5.111 Lecture 31
Kinetics
Topics: Rates of Chemical Reactions and Rate Law
Chapter 13.1-13.5

When considering a chemical reaction, one must ask whether the reaction will go (thermodynamics), and how fast the reaction will go (kinetics).

A kinetics experiment measures the rate at which the concentration of a substance taking part in a chemical reaction changes with time.

## Oxidation of Glucose

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta H° = -2816$ kJ/mol
$T\Delta S°$ or $\Delta S°$ is (+)
$\Delta G° = -2{,}885$ kJ/mol

Thermodynamically favorable.

But to be useful as an energy source, the oxidation of glucose must be fast enough.

Glucose oxidation is slow. Body uses protein catalysts called enzymes to speed up the reactions.

## Factors affecting rates of reactions

1.

2.

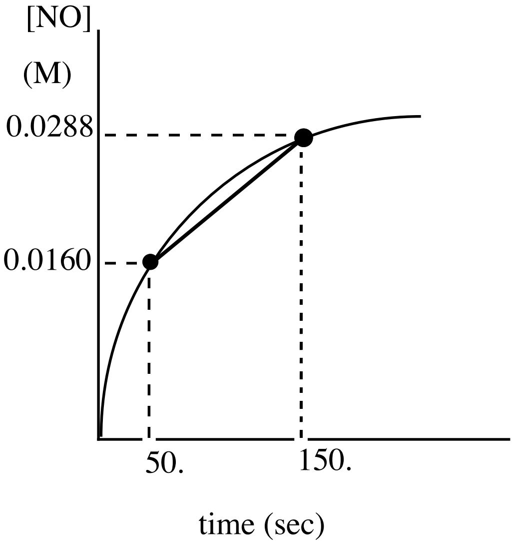
3.

4.

5.

Measuring reaction rates

Consider: $NO_2$ (g) + CO (g) → NO (g) + $CO_2$ (g)



Can monitor the changes in concentration of NO

$$\text{average rate} = \frac{\text{change in concentration}}{\text{change in time}}$$

$$\text{average rate} = \frac{\Delta[NO]}{\Delta t}$$

$$\text{average rate} = \frac{0.0288 - 0.0160 \text{ M}}{150. - 50. \text{ sec}} = 1.28 \times 10^{-4} \text{ M s}^{-1}$$

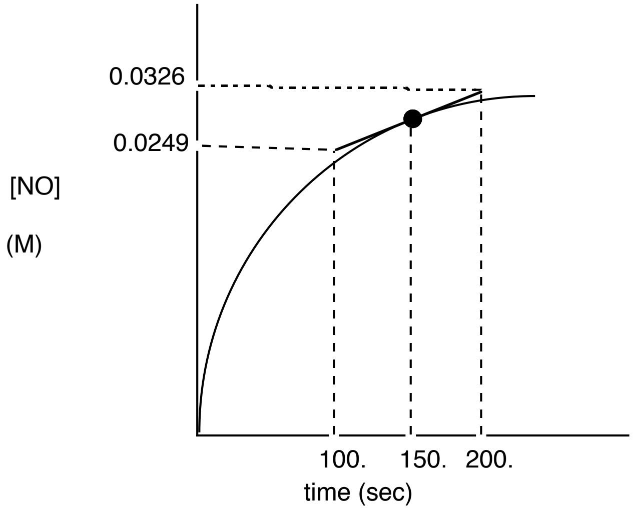
average rate depends on time interval chosen

$$\text{Instantaneous rate} = \text{limit}_{\Delta t \to 0} \frac{[NO]_{t+\Delta t} - [NO]_t}{\Delta t} = \frac{d[NO]}{dt}$$

As Δt approaches 0, the rate becomes the slope of the line tangent to the curve at time t.

$$\text{Instantaneous rate at } t=150 \text{ sec is } \frac{0.0326 - 0.0249 \text{ M}}{200. - 100. \text{ sec}} = 7.7 \times 10^{-5} \text{ M s}^{-1}$$

Initial rate = Instantaneous rate at time equals 0 sec



## Rate expressions

Consider again: $NO_2 \text{ (g)} + CO \text{ (g)} \rightarrow NO \text{ (g)} + CO_2 \text{ (g)}$
Can monitor NO or $CO_2$ increase or $NO_2$ or CO decrease

$$\text{rate} = \frac{-d[NO_2]}{dt} = \frac{-d[CO]}{dt} = \qquad\qquad = $$

Assuming no intermediate species and/or that the concentration of intermediates is independent of time

Generally $\quad aA + bB \rightarrow cC + dD$

$$\text{rate} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Example $\quad 2HI \text{ (g)} \rightarrow H_2 \text{ (g)} + I_2 \text{ (g)}$

$$\text{rate} = \qquad\qquad = \qquad\qquad =$$

## Rate Laws

The rate law is the relationship between the rate and the concentration, which are related by a proportionality constant, k, called the rate constant.

| | |
|---|---|
| $aA + bB \rightarrow cC + dD$ | rate = $k\,[A]^m[B]^n$..... |
| | m and n are order of reaction in A and B, respectively |
| | k is the rate constant |

## Truths about rate laws

(1) Rate law is a result of experimental observation. You can't look at the stoichiometry of the reaction and predict the rate law (unless the reaction is an elementary reaction - we will come back to this later).

