

Lecture Presentation

Chapter 13

Chemical Kinetics

John E. McMurry Robert C. Fay

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

Chemical Kinetics: The area of chemistry concerned with reaction rates and the sequence of steps by which reactions occur

Reaction Rate: Either the *increase* in the concentration of a product per unit time or the *decrease* in the concentration of a reactant per unit time

TABLE 13.1 Concentrations as a Function of Time at 55 °C for the Reaction $2 N_2O_5(g) \longrightarrow 4 NO_2(g) + O_2(g)$

		Concentration (M)		
Time (s)	N_2O_5	NO ₂	O ₂	
0	0.0200	0	0	
100	0.0169	0.0063	0.0016	
200	0.0142	0.0115	0.0029	
300	0.0120	0.0160	0.0040	
400	0.0101	0.0197	0.0049	
500	0.0086	0.0229	0.0057	
600	0.0072	0.0256	0.0064	
700	0.0061	0.0278	0.0070	

Note that the concentrations of NO₂ and O₂ increase as the concentration of N₂O₅ decreases.

$2 \operatorname{N}_2\operatorname{O}_5(g) \longrightarrow 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$

The concentrations of O_2 and NO_2 increase as the concentration of N_2O_5 decreases.



The rate of formation of O_2 is one-fourth the rate of formation of NO_2 and one-half the rate of decomposition of N_2O_5 .

$$2 \operatorname{N}_2\operatorname{O}_5(g) \longrightarrow 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$$

Rate of decomposition of N_2O_5 :

$$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{-(0.0101 \text{ M} - 0.0120 \text{ M})}{(400 \text{ s} - 300 \text{ s})}$$
$$= 1.9 \times 10^{-5} \frac{\text{M}}{\text{s}}$$

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

$$2 \operatorname{N}_2\operatorname{O}_5(g) \longrightarrow 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$$

General rate of reaction:

rate =
$$-\frac{1}{2} \frac{\Delta [N_2 O_5]}{\Delta t} = \frac{1}{4} \frac{\Delta [NO_2]}{\Delta t} = \frac{\Delta [O_2]}{\Delta t}$$

$$aA + bB \longrightarrow dD + eE$$

rate = $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t} = \frac{1}{e} \frac{\Delta[E]}{\Delta t}$

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson





The slope of the tangent at time *t* is defined as the instantaneous rate at that particular time. The initial rate is the slope of the tangent to the curve at t = 0.

Rate Laws and Reaction Order

Rate Law: An equation that shows the dependence of the reaction rate on the concentration of each reactant

 $aA + bB \longrightarrow products$ rate $\alpha [A]^m [B]^n$ rate = $k[A]^m [B]^n$

k is the rate constant.

Rate Laws and Reaction Order

The values of the exponents in the rate law **must be determined by experiment**; they cannot be deduced from the stoichiometry of the reaction.

TABLE 13.2 Balanced Chemical Equations and Experimentally Determined Rate Laws for Some Reactions				
Reaction*	Rate Law			
$(CH_3)_3CBr(soln) + H_2O(soln) \longrightarrow (CH_3)_3COH(soln) + H^+(soln) + Br^-(soln)$	Rate = $k[(CH_3)_3CBr]$			
$HCO_2H(aq) + Br_2(aq) \longrightarrow 2 H^+(aq) + 2 Br^-(aq) + CO_2(g)$ Rate = k[Br_2]				
$\operatorname{BrO}_3^-(aq) + 5\operatorname{Br}^-(aq) + 6\operatorname{H}^+(aq) \longrightarrow 3\operatorname{Br}_2(aq) + 3\operatorname{H}_2O(l)$	Rate = $k[BrO_3^{-}][Br^{-}][H^{+}]^2$			
$H_2(g) + I_2(g) \longrightarrow 2 HI(g)$	$Rate = k[H_2][I_2]$			

In general, the exponents in the rate law **are not the same** as the stoichiometric coefficients in the balanced chemical equation for the reaction. *In the first reaction, "(*soln*)" denotes a nonaqueous solution.

$$2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$$

rate = $k[NO]^m [O_2]^n$

Compare the initial rates to the changes in initial concentrations.

