CHEE 321: Chemical Reaction Engineering

1. Introductory Material

1a. Reaction Rates, Rate Laws and Stoichiometry

(Fogler Chapter 1.1, 3.1-3.3)

Basic Elements of Reactor Design

- Reactor design usually involves the following:
  - Knowledge of nature of reaction
    - Products and reactants
    - Stoichiometry
    - Catalytic or Non-Catalytic, Homogeneous or Heterogeneous, Reversible or Irreversible

  - Selection of operating conditions
    - Temperature, Pressure, Concentrations
    - Type of catalyst (if applicable)
    - Flow rates

  - Selection of reactor type for a given application

  - Estimation of reactor volume required to process given amount (moles or molar rate) of raw material to desired amount of products
    - How fast the reaction occurs (reaction rates) dictates how large the reactor volume will be

Our approach to reactor design

- Reactors are complex beasts
    - Temperature is not uniform and/or constant
    - Multiple reactions almost always occur
    - Flow patterns are complex
    - Many reactors involve multiple phases
    - Reaction mechanisms and reaction kinetics are never perfectly known
    - Feedstock quality and product specs often change

- To gain an insight into basic concepts relevant to reactor design, we will first consider simplified and/or ideal reactor systems
    - Isothermal operation of ideal reactors
    - Single reaction, single phase

- We will start with some common terminology and notation that will be used throughout the course

# Material Balances: It all starts from here!

System with Rxn: use mole balances

Output Rate
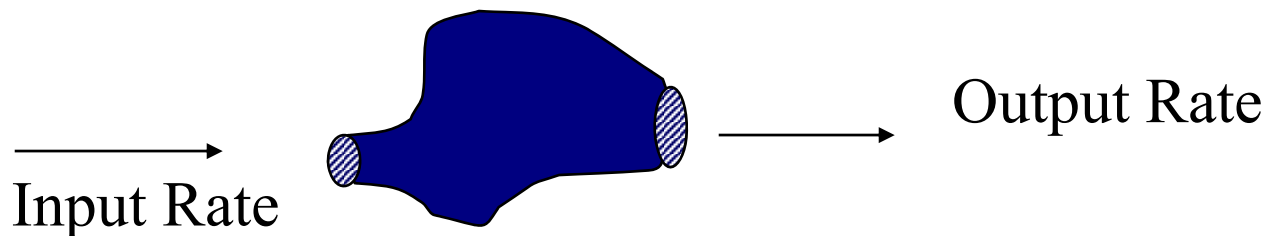
Input Rate

Rate of INPUT – Rate of OUTPUT + Rate of GENERATION – Rate of CONSUMPTION

= Rate of ACCUMULATION

Note: Rates refer to molar rates (moles per unit time).

Before we get into the details of the mole balance equation, we must introduce a definition for reaction rate as well as associated notation.

Notation: Reaction Rate for Homogeneous Reactions

$(-r_A)$ = rate of <u>consumption</u> of species A (A is a reactant)

= moles of A <u>consumed</u> per unit volume per unit time

$$\boxed{A + B \rightarrow C}$$
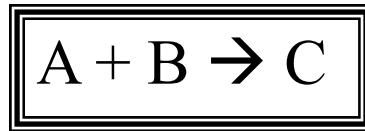
(r_A) = rate of <u>formation</u> of species A (A is a product)

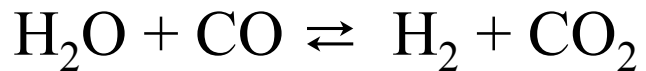$$D \rightarrow A$$

Units of (r_A) or $(-r_A)$

- moles per unit volume per unit time
- mol/L-s or kmol/m^3-s

Reaction definitions

<u>Irreversible Reactions:</u> Reactions that proceed uni-directionally under the conditions of interest

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

<u>Reversible Reactions:</u> Reactions that proceed in both forward and reverse directions under conditions of interest.

$$SO_2 + 0.5\ O_2 \rightleftarrows SO_3$$

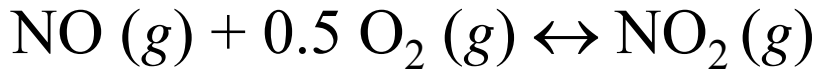$$H_2O + CO \rightleftarrows H_2 + CO_2$$

Thermodynamics tells us that all reactions are reversible. However, in many cases the reactor is operated such that the rate of the reverse reaction can be considered negligible.

