

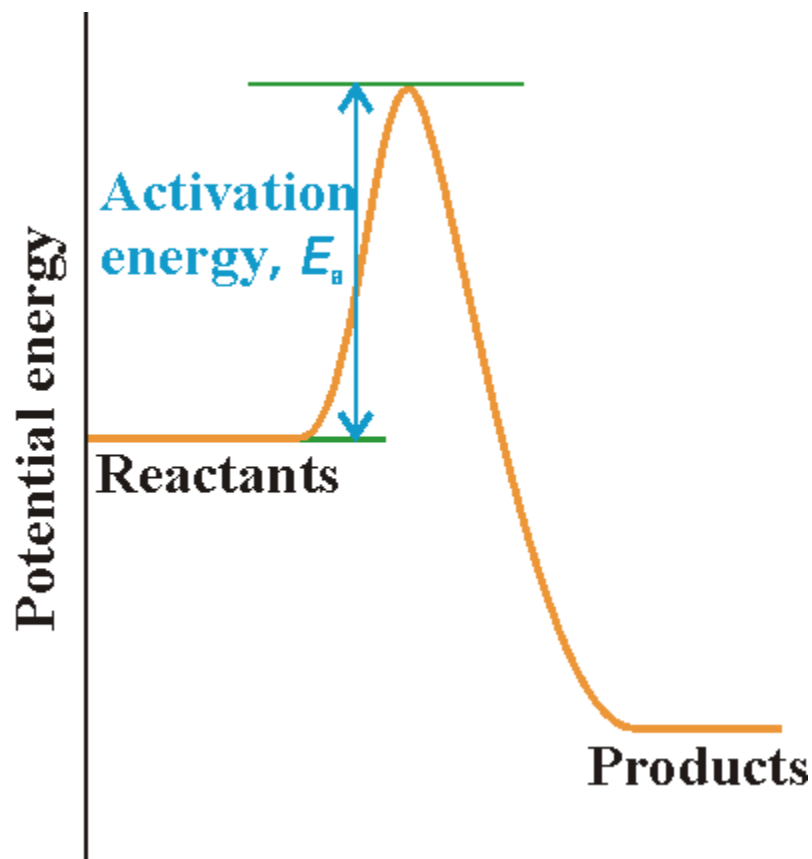
Chemical Kinetics



Energy



- Chemical reactions proceed if the products of the reaction have lower free energies than do the reactants



The fundamental equations of thermodynamics



- The first law of thermodynamics

$$\Delta U = \Delta Q + \Delta w$$

the total energy of a system is constant.

- Enthalpy, H, is a function that describes energy changes at constant pressure.