TABLE 13.3	Initial Concentration and Rate Data for the Reaction
$2 \operatorname{NO}(g) + \operatorname{O}_2$	$(g) \longrightarrow 2 \operatorname{NO}_2(g)$

Initial Reaction Rate

Experiment	Initial [NO]	Initial [O ₂]	(M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

$$2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$$

rate = $k[NO]^2 [O_2]^n$

The concentration of NO **doubles**, the concentration of O_2 remains constant, and the rate **quadruples**.

$$2^m = 4 \qquad m = 2$$

TABLE 13.3 Initial Concentration and Rate Data for the Reaction $2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$

Experiment	Initial [NO]	Initial [O ₂]	(M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

Initial Deaction Data

$$2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$$

rate = $k[\operatorname{NO}]^2[\operatorname{O}_2]$

The concentration of O_2 **doubles**, the concentration of NO remains constant, and the rate **doubles**.

$$2^n = 2$$
 $n = 1$

TABLE 13.3 Initial Concentration and Rate Data for the Reaction $2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$

Initial Reaction Rate

Experiment	Initial [NO]	Initial [O ₂]	(M/s)
1	0.015	0.015	0.024
2	0.030	0.015	0.096
3	0.015	0.030	0.048
4	0.030	0.030	0.192

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

$$2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$$

rate = $k[\operatorname{NO}]^2[\operatorname{O}_2]$

Reaction Order With Respect to a Reactant

- NO: second-order
- O₂: first-order

Overall Reaction Order

• 2 + 1 = 3 (third-order)

$$2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$$

rate = $k[\operatorname{NO}]^2[\operatorname{O}_2]$

Units of *k* for this third-order reaction:



 $2 \operatorname{NO}(g) + \operatorname{O}_2(g) \longrightarrow 2 \operatorname{NO}_2(g)$ $\operatorname{rate} = k[\operatorname{NO}]^2[\operatorname{O}_2]$

Rate Law	Overall Reaction Order	Units for k
Rate $= k$	Zeroth order	$M/s \text{ or } M s^{-1}$
Rate = $k[A]$	First order	$1/s \text{ or } s^{-1}$
Rate = $k[A][B]$	Second order	$1/(M \cdot s)$ or $M^{-1} s^{-1}$
Rate = $k[A][B]^2$	Third order	$1/(M^2 \cdot s)$ or $M^{-2} s^{-1}$

Zeroth-Order Reactions

A plot of **[A]** versus **time** gives a straight-line fit and the **slope** will be **-***k*.



Time \rightarrow

Zeroth-Order Reactions

For a zeroth-order reaction, the rate is independent of the concentration of the reactant.

$$A \longrightarrow \text{product(s)}$$

rate = $k[A]^0 = k \qquad -\frac{\Delta[A]}{\Delta t} = k$

Calculus can be used to derive an **integrated** rate law.



 $[A]_t$ concentration of A at time t $[A]_0$ initial concentration of A

Zeroth-Order Reactions

$$2 \operatorname{NH}_{3}(g) \longrightarrow \operatorname{N}_{2}(g) + 3 \operatorname{H}_{2}(g)$$

rate = $k[\operatorname{NH}_{3}]^{0} = k$

Most of the NH_3 molecules are in the gas phase above the surface and are unable to react.

As NH_3 molecules on the surface decompose, they are replaced by molecules from the gas phase, so the number of NH_3 molecules on the surface remains constant.



Because only the NH_3 molecules on the surface react under these conditions, the reaction rate is independent of the total concentration of NH_3 .

$$A \longrightarrow \text{product(s)}$$

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

Calculus can be used to derive an **integrated** rate law.

$$\ln\left(\frac{[A]_{t}}{[A]_{0}}\right) = -kt - \begin{cases} [A]_{t} & \text{concentration of A at time } t \\ [A]_{0} & \text{initial concentration of A} \end{cases}$$

Using:
$$\ln\left(\frac{x}{y}\right) = \ln(x) - \ln(y) \quad \left(\frac{\ln[A]_{t} = -kt + \ln[A]_{0}}{y = mx + b}\right)$$

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

$$y = mx + b$$

A plot of **In[A]** versus **time** gives a straight-line fit and the **slope** will be **-***k*.