Homogeneous & Heterogeneous Reactions

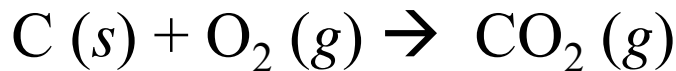**Homogeneous Reactions**: reactions that occur in a single-phase (gas or liquid)

<u>NOx formation</u>
$$NO\ (g) + 0.5\ O_2\ (g) \leftrightarrow NO_2\ (g)$$

<u>Polyethylene Production</u>
$$n\ C_2H_4\ \rightarrow \sim\sim(C_2H_4)_n\sim\sim$$

Heterogeneous Reactions: reactions that require the presence of two distinct phases (reaction usually occurs at the interface)

<u>Coal combustion</u>
$$C\ (s) + O_2\ (g) \rightarrow\ CO_2\ (g)$$

<u>SO_3(for sulphuric acid production)</u>
$$SO_2\ (g) + 1/2\ O_2\ (g) \leftrightarrow SO_3\ (g) \qquad \textit{Vanadium catalyst}$$

# Notation: Reaction Rate for Heterogeneous Reactions

For a heterogeneous reaction, rate of consumption of species A is denoted as $(-r_A')$

Heterogeneous reactions of interest are primarily catalytic in nature. Consequently, the rates are defined in term of mass of catalyst present

Units of $(-r_A')$

- mol per unit time per mass of catalyst
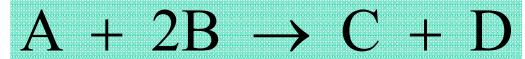- mol/(g cat)-s or kmol/(kg cat)-h

Stoichiometry

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

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D$$
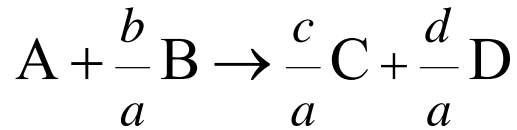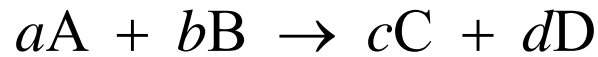
For every mole of A consumed:

b/a moles of B are consumed,
c/a moles of C are produced,
d/a moles of D are produced.

Relative reaction rates follow the same stoichiometric ratios

$$-\frac{r_A}{a} = -\frac{r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

$$r_B = \frac{b}{a}r_A \; ; r_C = -\frac{c}{a}r_A \; ; r_C = -\frac{d}{a}r_D$$

$$A + 2B \rightarrow C + D$$

If $-r_A$=4 mol-A/(L-s)

then

r_A=−4 mol-A/(L-s)
$-r_B$=8 mol-B/(L-s)
r_C=r_D=4 mol/(L-s)

Fogler 3.1

Reaction Rate and Rate Law

Rate Law: is an algebraic equation that relates reaction rate to species concentration

$$(-r_A) = k \cdot [f(C_A, C_B, ..)]$$

e.g. $(-r_A) = k \, C_A$ or $(-r_A) = k \, C_A^2$

where k is the reaction rate coefficient

Note: k is constant at a given temperature

The terms within the brackets $[f(C_A, C_B, ..)]$ denote dependency of reaction rate on the concentrations of the reactants (and for reversible reactions on the concentration of products as well)

RATE LAW IS INDEPENDENT OF REACTOR

Dependence on Concentration - Reaction Order

Consider the following reaction:

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

The rate law may be written as follows:

$$(-r_A) = k\, C_A{}^{\alpha}\, C_B{}^{\beta} \qquad \text{(Power Law Model)}$$

α = reaction order with respect to species "A"
β = reaction order with respect to species "B"

$$n = \alpha + \beta = overall\ order\ of\ reaction$$

The units of k depend on the overall reaction order.

Rate laws are determined by experimental observation, and do not have to match the reaction stoichiometry

Rate Laws: Elementary vs. Non-Elementary Reactions

In the previous example, i.e., $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$

The rate law (in terms of the rate of consumption of A) was written as:

$$(-r_A) = k\, C_A^{\alpha}\, C_B^{\beta}$$

If $\alpha = a$ and $\beta = b$, the reaction is considered to follow an *elementary rate law*.