$$\Delta H_p = c_p(\Delta T)_p$$

- For a biological system it defines the internal energy of a system

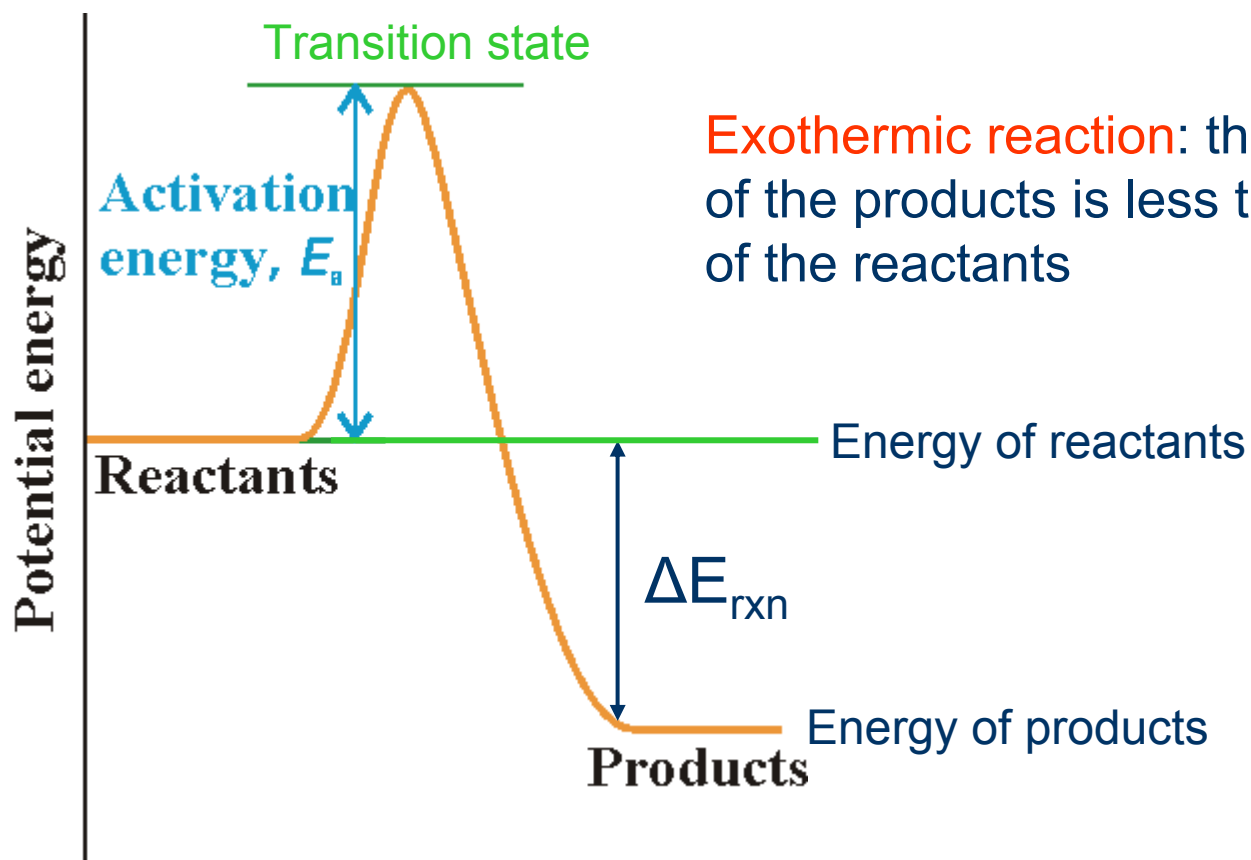
– **HEAT**

$\Delta H = +ve \Rightarrow$ heat is absorbed \Rightarrow ENDOTHERMIC

$\Delta H = -ve \Rightarrow$ heat is evolved (given out) \Rightarrow EXOTHERMIC



The reaction profile





The fundamental equations of thermodynamics



- **The second law of thermodynamics**
Spontaneous processes are those which **increase** the entropy of the **universe** (i.e. system + surroundings).
- Entropy is equal to a measurement of the randomness of a system.

$$dS = \frac{dq_{rev}}{T}$$

The fundamental equations of thermodynamics



- The Gibbs Free Energy



$$\Delta_r G^0 = \sum v_i \Delta_f G^0(\text{products}) - \sum v_i \Delta_f G^0(\text{reactants})$$

$$dG = dH - TdS \quad \text{or} \quad \Delta G = -RT \ln K_{\text{eq}}$$

- i) If $\Delta G^0 < 0$ (exergonic, from the Greek word for work-producing)
the **forward** reaction is spontaneous.
- (ii) If $\Delta G^0 > 0$ (endergonic, signifying work-consuming)
the **reverse** reaction is spontaneous.
- (iii) If $\Delta G^0 = 0$ the reaction is at equilibrium.



