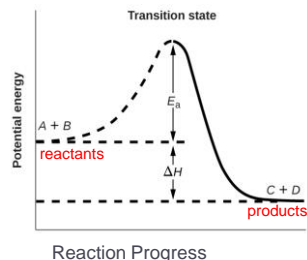
ΔH = Heat of reaction

$$\Delta H = \Delta H(\text{products}) - \Delta H(\text{reactants})$$

E_a shown for curve is the activation energy for the forward reaction, $E_a(\text{forward})$. This is the difference in energy between the transition state and the reactants.

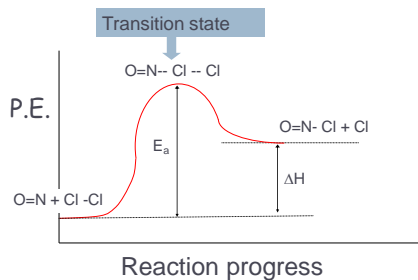
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P.E. Curve for Exothermic Reaction ($\Delta H = -$)



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P.E. Curve for Endothermic Reaction ($+\Delta H$)



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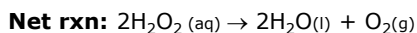
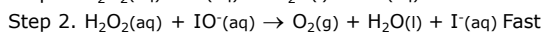
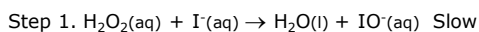
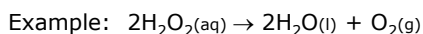
Catalysts

- A **Catalyst** is a substance that increases the rate of a reaction, but is **not** itself used up.
- A catalysts works by lowering E_a - usually they help weaken or break reactant bonds.
- A catalyst alters the reaction mechanism, but does not change the overall reaction.
- Catalyst may show up in experimental rate law – a reaction may have more than one rate law.
- Enzymes are large protein molecules with one or more active sites that serve as biological catalysts in living organisms.

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Homogeneous Catalyst

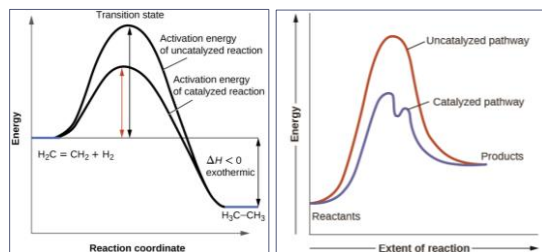
- A homogeneous catalyst is one that is in the same phase as the reactants.



- $\text{I}^-(\text{aq})$ is the catalyst

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Energy profiles with Catalyst

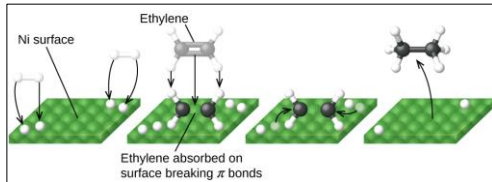


Note: E_a is lower but ΔH is same.

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HETEROGENOUS Catalysts

- Catalysts can be classified as **heterogeneous**: the catalyst and reactants are in different phases.

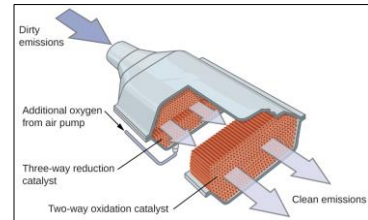


Ni is a catalyst for the reaction $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$.

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Catalytic Converters

- Convert pollutants (hydrocarbons, carbon monoxide, and nitric oxide) into CO_2 , H_2O , N_2 , and O_2 using a heterogeneous catalyst (Pt, Pd, Rh).



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