SUMMARY: CHAPTER 2
Introductory Concepts

Stoichiometry

- Invented by Lavosier
- Molecules react in fixed proportions

$$\alpha_1 A + \alpha_2 B \Rightarrow \alpha_3 C + \alpha_4 D$$

Stoichiometric Coefficent, β_n

- Number of molecules produced when reaction goes once

Example

$$2CO + O_2 \Rightarrow 2CO_2$$

$$CO + \tfrac{1}{2} O_2 \Rightarrow CO_2$$

New Topic: Reaction rate:

Original definition due to Priestley - moles/hr produced by a reactor.

Van't Hoff showed that as you make a reactor bigger, you produce more product. The production rate is proportional to the volume. i.e.

total production(moles/hr)=constant×Volume.

Van't Hoff defined

$$r_A = \frac{\text{production rate}\left(\text{Moles}/\text{hr}\right)}{\text{reactor volume}\left(\text{liter}\right)} \qquad (1)$$

- r_A called the Rate of production of A
- r_A has dimensions moles/lit-hr
- r_A is positive for a product, negative for a reactant

Equ 1 applies to homogeneous reactions
Different equation applies to heterogeneous reactions

Some reactions scale as surface area instead

$$R_A = \frac{\text{production rate}\left(\text{Moles}/\text{hr}\right)}{\text{surface area}\left(\text{cm}^2\right)}$$

- R_A is also called the Rate of production of A
- R_A has dimensions moles/cm^2-hr
- R_A is positive for a product, negative for a reactant

It is also useful to define r_i the rate of a reaction i by

$$r_i = \frac{1}{\beta_A} r_A$$

Table 2.1 Summary of the key definitions.	
Stoichiometric coefficient	The amount of product produced when the reaction goes once. The stoichiometric is positive for a product and negative for a reactant.
r_{A1}	The net rate of production of a species A. r_A is positive for a product and negative for a reactant.
Rate of reaction 1 r_1	$r_1 = \frac{1}{\beta_A} r_A$ for any species A participating in reaction 1.
Homogeneous reaction	A reaction which happens throughout the reacting phase.
Heterogeneous reaction	A reaction which happens near the boundary of a reacting phase.

New Topic: Variations in rate with conditions

Rates vary with:

- Concentrations of all species (reactants, products, inerts) (factors of 10-100)
- Temperature (factors of 100 or more)
- The presence of solvents (factors of 10^{12} or more)
- The presence of catalysts (factors of 10^{12} or more)

Next Topic: Rate equations

definition:

- Rate as a function of the concentration of all of the speices in the reactor.

Typical rate laws for simple A⇒C reactions:

$r_A = -k(C_A)$ First order

$r_A = -k(C_A)^2$ Second order

$r_A = -k(C_A)^3$ Third order

$r_A = -k(C_A)^n$ nth order

n is the order

k is the rate constant

For reactions A + B ⇒ C

$r_A = -k(C_A)^n(C_B)^m$

nth order in A, mth order in B

overall (m+n)th order

$r_A = -k(C_A)(C_B)^2$

first order in A, second order in B, third order overall.

Table 2.4 The key definitions from Section 2.3.	
Rate equation	The rate as a function of the concentration of the reactants.
Order	The exponent n is the expression.
First order reaction	A reaction whose rate is preparation to the reactant concentration to the first power (i.e. n = 1 in eqn. (2.11)).
Second order reaction	A reaction whose rate is proportional to the reactant concentration to the second order.
Overall order of reaction	The sum of the orders for each of the reactants.

notation

k_1, k_2 rate constants
K_1, K_2 equilibrium constants
C_A=[A] concentration of species A

Discussion Problems:

Table2.2 Sample rate data to illustrate equation (2.11).			
C_A Moles/Lit	rate Moles/Lit/ Min	C_A Moles/Lit	rate Moles/Lit/ hrs
0.25	0.13	1	0.5
0.5	0.25	2	1.0

1. what is the order of the reaction?

Table2.3 Sample data to illustrate equation (2.12).					
C_A moles/liter	C_B moles/liter	rate moles/liter-min	C_A moles/lit er	C_B moles/liter	rate moles/liter-min
1	0.25	0.031	0.25	1	0.13
1	0.5	0.13	0.5	1	0.25
1	1	.5	1	1	0.5
1	2	2.0	2	1	1.0

2. what is the order of the reaction?