Chemical Kinetics

- Study of the rates of chemical reactions and the factors that influence the rates.
- Collision Theory
 - Collisions between reacting molecules are necessary before a reaction can occur
 - Only those collisions having sufficient energy are effective in bringing about a reaction → activation energy
 - Colliding molecules must be properly oriented with respect to one another for the reaction to take place



Chemical kinetics

Factors affecting *reaction rate*:

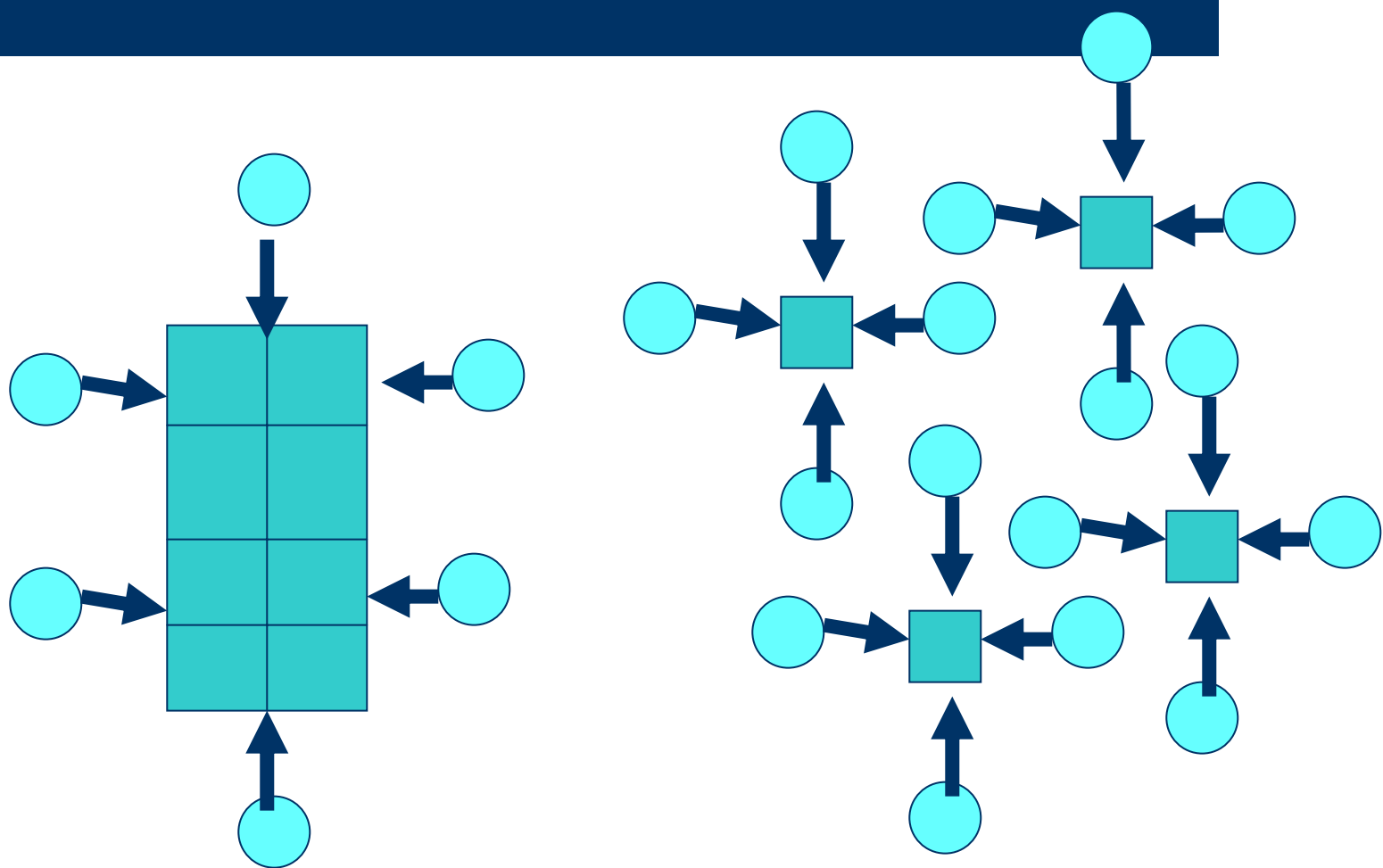
Concentrations of reactants

Catalyst

Temperature

Surface area of solid reactants or catalyst

Surface Area





Example

- The reaction:



Catalyst	E_a	n_1/n	Relative rate
None	18,000	5.6×10^{-14}	1
I ⁻	13,500	1.16×10^{-10}	2.07×10^3
Catalase	6,400	1.95×10^{-5}	3.47×10^8