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

(a) Reactant concentration versus time



This is a plot of **[A]** versus **time**.

The best-fit is a *curve* and not a *line*.

```
\ln[\mathbf{A}]_t = -kt + \ln[\mathbf{A}]_0
```



$$2 \operatorname{N}_2\operatorname{O}_5(g) \longrightarrow 4 \operatorname{NO}_2(g) + \operatorname{O}_2(g)$$

rate = $k[\operatorname{N}_2\operatorname{O}_5]$

					0 50	
	Time (s)	[N ₂ O ₅]	ln [N ₂ O ₅]		-3.50	
27					-4.00	
	0	0.0200	-3.912			
	100	0.0169	-4.080	² 0	4 50	
	200	0.0142	-4.255	Z	-4.50	Δy Slope = $-k$
	300	0.0120	-4.423	lr		
	400	0.0101	-4.595		-5.00	
	500	0.0086	-4.756			
	600	0.0072	-4.934		-5.50	
	700	0.0061	-5.099		(0 200 400 600 800
	,	0.0001				Time (s)

$$2 \text{ N}_2\text{O}_5(g) \longrightarrow 4 \text{ NO}_2(g) + \text{O}_2(g)$$
$$\text{rate} = k[\text{N}_2\text{O}_5]$$



Calculate the slope:

$$\frac{-5.02 - (-4.17)}{650 \text{ s} - 150 \text{ s}} = -0.0017 \frac{1}{\text{ s}}$$
$$k = 0.0017 \frac{1}{\text{ s}}$$



Half-Life of a First-Order Reaction

Half-Life: The time required for the reactant concentration to drop to one-half of its initial value



Half-Life of a First-Order Reaction

$$t_{1/2} = \frac{0.693}{k}$$

For a first-order reaction, the half-life is independent of the initial concentration.

Each successive half-life is an equal period of time.

Each successive half-life is an equal period of time in which the reactant concentration decreases by a factor of 2.



Radioactive Decay Rates

$${}^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e$$
$$t_{1/2} = 5715 \text{ y}$$
$$\text{Decay rate} = -\frac{\Delta N}{\Delta t} = kN$$

$$A \longrightarrow \text{product(s)}$$

rate = $k[A]^2 \qquad -\frac{\Delta[A]}{\Delta Dt} = k[A]^2$

Calculus can be used to derive an **integrated** rate law.



concentration of A at time t

$$2 \operatorname{NO}_2(g) \longrightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$$

Time (s)	[NO ₂]	ln[NO ₂]	1/[NO ₂]
0	8.00×10^{-3}	-4.828	125
50	6.58×10^{-3}	-5.024	152
100	5.59×10^{-3}	-5.187	179
150	4.85×10^{-3}	-5.329	206
200	4.29×10^{-3}	-5.451	233
300	3.48×10^{-3}	-5.661	287
400	2.93×10^{-3}	-5.833	341
500	2.53×10^{-3}	-5.980	395

 $2 \operatorname{NO}_2(g) \longrightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$



Plotting **In[NO₂]** versus **time** gives a curve and not a straight-line fit.

Therefore, this is **not** a firstorder reaction.

$$2 \operatorname{NO}_2(g) \longrightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$$

Plotting $\frac{1}{[NO_2]}$ versus

time gives a straight-line fit.

Therefore, this is a secondorder reaction.





$$2 \operatorname{NO}_2(g) \longrightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$$

Calculate the slope:

$$\frac{(340 - 150)\frac{1}{M}}{400 \text{ s} - 50 \text{ s}} = 0.54 \frac{1}{\text{M s}}$$
$$k = 0.54 \frac{1}{\text{M s}}$$

$$\boxed{\text{Slope} = k}$$





Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

$$t_{1/2} = \frac{1}{k[A]_0}$$

For a second-order reaction, the half-life is dependent on the initial concentration.