(2) Rate law is not limited to reactants. It can have product terms, i.e., rate = $k[A]^m[B]^n[C]^c$

(3) For rate = $k[A]^m[B]^n$, m is the order of reaction in A, n is the order of reaction in B. m and n can be integers, fractions, negative or positive.

| | | | |
|---|---|---|---|
| $m = 0$ | | | |
| $m = 1/2$ | | | |
| $m = 1$ | First order | $k[A]$ | Double concentration/ |
| $m = 2$ | Second order | $k[A]^2$ | Double concentration/<br>Triple concentration/ |
| $m = -1$ | | | |
| $m = -1/2$ | | | |

(4) The overall reaction order is the sum of the exponents in the rate law. For rate = $k[A]^2[B]$, the overall reaction order is _________ order.

(5) The units for k vary. Determine units for k by considering units for rate and for concentration.

Integrated Rate Laws

Measuring initial rates can be difficult because it involves determining small changes in concentrations that occur during short intervals in time. An alternative is to use the integrated rate law, which expresses concentrations directly as a function of time.

First Order $\quad A \rightarrow B$

$$\text{rate} = \frac{-d[A]}{dt} = k[A]$$

separate concentration and time terms

$$\frac{1}{[A]} \bullet d[A] = -k\,dt$$

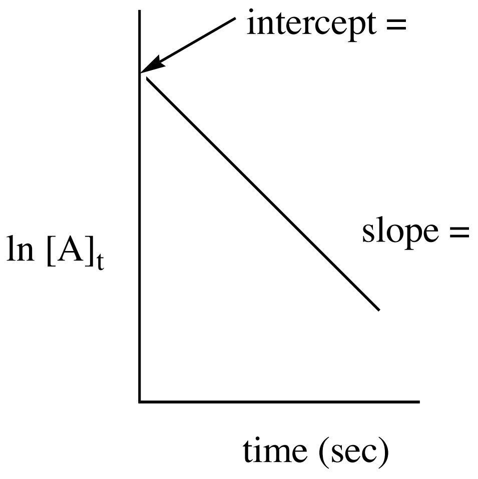
$$\int_{[A]_0}^{[A]_t} \frac{1}{[A]}\, d[A] = -k \int_{o}^{t} dt$$

$$\ln [A]_t - \ln [A]_0 = -kt \qquad \text{or} \qquad \boxed{\ln [A]_t = -kt + \ln [A]_0}$$

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

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

$$\boxed{[A]_t = [A]_0\, e^{-kt}}$$



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

First order Half-life

Half-life is the time it takes for the original concentration to be reduced by half ($t_{1/2}$)

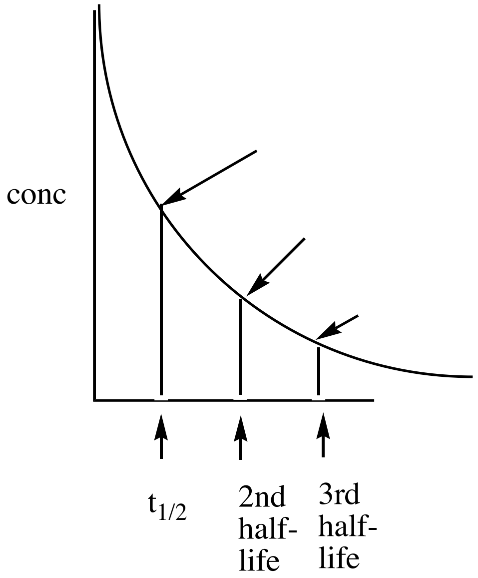
From above $$\ln \frac{[A]_t}{[A]_0} = -kt$$

$$\ln \frac{\left(\frac{[A]_0}{2}\right)}{[A]_0} = -kt_{1/2}$$

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

$$-0.6931 = -kt_{1/2}$$

$$t_{1/2} = \frac{0.6931}{k}$$



For the same material does it take longer to go from 1 ton to a ½ ton or 1 gram to a ½ gram?

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