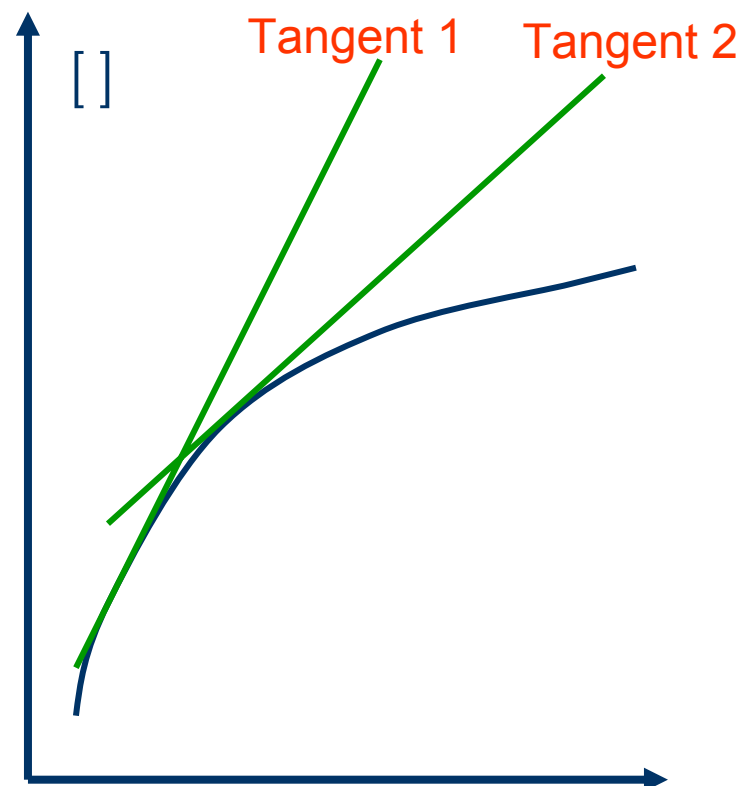
Reaction Rate Defined

Reaction rate: changes in a concentration of a product or a reactant per unit time.

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

$\Delta[\]$ → concentration
 Δt → change

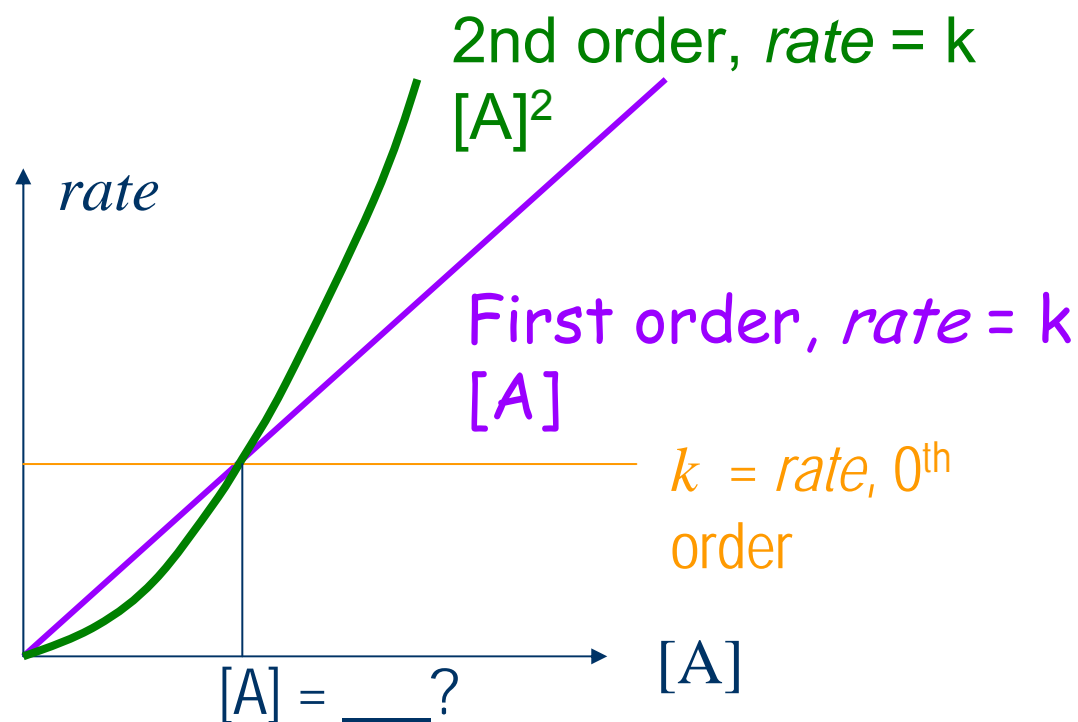
- Non-disruptive techniques
- Disruptive techniques: Chemical Analysis Method