More complex rate equations

Very few real reactions have simple reaction orders over a wide range of conditions:

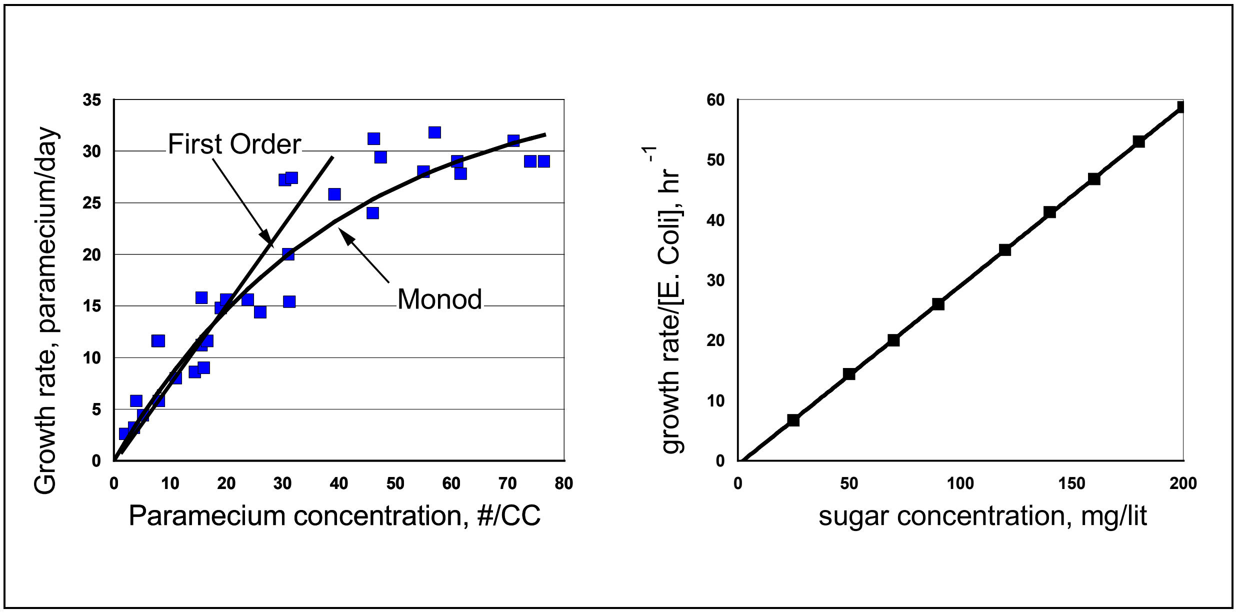

Figure 2.1 The reproduction rate of paramecium as a function of the paramecium concentration and the rate of E. Coli growth in sugar solutions as a function of the sugar concentration. Paramecium data of Meyers, H. Experim. Zoology **49** (1927) 1. E. Coli data from Monod[1942].

$$r_{ecoli} = \frac{k_1 K_2 [E..Coli]\,[Sugar]}{(1 + K_2 [Sugar])}$$

(2.18)

