The Phenomenology of Chemical Reaction Rates

- Non-equilibrium distributions occur when compounds react.
- When reactive species are mixed at constant temperature and pressure, the reaction proceeds until the free energy is minimized
    - Thermodynamics tells us about the equilibrium.
    - Diffusion gradients gives us some idea of how long the reaction might take.
- "Kinetics" addresses the timescales on which reactions occur.

Basic Ideas - Reactants go, Products appear

- Consider the general reaction:

$$\alpha\mathrm{A} + \beta\mathrm{B} \rightleftharpoons \gamma\mathrm{C} + \delta\mathrm{D}$$

  where:
    - α, β, γ and δ are stoichiometric coefficients.
- Therefore, the disappearance of α moles of A is accompanied by:
    - the disappearance of β moles of B.
    - the appearance of γ moles of C.
    - the appearance of δ moles of D.
- Define extent of reaction, ξ:

$$\xi = \frac{n_A^\circ - n_A}{\alpha} = \frac{n_B^\circ - n_B}{\beta} = \frac{n_C^\circ - n_C}{-\gamma} = \frac{n_D^\circ - n_D}{-\delta}$$

    - We will see cases where $d\xi/dt$ is **not** equivalent to the rate of reaction.
- If the reaction is an *elementary* process then $d\xi/dt$ is equivalent to the rate of reaction.
    - In concentration units, the rate of reaction $\Re$ is:

$$\Re = \frac{1}{V}\frac{d\xi}{dt} = -\frac{1}{\alpha V}\frac{dn_A}{dt} = -\frac{1}{\beta V}\frac{dn_B}{dt}$$

$$= \frac{1}{\gamma V}\frac{dn_C}{dt} = \frac{1}{\delta V}\frac{dn_D}{dt}$$

  or

$$\Re = -\frac{1}{\alpha}\frac{d[A]}{dt} = -\frac{1}{\beta}\frac{d[B]}{dt} = \frac{1}{\gamma}\frac{d[C]}{dt} = \frac{1}{\delta}\frac{d[D]}{dt}$$

- This may break down if the reaction is not elementary, (i.e. if there is an intermediate involved).
    - Overall stoichiometric equation obeyed.
    - Entities not in reaction equation involved.
    - Net reaction occurs in a sequence of reactions.
    - As a results not all equalities are obeyed at all points in the reaction.

- **Example:** Radioactive Decay sequence.
  - Net reaction: $A \rightarrow C$
  - Actual reaction in two stages:

    $$A \rightarrow E$$

    $$E \rightarrow C$$

    where the first reaction is fast and the second is slow.
  - Therefore the rate of disappearance of A is not the rate of appearance of C at all times.
- When multiple steps are involved, the rate of disappearance of reactants is related to the rate of appearance of products, but the relationship is more complex.

- Rates of reactions are time dependent.
- Rates of reactions may be studied by any physical property of the system that can be related *unambiguously* to the concentration of the species of interest.
  - Optical absorbance
  - Electrical conductance
  - Electrochemical potential
  - Total pressure
  - Intensity of fluorescence
- The chosen property is followed as a function of time.
  - Continuously for fast reactions.
  - Periodically for slow reactions.
- If a reaction is slow, additional methods possible:
  - Sample the mixture periodically.
  - Sampling time is much less than the reaction time.
  - Quench the reaction by rapid cooling or dilution.

  - Analyze the sample when convenient.
  - Relate the concentrations to the sampling time.
  - Plot concentrations versus time, so that the slope is the rate.
- The rate itself is a function of time
  - Therefore rates are usually measured when the system is far from equilibrium (i.e. it initial rate).
- The phenomenlogical rate decreases as equilibrium is approached.
  - Because the rate depends on concentration and concentrations change as equilibrium is approached.
- The relationship between the phenomenological rate and the concentrations of species involved is the *rate law*:

  $$\Re = f([A],[B],[C],[D],[E],[F],\ldots)$$

  - k is a proportionality constant, known as the rate coefficient.

  - Usually determined for initial conditions with no products present.
- Rates may depend on species not present in the overall reaction such as catalysts.

More About Rate Laws

- A rate law **cannot** be predicted *a priori* from a reaction equation!!!
  - Additional information **must** be gathered from experiments.
  - The rate law and the reaction equation may have no obvious connection.
  - The mechanism of the reaction must be elucidated in terms of *elementary reactions*.