Each successive half-life is twice as long as the preceding one. Each successive half-life is an equal period of time in which the reactant concentration decreases by a factor of 2.



TABLE 13.4 Characteristics of Zeroth-, First-, and Second-Order Reactions of the Type $A \rightarrow Products$ Zeroth-Order **First-Order** Second-Order $-\frac{\Delta[\mathbf{A}]}{\Delta t} = k$ $-\frac{\Delta[\mathbf{A}]}{\Delta t} = k[\mathbf{A}]$ $-\frac{\Delta[\mathbf{A}]}{\Delta t} = k[\mathbf{A}]^2$ Rate law $\frac{1}{[\mathbf{A}]_t} = kt + \frac{1}{[\mathbf{A}]_0}$ $\ln [A]_t = -kt + \ln [A]_0$ $[A]_t = -kt + [A]_0$ Integrated Rate Law Linear graph [A] versus t ln [A] versus t $\frac{1}{[A]}$ versus t $\ln [A]_0$ $[A]_0$ Slope = -kSlope = -k[A] <u>1</u> [A] Slope = k $[A]_0$ Graphical k = -(Slope)k = -(Slope)k = Slopedetermination of *k* Half-life $t_{1/2} = \frac{[A]_0}{2k}$ $t_{1/2} = \frac{0.693}{k}$ $t_{1/2} = \frac{1}{k[A]_0}$

(constant)

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

(not constant)

(not constant)

Typically, as the temperature increases, the rate of reaction increases.

$$2 \text{ N}_2 \text{O}_5(g) \longrightarrow 4 \text{ NO}_2(g) + \text{O}_2(g)$$
$$\text{rate} = \mathbf{k}[\text{N}_2 \text{O}_5]$$

The rate constant is dependent on temperature.

Magnesium is inert in cold water.





$Mg(s) + 2 H_2O(l) \longrightarrow Mg^{2+}(aq) + 2 OH^{-}(aq) + H_2(g)$

The formation of bubbles of gas and the pink color of phenolphthalein, which indicates an alkaline solution, provide evidence of the reaction.

Transition State: The configuration of atoms at the maximum in the potential energy profile. This is also called the activated complex.



Reaction progress →

Collision Theory: As the average kinetic energy increases, the average molecular speed increases, and thus the collision rate increases.



Collision energy \rightarrow

The fraction of collisions that are sufficiently energetic to result in reaction increases exponentially with increasing temperature.

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

- **k** Rate constant
- **A** Collision frequency factor
- *E*_a Activation energy
- **R** Gas constant

Temperature (K)

Using the Arrhenius Equation

$$\ln(k) = \ln(A) + \ln\left(e^{-E_a/RT}\right)$$



Reaction Mechanism: A sequence of reaction steps that describes the pathway from reactants to products

Elementary Reaction (step): A single step in a reaction mechanism

An **elementary reaction** describes an individual molecular event.

The **overall reaction** describes the reaction stoichiometry and is a summation of elementary reactions.

Experimental evidence suggests that the reaction between NO₂ and CO takes place by a two-step mechanism:

 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ elementary reaction $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ elementary reaction $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ overall reaction

 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$



Experimental evidence suggests that the reaction between NO₂ and CO takes place by a two-step mechanism:

$$NO_2(g) + NO_2(g) \longrightarrow NO(g) + [NO_3(g)]$$
 elementary reaction
 $\boxed{NO_3(g)} + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ elementary reaction
 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ overall reaction

A **reactive intermediate** is formed in one step and consumed in a subsequent step.