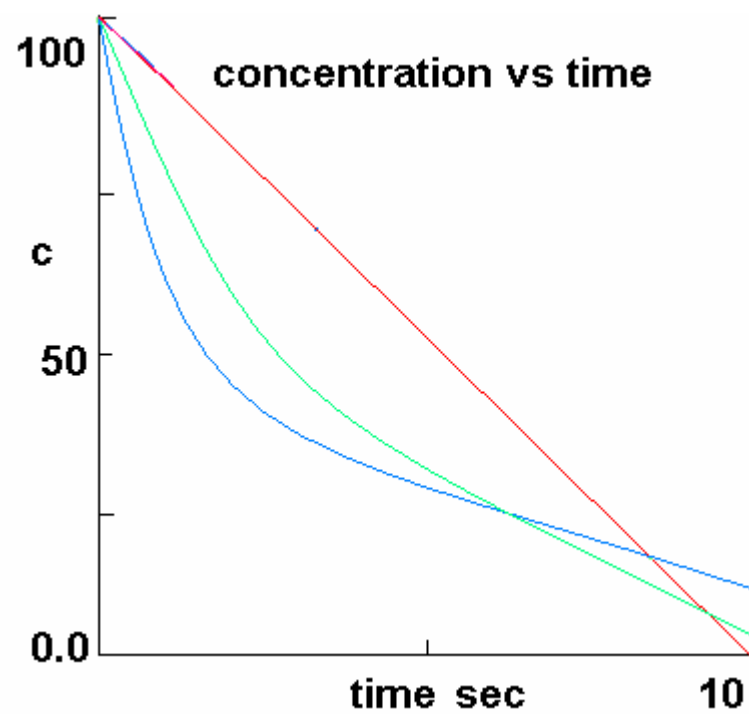
Reaction Order

$$-\frac{dA}{dt} = k_A [A]^n$$





Reaction Plots





Integrated Rate Laws

concentrations as functions of time

One reactant A decomposes in 1st or 2nd order rate law.