Some Common Rate Laws

- Many rate laws have the general form:

$$\Re = k \prod_i A_i^{\alpha_i}$$

  where:
  - α_i is the order of the reaction with respect to compound A_i and is usually integral or half-integral.
  - $\sum_i \alpha_i \leq 3$ and is the overall order of the reaction.
  - The order may be zero with respect to compounds that appear in the net reaction equation.
  - The order may be non-zero with respect to compounds that do not appear in the net reaction equation.
- Many rate laws are not of this form.

Molecularity

- Reserved for three cases of overall reaction order:
  - Unimolecular refers to a first order reaction.
  - Bimolecular refers to a second order reaction.
  - Termolecular refers to a third order reaction.

Units for Rate Coefficients

- The rate $\Re$ has units of concentration per unit time.
  - Therefore the units for the rate coefficient depends on the order of the rate law.
- For a first order reaction, k has units of time^{-1}
- For a second order reaction, k has units of concentration^{-1} time^{-1}
- For a third order reaction, k has units of concentration^{-2} time^{-1}
- For a nth order reaction, k has units of concentration^{-n+1} time^{-1}

Reaction Dynamics

- Reaction dynamics addresses issues such as:
  - Why don't all collisions of reactants lead to reaction.
  - How does internal energy affect reaction rate.
  - How does relative orientation affect the rate of reaction?

Mechanisms and Integrated Rate Equations

- It is desirable to connect experimental measurements with rate laws.
  - Experimental conditions selected to simplify analysis as much as possible.
- Often the dependence of the rate on species concentration is elucidated by designing an experiment such that the concentration of only one species is considered at a time.
  - This is achieved by having large concentrations of all reactants except the one of interest.
  - Thus the other reactants do not significantly change concentration while the reaction is proceeding.

First Order Reactions

- We wish to find an expression that allows us to determine the concentration of the species as a function of time.
- Consider at first order reaction of the general form:

$$A \rightarrow \text{products}$$

- The rate law in differential form is:

$$\Re = -\frac{d[A]}{dt} = k_1[A]$$

  where:
  - k_1 is the first order rate coefficient.
- Let $[A] = [A]_0$ at $t = 0$
- Then to find [A] at any time integrate:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k_1 \int_0^t dt = \ln \frac{[A]}{[A]_0} = -k_1 t$$

- This may be rewritten as:

$$[A] = [A]_0 e^{-k_1 t}$$

- Processes that follow this rate law are:
  - Spontaneous emission from an excited state.

$$N(t) = N^\circ e^{-t/\tau_{rad}}$$

    where τ is the radiative life time.

  - Relaxation of a nonequilibrium velocity distribution (time scale is τ_{coll})
  - Unimolecular reactions such as decomposition or isomerization.
  - Radioactive decay.
- For a first order process a plot of $\ln[A]$ (or the ln of a quantity proportional to concentration) vs time will be linear.

$$\ln[A] = \ln[A]_0 - k_1 t$$

  - The slope will be $-k_1$.
- The half-life for a reaction is:

$$\frac{[A]_0}{2} = [A]_0 e^{-k_1 t_{1/2}}$$

or

$$t_{1/2} = \frac{-\ln(1/2)}{k_1} = \frac{0.6931}{k_1}$$

  - After one half-life, half of $[A]_0$ is left.
  - After two half-lives, one quarter of $[A]_0$ is left.

Second-Order Reactions

- Must consider two cases:
  - Case 1: Second order in one reactant:

$$A + A \rightarrow \text{Products}$$

$$\Re = \frac{-1}{2}\frac{d[A]}{dt} = k_2[A]^2$$

  - Case 2: First order in each of two reactants:

$$A + B \rightarrow \text{Products}$$

$$\Re = -\frac{d[A]}{dt} = k_2'[A][B]$$

- Consider the first case where $[A] = [A]_0$ at $t = 0$:

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -2k_2 \int_0^t dt$$

$$\frac{-1}{[A]} - \frac{-1}{[A]_0} = -2k_2 t$$

or

$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2k_2 t$$

  - The time required to drop to half the initial concentration is:

$$t_{1/2} = \frac{1}{2[A]_0 k_2}$$

    which depends on initial concentration.