Molecularity: A classification of an elementary reaction based on the number of molecules (or atoms) on the reactant side of the chemical equation

Unimolecular Reaction

 $O_3^*(g) \longrightarrow O_2(g) + O(g)$



Bimolecular Reaction

 $O_3(g) + O(g) \longrightarrow 2 O_2(g)$



Termolecular Reaction

 $O(g) + O(g) + M(g) \longrightarrow O_2(g) + M(g)$



Rate Laws for Elementary Reactions

The rate law for an elementary reaction follows directly from its molecularity because an **elementary reaction is an individual molecular event.**

Rate Laws for Elementary Reactions

Unimolecular Reaction $O_3^*(g) \longrightarrow O_2(g) + O(g)$ rate = $k[O_3]$ **Bimolecular Reaction** $O_3(g) + O(g) \longrightarrow 2 O_2(g)$ rate = $k[O_3][O]$ **Termolecular Reaction** $O(g) + O(g) + M(g) \rightarrow O_2(g) + M(g)$ rate = $k[O]^2[M]$

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

© 2016 Pearson Education, Inc.

Rate Laws for Elementary Reactions

TABLE 13.5 Rate Laws for Elementary Reactions

Elementary Reaction	Molecularity	Rate Law
$A \rightarrow Products$	Unimolecular	Rate = $k[A]$
$A + A \rightarrow Products$	Bimolecular	Rate = $k[A]^2$
$A + B \rightarrow Products$	Bimolecular	Rate = $k[A][B]$
$A + A + B \rightarrow Products$	Termolecular	Rate = $k[A]^2[B]$
$A + B + C \rightarrow Products$	Termolecular	Rate = $k[A][B][C]$

Rate-Determining Step: The slow step in a reaction mechanism since it acts as a bottleneck and limits the rate at which reactants can be converted to products

Multistep Reactions with an Initial Slow Step

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO(g) + NO_3(g)$$
 slow step
 $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$ fast step

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$
 overall reaction

Based on the slow step: $rate = k_1 [NO_2]^2$

Multistep Reactions with an Initial Fast Step

$$2 \operatorname{NO}(g) \stackrel{k_1}{\longrightarrow} \operatorname{N_2O_2}(g) \qquad \text{fast step, reversible}$$

$$\operatorname{N_2O_2}(g) + \operatorname{H_2}(g) \stackrel{k_2}{\longrightarrow} \operatorname{N_2O}(g) + \operatorname{H_2O}(g) \qquad \text{slow step}$$

$$\frac{\operatorname{N_2O}(g) + \operatorname{H_2}(g) \stackrel{k_3}{\longrightarrow} \operatorname{N_2}(g) + \operatorname{H_2O}(g) \qquad \text{fast step}}{\operatorname{NO}(g) + 2\operatorname{H_2}(g) \longrightarrow \operatorname{N_2}(g) + 2\operatorname{H_2O}(g)} \qquad \text{fast step}$$

Based on the slow step: $rate = k_2[N_2O_2][H_2]$

2

rate =
$$k_2[N_2O_2][H_2]$$

intermediate
First step: Rate_{forward} = $k_1[NO]^2$ Rate_{reverse} = $k_{-1}[N_2O_2]$
 $k_1[NO]^2 = k_{-1}[N_2O_2]$
 $[N_2O_2] = \frac{k_1}{K_{-1}}[NO]^2$
Slow step: rate = $k_2[N_2O_2][H_2]$ rate = $k_2 \frac{k_1}{K_{-1}}[NO]^2[H_2]$

Instructor's Resource Materials (Download only) for *Chemistry*, 7e John E. McMurry, Robert C. Fay, Jill Robinson

Procedure for Studying Reaction Mechanisms



Using the Arrhenius Equation



Catalyst: A substance that increases the rate of a reaction without itself being consumed in the reaction. A catalyst is used in one step and regenerated in a later step.

$$H_{2}O_{2}(aq) + \boxed{I^{1-}(aq)} \longrightarrow H_{2}O(l) + IO^{1-}(aq) \qquad \text{rate-determining} \\ H_{2}O_{2}(aq) + IO^{1-}(aq) \longrightarrow H_{2}O(l) + O_{2}(g) + \boxed{I^{1-}(aq)} \qquad \text{fast step} \\ 2H_{2}O_{2}(aq) \longrightarrow 2H_{2}O(l) + O_{2}(g) \qquad \text{overall reaction} \end{cases}$$