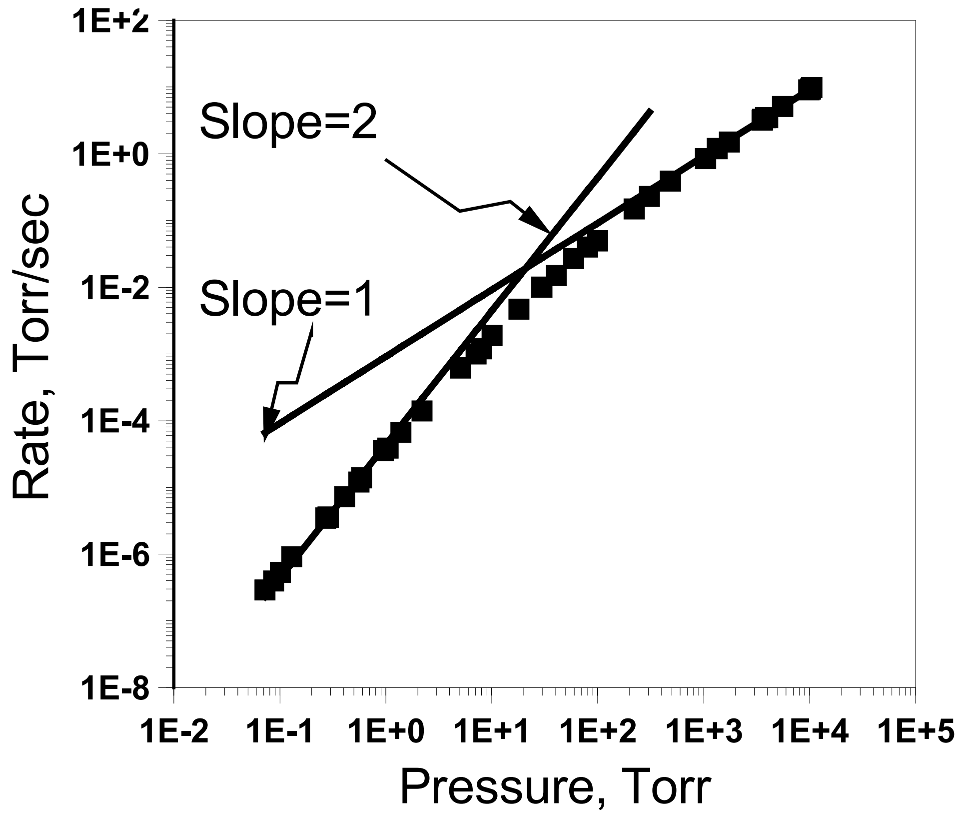

Figure 2.3 The rate of CH_3NC isomerization to CH_3CN as a function of the CH_3NC pressure.

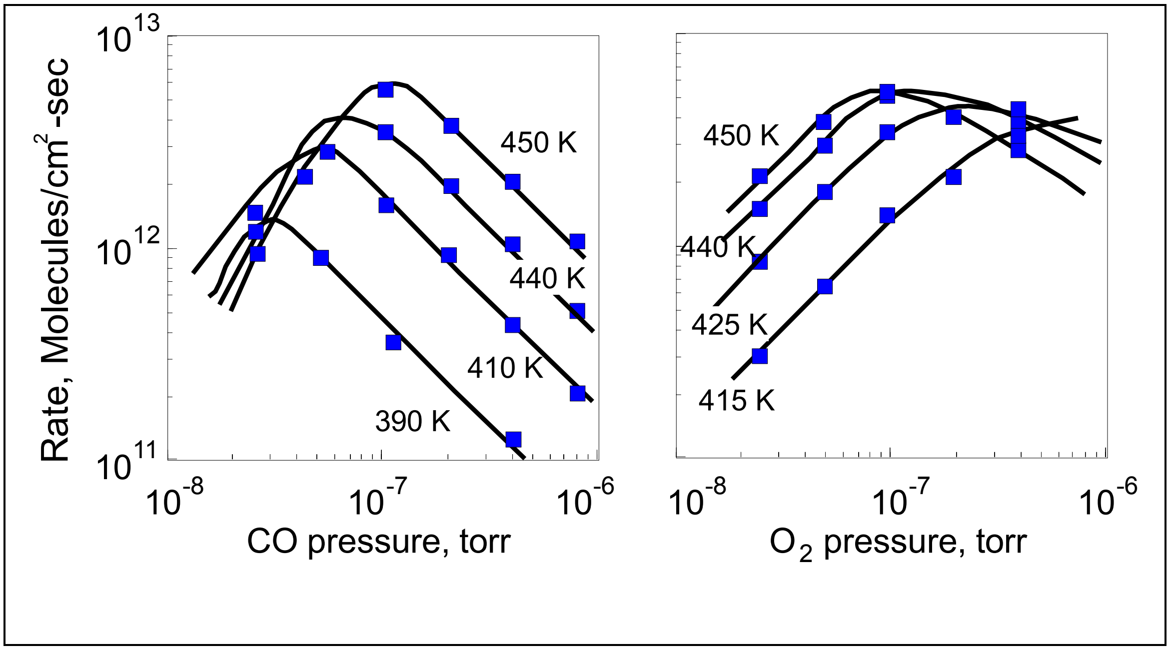

Figure 2.15 The influence of the CO pressure on the rate of CO oxidation on Rh(111). Data of Schwartz, Schmidt, and Fisher.

$$r_{CO} = \frac{k_1 P_{CO} P_{O_2}}{(1 + K_2 P_{CO})^2}$$

Called a **Langmuir-Hinshelwood** rate law.
also called **Monod** rate law

Arises because reaction occurs on catalyst surface:

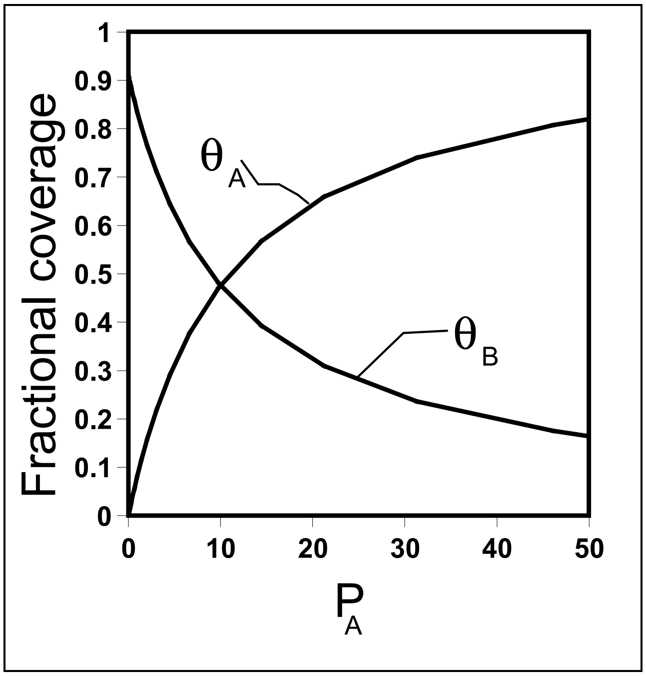

Figure 12.33 The changes in θ_A and θ_B as a function of P_A with $K_B P_B = 10$.

No industrially important reaction is first or second order over a wide range of conditions

Not all reactions have rate equations:

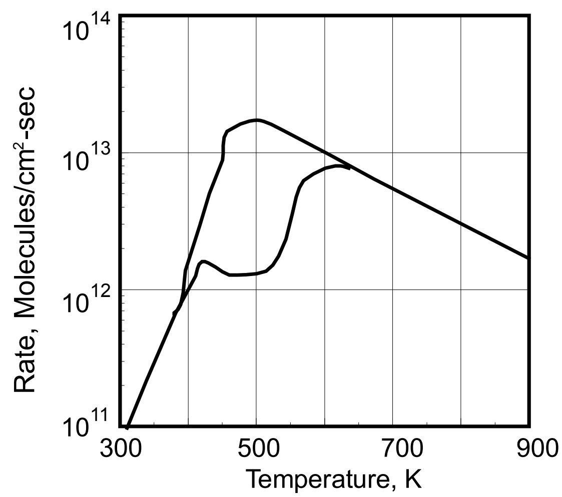

Figure 2.22 Rate Data for CO Oxidation on Rh(100) catalyst. Data of Schwartz et al.[1986].

Summary

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Overall order of reaction	The sum of the orders for each of the reactants.

- Real reactions rarely follow these simple rate laws.
- Some reactions do not have a rate law

Next Topic: Temperature dependence of the rate equation:

Harcourt Equation (assumes energy transfer dominates):

$$k=k^T T^n$$

k=rate constant

k^T=preexponential

n = constant between 1 and 4.

Arrhenius' model (assumes activation barrier to reaction controls rate)

$k=k_o\exp(-E_a/k_BT)$

k_o=preexponential

E_a = activation barrier, kj/molecule

k = boltzman's constant, 1.381×10^{-23} j/K

T= temp (kelvin).