Differential rate law

$$- d[A] / dt = k$$

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

$$- \frac{d[A]}{dt} = k [A]^2$$

Integrated rate law

$$[A] = [A]_0 - k t$$

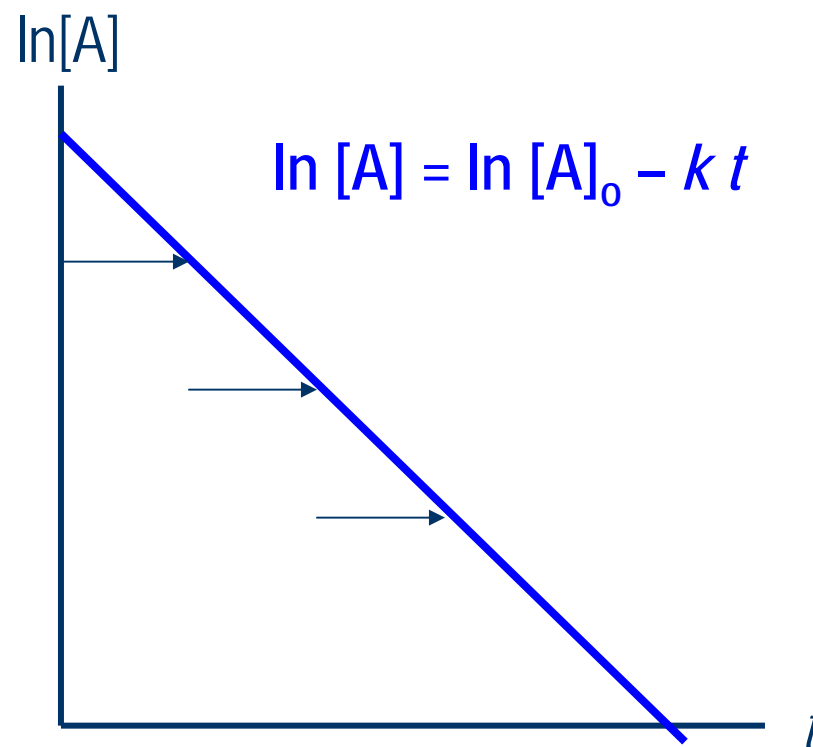
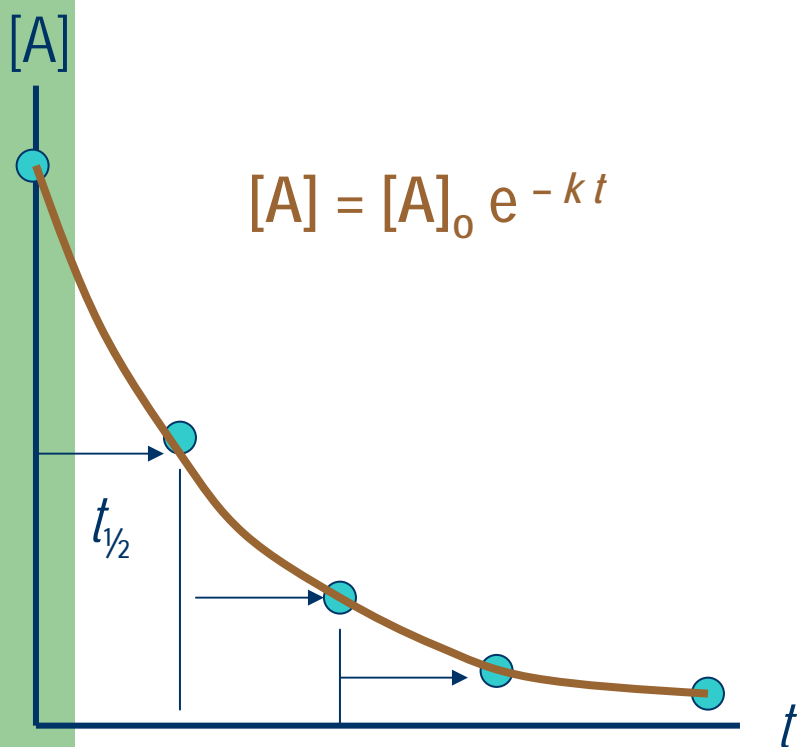
$$[A] = [A]_0 e^{-k t} \text{ or } \ln [A] = \ln [A]_0 - k t$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = k t$$

[A] conc at t

[A]₀ conc at $t = 0$

Concentration and time of 1st order reaction



Half life & k of First Order Decomposition



The time required for half of A to decompose is called half life $t_{1/2}$.

Since $[A] = [A]_0 e^{-k t}$ or $\ln [A] = \ln [A]_0 - k t$

When $t = t_{1/2}$, $[A] = \frac{1}{2} [A]_0$

Thus

Radioactive decay usually follow 1st order kinetics, and half life of an isotope is used to indicate its stability.



