Overview of Chapter 15: Kinetics

Rates of Reactions

Effects on reaction rates:

- Temperature effects
- Concentration effects
- Effects of catalysts

Integrated Rate Laws

Reaction Mechanisms

Today's questions to consider:

How fast does ethanol break down in the body?

How can we affect this rate?

Today's Topics

- Rate equations
- Factors affecting rates
- 1st, 2nd, and 0 order reactions

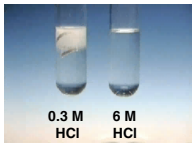
Factors Affecting Rates

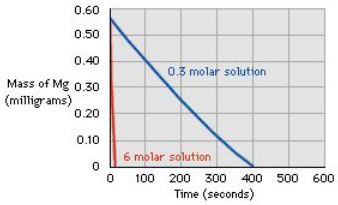
1. Concentrations
2. Physical state of reactants and products
3. Temperature
4. Catalysts

Factors Affecting Rates

1. Concentrations

$Mg(s) + 2\ HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$





Factors Affecting Rates

2. Physical state of reactants

Factors Affecting Rates

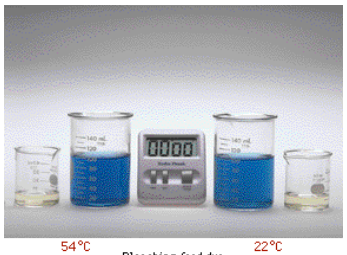
3. Catalysts:

Mn^{++} decomposition of H_2O_2

$2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

Factors Affecting Rates

4. Temperature



Concentrations and Rates

To determine a reaction's mechanism, we study the reaction's

rate and

concentration dependence

Concentrations, Rates, & Rate Laws

In general, for

$a\,A + b\,B \rightarrow x\,X$ with a catalyst C

$\text{Rate} = k\,[A]^m[B]^n[C]^p$

The exponents m, n, and p

- are the reaction order
- can be 0, 1, 2 or fractions
- **must be determined by experiment**

Interpreting Rate Laws

$\text{Rate} = k\,[A]^m[B]^n[C]^p$

- If m = 1, rxn. is 1st order in A
  $\text{Rate} = k\,[A]^1$
  If [A] doubles, then rate goes up by factor of __
- If m = 2, rxn. is 2nd order in A.
  $\text{Rate} = k\,[A]^2$
  Doubling [A] increases rate by _____
- If m = 0, rxn. is zero order.
  $\text{Rate} = k\,[A]^0$
  If [A] doubles, rate _____

Ethanol Oxidation Rates

One mole of ethanol (CH_3CH_2OH) = 46 g by mass
= 60 ml by volume

3 beers (6.4% ethanol by volume) = 3 x 355 ml x 0.064
= 68 ml ethanol
= 1.1 mole ethanol

3 cocktails with 45 ml (1.5 oz) each of 80 proof (40%) ethanol:
= 3 x 45 ml x 0.40
= 54 ml ethanol
= 0.9 mole ethanol

1/2 bottle of wine (750 ml) at 14% ethanol:
= 1/2 x 750 ml x 0.14
= 52 ml ethanol
= 0.9 mole ethanol

Ethanol Oxidation Rates

- In Massachusetts, legal intoxication is 0.08% by volume
- Adults average 40 L of fluids
  At intoxication, 40 L x 0.08% = 32 ml ethanol in the bloodstream
  = 0.533 moles ethanol
  = 0.533 moles/40 L = 0.0133M
  = 0.08% ethanol by volume
- **Uptake**: The small intestine takes up ethanol with a first order reaction with $t_{1/2}$ = 4 minutes (+/- 25% in different individuals)
- **Breakdown**: The liver oxidizes ethanol with a zero order rate constant of 0.00425 mole/(L hour) using an enzyme called Liver Alcohol Dehydrogenase (LAD)

$$\text{Ethanol} + NAD^+ \xrightarrow{\text{LAD}} \text{Acetaldehyde} + NADH + H^+$$

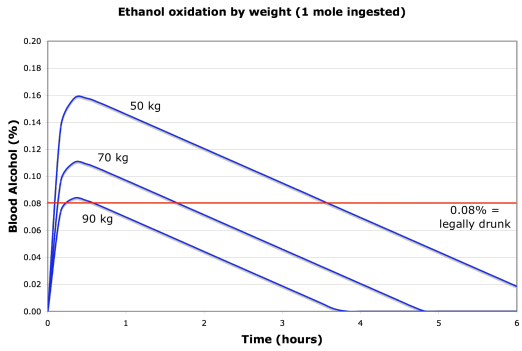
Ethanol Oxidation Rates

Calculate the ethanol oxidation of 3 people:
50, 70, and 90 kg (110, 154, and 198 lbs)

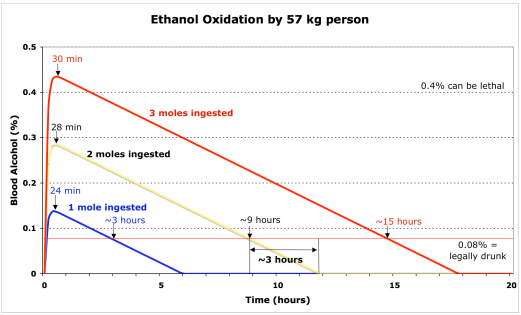
Assumptions:
70% of a person's weight is fluid (typically 65-75%)
An average liver is 1.6 kg (typical is 1.4-1.8 kg) (a)
An LAD enzyme rate constant of
0.00425 mole/(L hour) (b)

(a) Sabiston's Textbook of Surgery, 15th ed, 1997
(b) Umlis et al., (2005) Alcohol 35: 3-12.

Ethanol Oxidation Rates



Ethanol Oxidation Rates

Now calculate what happens when a 57 kg (125 lb) person ingests 1, 2, and 3 moles of ethanol:

Ethanol Oxidation Rates