Elementary Reaction
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ $\qquad (r_{\text{HI}}) = k\, C_{\text{H2}}\, C_{\text{I2}}$

Non-elementary
$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2 \quad (-r_{\text{CO}}) = k\, C_{\text{CO}}\, C_{\text{Cl2}}^{3/2}$

See Fogler Table 3-1 for examples

Units of rate coefficient depend on reaction order

$(r_A) = k \times$ [conc. terms]

units of k = units of (r_A)/units of [conc. terms]

Zero-order reaction
$(r_A) = k$ $\qquad\qquad\qquad\qquad\qquad$ k in mol/m^3·s or mol/L·s

First order reaction
$(r_A) = kC_A$ or $= kC_A^{3/2} C_B^{-1/2}$ $\qquad$ k in s^{-1}

Second-order reaction
$(r_A) = kC_A^2$ or $= kC_A C_B$ $\qquad\qquad$ k in m^3/mol ·s or L/mol·s

Factors influencing rate of reaction (r_j)

- <u>Factors affecting rate coefficient (k)</u>
  - temperature
  - catalyst type (if present in system)
  - pressure   Generally negligible

- <u>Factors affecting concentration</u>
  - pressure (especially for gas-phase system)
  - temperature

Temperature dependence of rate: the Arrhenius Law

$$k = A \exp(-E_a/RT)$$

A = frequency factor or pre-exponential factor
E_a = Activation Energy
R = Universal gas Constant
T = absolute temperature (K)

<u>Vignette on Svante Arrhenius</u>

Arrhenius studied reaction rates as a function of temperature, and in 1889 he introduced the concept of activation energy as the critical energy that chemicals need to react. He also pointed out the existence of a "greenhouse effect" in which small changes in the concentration of carbon dioxide in the atmosphere could considerably alter the average temperature of a planet.

For his PhD thesis in 1884 he presented his "ionic theory", but it turned out to be a bit too revolutionary for his examiners' taste. He barely passed with a fourth class rank, "not without merit".
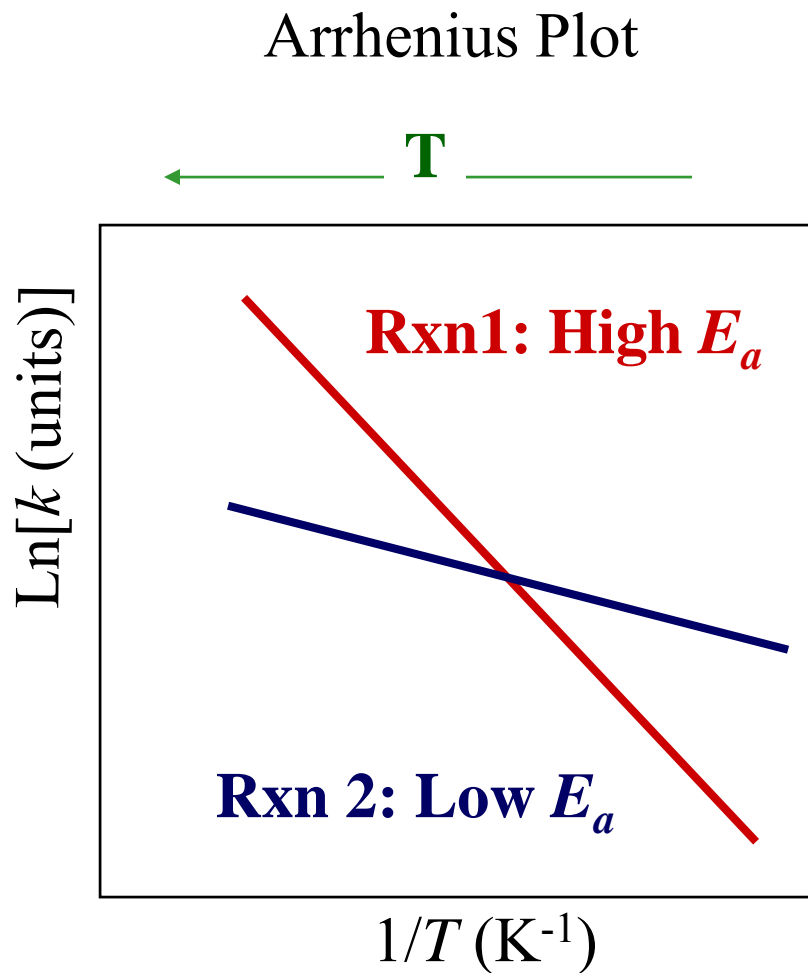
Implications of Arrhenius Law