Real data somewhere in between

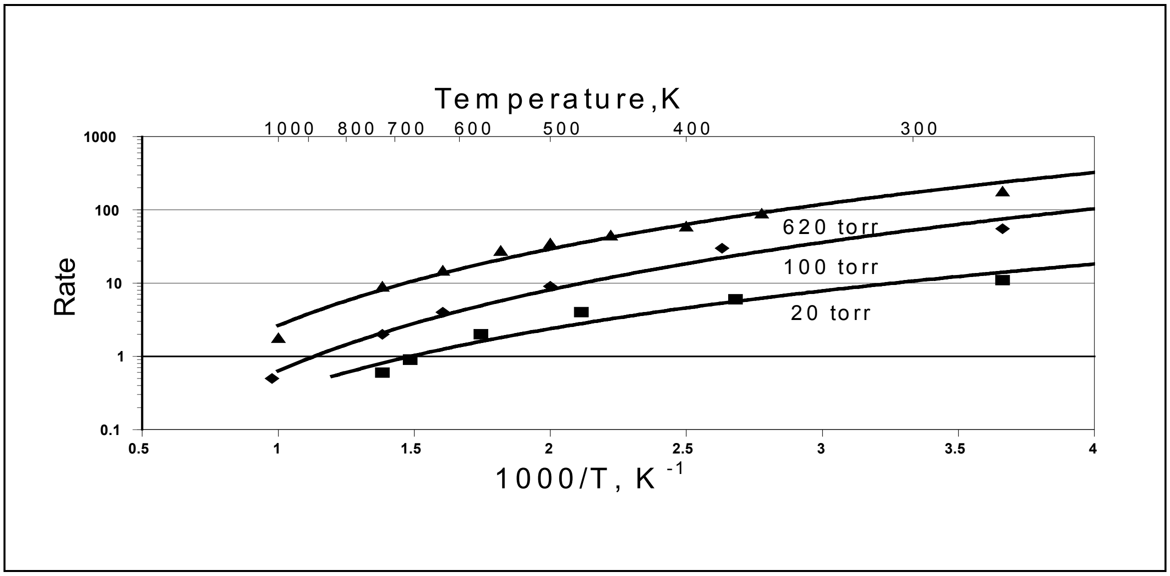

Figure 2.6 The rate of the reaction $CH + N_2 \rightarrow HCN + N$ as a function of the temperature. Data of Becker, Gelger and Wresen[1996].

$$k_1 = k_m^0 (T)^m e^{-E_A / k_B T}$$

(2.28)

Arrhenius' effect much larger than Harcourt and Essen.

Key implications of Arrhenius' Law

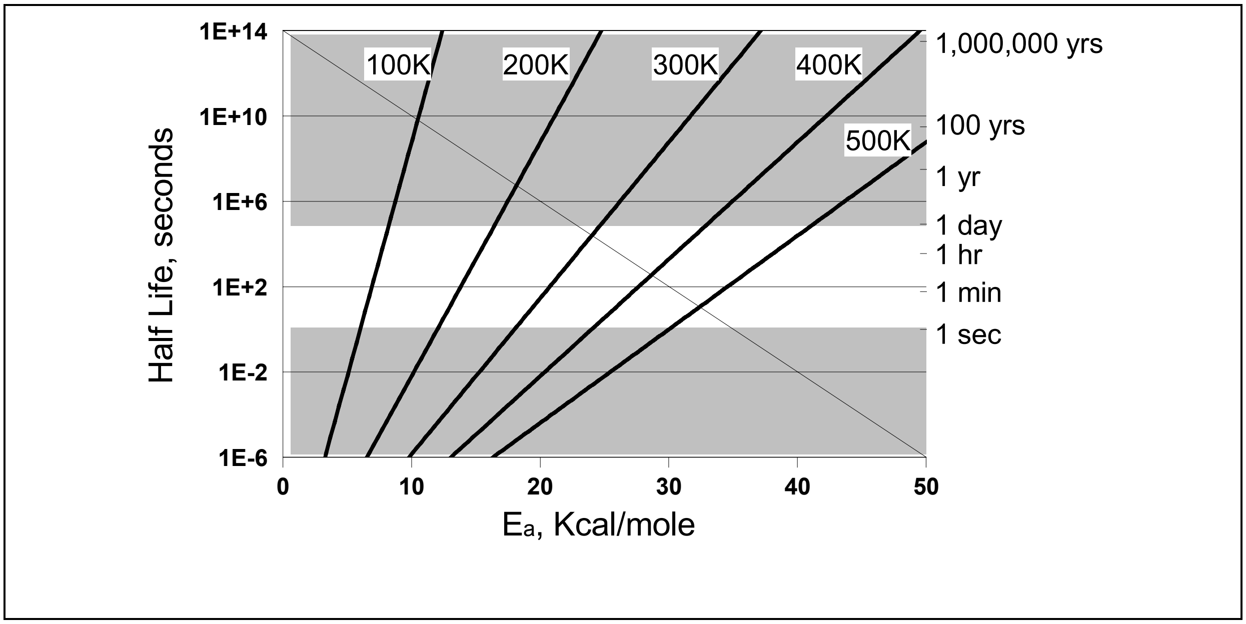

Figure 2.8 A plot of $\tau_{1/2}$ vs. E_A at 100, 200, 300, 400, and 500 K.