Since the catalyst is involved in the **rate determining step**, it often appears in the rate law.

rate = $k[H_2O_2][I^{1-}]$

$$\begin{array}{l} H_2O_2(aq) + \overbrace{I^{1-}(aq)}^{1-} \longrightarrow H_2O(l) + IO^{1-}(aq) & \begin{array}{c} \textbf{rate-determining} \\ \textbf{step} \\ \end{array}$$

$$H_2O_2(aq) + IO^{1-}(aq) & \longrightarrow H_2O(l) + O_2(g) + \overbrace{I^{1-}(aq)}^{1-} & \begin{array}{c} \textbf{fast step} \\ \end{array}$$

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g) & \begin{array}{c} \textbf{overall reaction} \\ \end{array}$$

The rate of decomposition of aqueous hydrogen peroxide can be monitored qualitatively by collecting the evolved oxygen gas in a balloon.



In the absence of a catalyst, little O_2 is produced.



After addition of aqueous sodium iodide, by opening the stopcock to add Nal, the balloon rapidly inflates with O_2 .

(a) Catalyzed pathway

٨

Potential energy



(b) Uncatalyzed pathway

Reaction progress \rightarrow

Reaction progress →

The activation energy E_a is lower for the catalyzed pathway. The shape of the barrier for the catalyzed pathway applies to the decomposition of H₂O₂.

Homogeneous and Heterogeneous Catalysts

Homogeneous Catalyst: A catalyst that exists in the same phase as the reactants

Heterogeneous Catalyst: A catalyst that exists in a different phase from that of the reactants

Homogeneous and Heterogeneous Catalysts



(a) H_2 and C_2H_4 are adsorbed on the metal surface.



(b) The H–H bond breaks as H–metal bonds form, and the H atoms move about on the surface.



(c) One H atom forms a bond to a C atom of the adsorbed C_2H_4 to give a metal-bonded C_2H_5 group. A second H atom bonds to the C_2H_5 group.



(d) The resulting C_2H_6 molecule is desorbed from the surface.

Homogeneous and Heterogeneous Catalysts

TABLE 13.6 Some Heterogeneous Catalysts Used in Commercially Important Reactions

Reaction	Catalyst	Commercial Process	Product: Commercial Uses
$2 \operatorname{SO}_2 + \operatorname{O}_2 \longrightarrow 2 \operatorname{SO}_3$	Pt or V_2O_5	Intermediate step in the contact process for synthesis of sulfuric acid	H ₂ SO ₄ : Manufacture of fertilizers, chemicals; oil refining
$4 \text{ NH}_3 + 5\text{O}_2 \longrightarrow 4 \text{ NO} + 6\text{H}_2\text{O}$	Pt and Rh	First step in the Ostwald process for synthesis of nitric acid	HNO ₃ : Manufacture of explosives, fertilizers, plastics, dyes, lacquers
$N_2 + 3H_2 \longrightarrow 2 NH_3$	Fe, K_2O , and Al_2O_3	Haber process for synthesis of ammonia	NH ₃ : Manufacture of fertilizers, nitric acid
$H_2O + CH_4 \longrightarrow CO + 3 H_2$	Ni	Steam-hydrocarbon re-forming process for synthesis of hydrogen	H ₂ : Manufacture of ammonia, methanol
$CO + H_2O \longrightarrow CO_2 + H_2$	ZnO and CuO	Water–gas shift reaction to improve yield in the synthesis of H_2	H ₂ : Manufacture of ammonia, methanol
$CO + 2H_2 \longrightarrow CH_3OH$	Cu, ZnO, and Al_2O_3	Industrial synthesis of methanol	CH ₃ OH: Manufacture of plastics, adhesives, gasoline additives; industrial solvent
$ \ \ \ \ \ \ \ \ \ \ \ \ \ $	Ni, Pd, or Pt	Catalytic hydrogenation of compounds with $C = C$ bonds as in conversion of unsaturated vegetable oils to solid fats	Food products: margarine, shortening