$$k = A \exp(-E_a/RT)$$
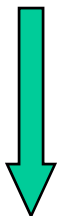
$$\ln(k) = \ln(A) - (E_a/R) \cdot 1/T$$

- Rate increases exponentially with increasing T

- k with high value for *activation energy* E_a is more sensitive to temperature than those with lower values

Arrhenius Plot

T

Rxn1: High E_a

Rxn 2: Low E_a

Ln[k (units)]

$1/T$ (K^{-1})

Fogler 3.3

Interpretation of Arrhenius parameters

$$k = A \exp(-E_a/RT)$$

- For simple reaction in which two molecules collide and react, the pre-exponential term in the Arrhenius equation can be thought of as the frequency of collision of the molecules (entropic factor)

- The activation energy can be thought of as the energy barrier that must be overcome as reactants go through the *transition* to products: transition state theory

Activation Energy
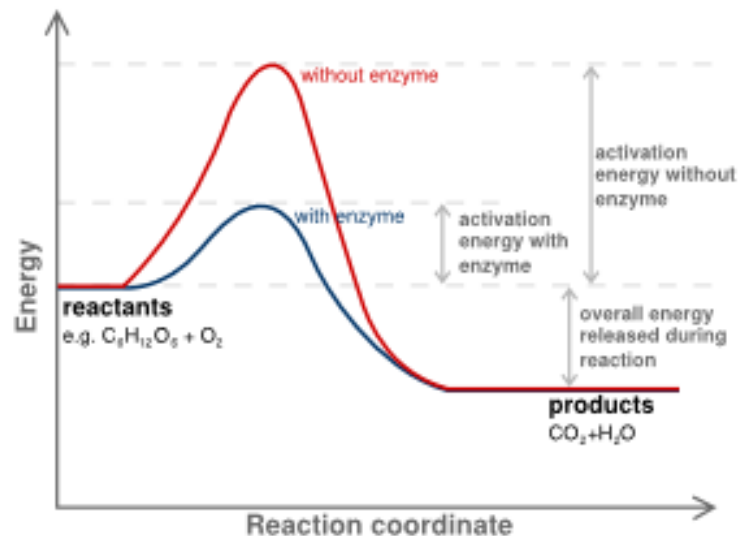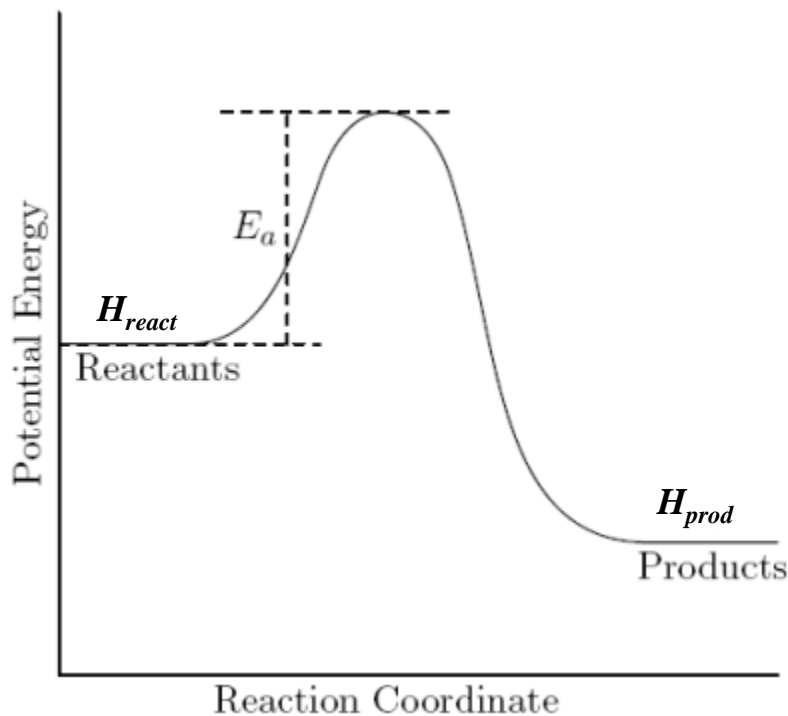
Enzyme = catalyst