$$E_A = (1/15 \text{ kcal/mole-}^\circ\text{ K})T_{minute}$$

(2.31)

$$E_A = (0.06 \text{ kcal/mole-}^\circ\text{ K})T_{sec}$$

(2.32)

$$T_{minute} = \frac{15 \text{ K - mole}}{\text{kcal}} E_A$$

(2.33)

Changes in rate with temp

$$r_2 = r_1 \exp\left(\frac{E_A}{k_B}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

(2.36)

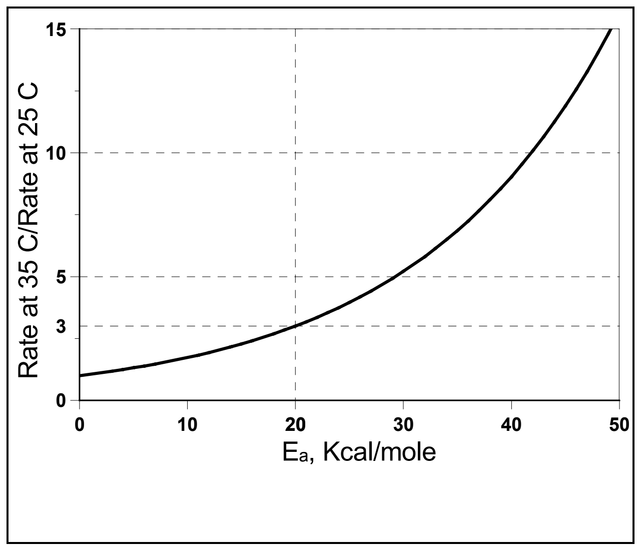

Figure 2.4 The fractional change in the rate of a nth order reaction when the temperature is changed from 25 to 35 °C.

Table 2.6 The variation in rate of a series of reactions with a 10^{o} K change in temperature. Data from Van't Hoff[1884].

Reaction	Temp. range C	Rate change with a 10 K temperature change
$CH_3COOCH_2CH_3 + H_2O \overset{H^+}{\Rightarrow} CH_3COOH + CH_3CH_2OH$	3.6-30.4	2.03
$CH_3CH_2Cl + NaOH \Rightarrow H_2C = CH_2 + NaCl + H_2O$	23.5-43.6	2.87
$CH_3CH_2CH_2Cl + NaOH \Rightarrow CH_3CH = CH_2 + NaCl$	24.5-43.6	2.68
$HPO_3 + H_2O \Rightarrow H_3PO_4$	0-61	3.0

Table 2.7 The variation in the respiration rate of plants with a 10° change in temperature. Data of Clausen[1890].

Wheat	2.47
Lilac	2.48
Lupine	2.46

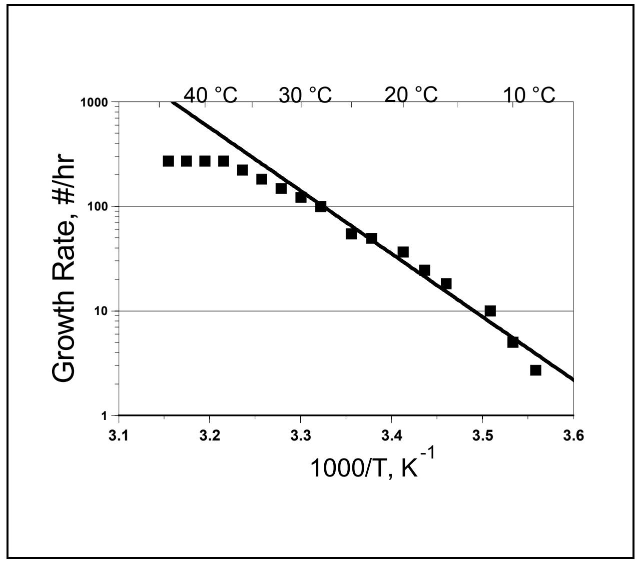

Figure 2.10 The rate of E. Coli growth as a function of temperature adapted from Bailey and Ollis [1977].