Arrhenius Equation

The temperature dependence of the rate constant k is best described by the Arrhenius equation:

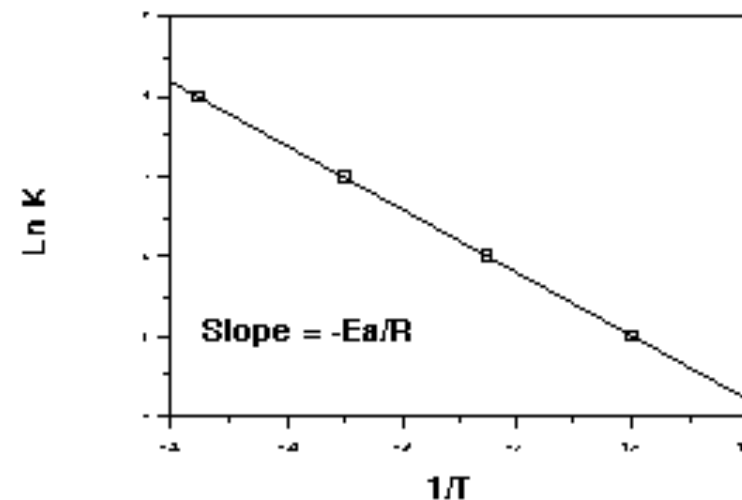
$$k = A e^{-E_a / RT}$$

or $\ln k = \ln A - E_a / RT$

If k_1 and k_2 are the rate constants at T_1 and T_2 respectively, then

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

Arrhenius Plot





Typical activation energies

	<u>Kcal/mole</u>
Diffusion controlled	0 - 8
Enzyme reactions	10 - 15
Hydrolysis	15 - 25
Lipid oxidation	10 - 25
Nonenzymatic browning	25 - 50
Spore destruction	60 - 80
Vegetative cell destruction	50 - 150
Protein denaturation	80 - 120



Q_{10} Reaction rate

- Alternative way of expressing temperature dependence

$$Q_{10} = \frac{\text{Rate @ } T + 10}{\text{Rate @ } T} \quad Q_{10} = 10^{\left[\frac{2.186 E_A}{(T)(T+10)} \right]}$$

- Extensively used by the food industry
- Model used to describe how much faster/slower a reaction will go if the product is held at some other temperature
- Used to predict expected product shelf life
 - ASLT



Q_{10} and shelf life prediction

T°C	Q_{10}			
	2	2.5	4	5
50	2	2	2	2 weeks
40	4	5	8	10 weeks
30	8	12.5	32	50 weeks
20	16 wk	31 wk	2.5 yr	4.8 yr



Q₁₀ Practical problems

- too large ΔT
- phase change
 - freeze range to refrigerated range
 - lipid melting
 - reactant crystallizes out or solubilizes
 - transition over glass - rubber point
- concentration due to freezing
- high temperatures: Protein denaturation
- simultaneous competing mechanisms - multiple pathways of different EA
- water activity change with temperature
- oxygen solubility (20% decrease per 10°C rise)
- moisture change due to humidity difference in chambers
- change in film permeability to oxygen, CO₂, water
- viscosity change of reaction phase free volume dependence
- change of mechanism
 - different microbes or NEB vs Lipid oxidation

Chemical Reaction and Molecular Collision



Molecular collisions lead to chemical reactions. Thus, the reaction constant, k is determined by several factors.

$$k = Zfp$$

Z : collision frequency

p , the fraction with proper orientation

f , fraction of collision having sufficient energy for reaction

f is related to the potential energy barrier called activation energy, E_a .

$$f \propto e^{-E_a / RT} \text{ or } \exp(-E_a / RT)$$

$$n_1/n = \exp(-E_a / RT)$$

n_1 = number of molecules with an energy of E_a or greater

n = the total number of molecules



Example

- The rate constant for color formation on the surface of grilled meat was calculated as a function of temperature. Plot the data as an Arrhenius plot and calculate the activation energy for the browning reaction

Temp/ °C	100	120	140	160	180	200
rate/h ⁻¹	0.001591	0.001875	0.002174	0.002487	0.002811	0.003146



Example

- The E_a for a non-enzymatic browning reaction is $\sim 30,000$ cal/mol
- The E_a for enzymatic denaturation is $\sim 100,000$ cal/mol

You know that 30 min at 80°C will inactivate the enzyme you are concerned with. You have, however, a very brown product.

A colleague recommends you to use 110°C for 1 sec.

Will this work?