Difference in energy content between products and reactants is the *heat of reaction*;

Difference in energy content between transition state and reactants is the *activation energy*

The role of catalyst is to lower the energy barrier to reaction, so that a higher fraction of molecules react when they collide.

Fogler 3.3

Why does increasing temperature result in increased reaction rate ?

Energy Distribution of Reactant Molecules
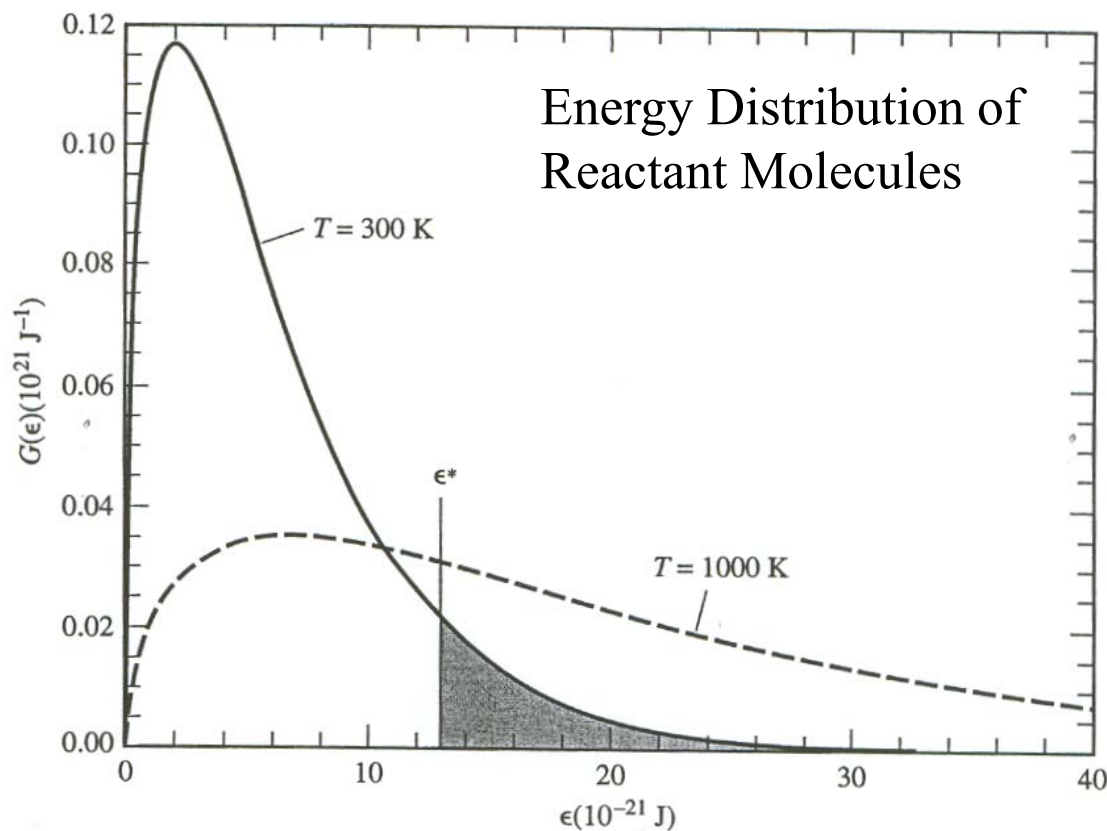
The case of ant walking:
Can we really represent it with Arrhenius Relation?