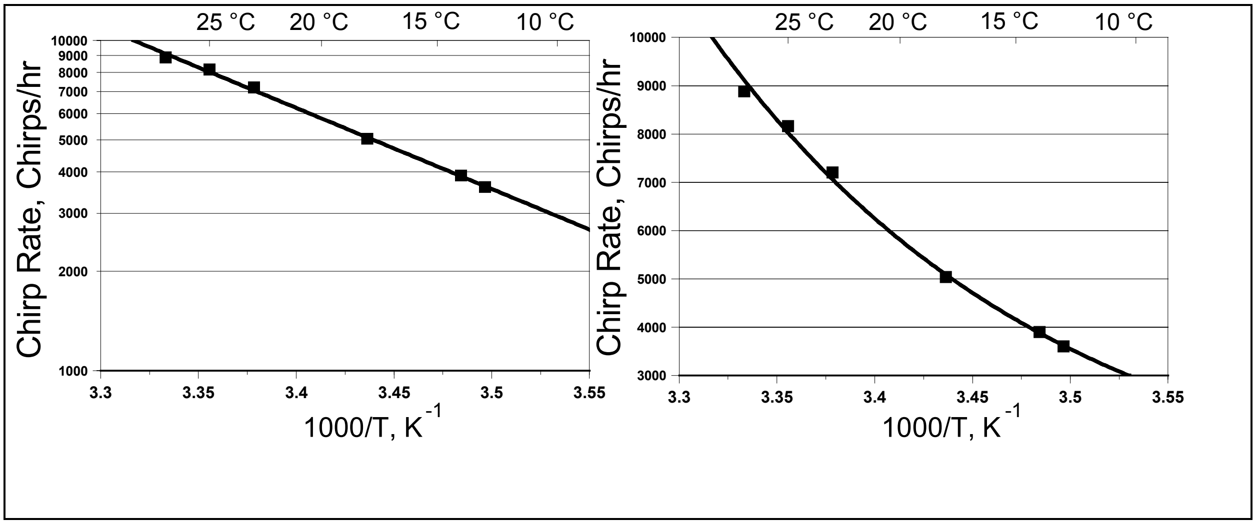

Figure 2.11 The rate that crickets chirp as a function of temperature. Data for field crickets (Gryllys pennsylvanicus)

Again: not all reactions work:

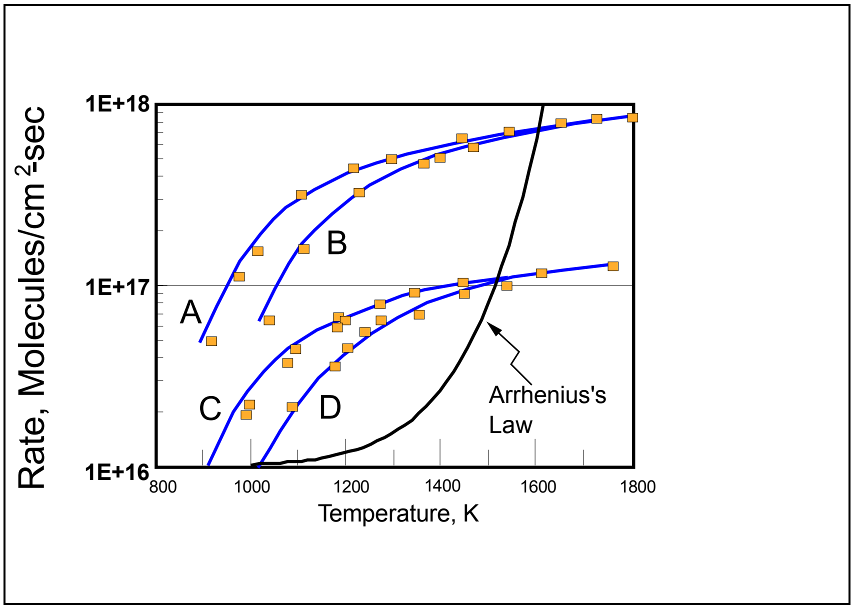

Figure 2.17 The variation in the rate of the reaction in Figure 2.16 with temperature. Data of Loffler and Schmidt[1976]. A) P_{NH_3} = 0.3, P_{H_2} =0.15, B) P_{NH_3} = 0.3, P_{H_2} =0.44, C) P_{NH_3} = 0.05, P_{H_2} =0.15, D) P_{NH_3} = 0.05, P_{H_2} =0.45

Discussion Problem

Your taste buds work by a chemical reaction where sugar molecules bind to nerve endings in your mouth.

a) What is the activation barrier for the process?

b) How much will the sweetness of bread change if you heat the bread enough that the temperature of your tongue rises by 5 C?