Harlow Shapley was a famous astronomer who discovered the Milky Way galaxy. As a sideline, on cloudy days, he measured the walking speed of ants outside the Mount Wilson Observatory. Shapley, *Proc. National Academy of Science*, **6**, (1920, 1924) 436 reported the following data:
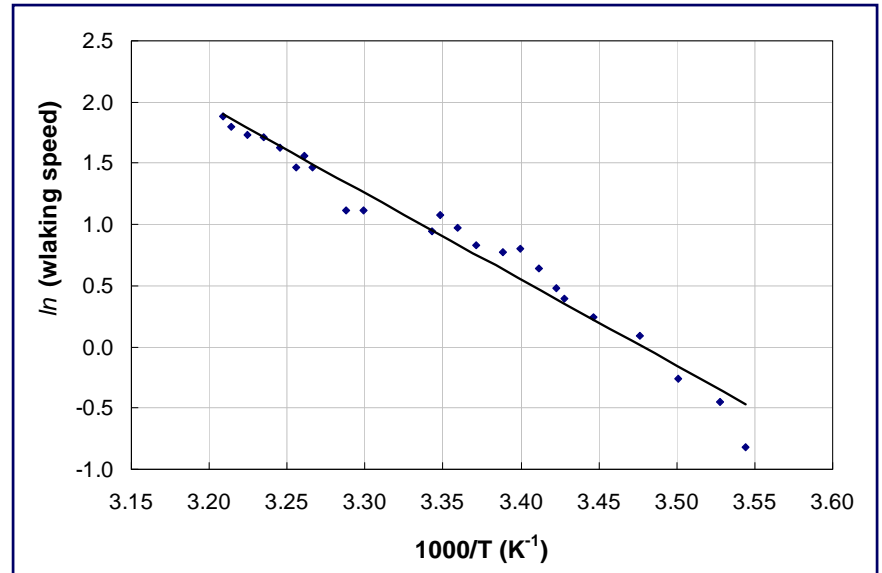
Temperature, °C	Running Speed, cm/second	Temperature, °C	Running Speed, cm/second	Temperature, °C	Running Speed, cm/second
9.0	0.44	21	2.23	33	4.32
10.3	0.64	22	2.16	33.5	4.77
12.5	0.77	23.5	2.29	34	4.35
14.5	1.10	24.5	2.65	35	5.08
17	1.28	25.5	2.94	36	5.57
18.6	1.48	26	2.56	37	5.67
19	1.62	30	3.05	38	6.06
20	1.90	31	3.06	38.5	6.60

•M. I. Masel, Chemical Kinetics and Catalysis

The Case of Ant walking
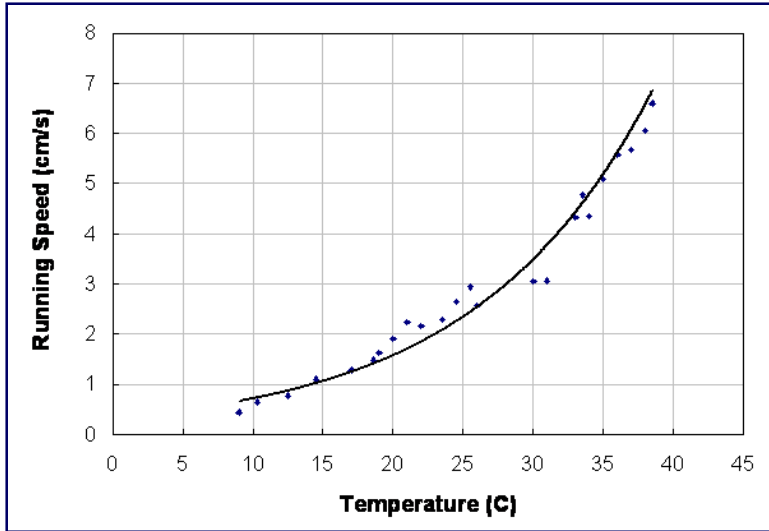
Raw data

Processed data

Kinetics of Many Processes in Nature follow Arrhenius Relationship

Some Examples

- Cricket chirping
- Ant walking
- Tumour growth
- Diffusion $[D = D_o \exp(-E_D/RT)]$

References:
M. I. Masel, Chemical Kinetics and Catalysis
Octave Levenspiel, Chemical Reaction Engineering

Rate of Cricket Chirping

Figure 2.11 The rate that crickets chirp as a function of temperature. Data for field crickets (*Gryllys pennsylvanicus*). From Heinrich (1993).