- Consider case 2:

$$A + B \rightarrow \text{Products}$$

$$\Re = -\frac{d[A]}{dt} = k_2'[A][B]$$

  - Must first use a variable transformation:

$$x = [A]_0 - [A] = [B]_0 - [B]$$

  - Thus the rate law becomes:

$$\frac{dx}{dt} = k_2'([A]_0 - x)([B]_0 - x)$$

  - Separation of variables yields:

$$k_2' \int_0^t dt = \int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)}$$

  - The integration in x requires partial fractions.

  - There exists some a and b such that:

$$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{a}{([A]_0 - x)} + \frac{b}{([B]_0 - x)}$$

- To find a and b bring the right had side of the equation to a common denominator.

$$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{a([B]_0 - x) + b([A]_0 - x)}{([A]_0 - x)([B]_0 - x)}$$

Therefore:

$$a[B]_0 + b[A]_0 = 1$$

$$-ax - bx = 0$$

and

$$a = -b$$

$$a = \frac{1}{[B]_0 - [A]_0}$$

$$b = \frac{1}{[A]_0 - [B]_0}$$

  - Note that this introduces the restriction that $[A]_0 \neq [B]_0$.

- Thus:

$$\begin{aligned} &\frac{1}{([A]_0 - x)([B]_0 - x)} \\ &= \left(\frac{1}{[B]_0 - [A]_0}\right)\left(\frac{1}{([A]_0 - x)}\right) \\ &+ \left(\frac{1}{[A]_0 - [B]_0}\right)\left(\frac{1}{([B]_0 - x)}\right) \\ &= \left(\frac{1}{[A]_0 - [B]_0}\right)\left[\frac{1}{([B]_0 - x)} - \frac{1}{([A]_0 - x)}\right] \end{aligned}$$

and

$$k_2't = \frac{1}{[A]_0 - [B]_0}\left(\ln\frac{[B]_0}{[B]_0 - x} - \ln\frac{[A]_0}{[A]_0 - x}\right)$$

or

$$k_2't = \frac{1}{[A]_0 - [B]_0}\ln\frac{[A]/[A]_0}{[B]/[B]_0}$$

- Consider the case where $[A]_0 >> [B]_0$.
  - Then $[A]/[A]_0 \approx 1$.
  - and

    $$k_2't = \frac{1}{[A]_0}\ln\frac{1}{[B]/[B]_0}$$

  - This can be rearranged to:

    $$[A]_0 k_2't = \ln\frac{[B]_0}{[B]}$$

    which is of the form of a first order reaction.

    $$[B] = [B]_0 e^{-k_1't}$$

    where

    $$k_1' = [A]_0 k_2'$$

  - This is an example of a pseudo first-order reaction.
- Not all chemical reactions have rate laws amenable to analytic solution.
  - Numerical methods need to be used.
- Many reactions occur as a sequence of elementary reactions.
  - Such reactions may have compliciated rate expressions.
  - The sequence of elementary reactions is a mechanism.

Sequential Reactions

- The net reaction proceeds as a series of steps that produce and use intermediates.
  - Intermediates are present only in small amounts at the end of the reaction.
  - The concentrations of intermediates vary with time during the reaction.
- Consider the reaction sequence:

  $$A \rightarrow B \rightarrow C$$

  with rate coefficients k_1 and k_1' respectively for each step.
  - The intermediate B is distinct from A and C, but usually less stable than either.
  - The resulting rate equations may be solved exactly.
  - A representative case is shown in Figure 26.2.

Exact Solution

- First, let us write the system of differential equations.

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B]$$

$$\frac{d[C]}{dt} = k_1'[B]$$

- It will be assumed that $[B]_0 = [C]_0 = 0$
  - Therefore at all times:

$$[A] + [B] + [C] = [A]_0$$

- Solve the first differential equation:

$$\frac{d[A]}{[A]} = -k_1 t$$

$$[A] = [A]_0 e^{-k_1 t}$$

- Define y_1 such that:

$$[A] = [A]_0 - y_1$$

- Define y_2 such that:

$$[C] = y_2$$

- Therefore:

$$[B] = y_1 - y_2$$

- The solution to the first differential equation becomes:

$$y_1 = [A]_0(1 - e^{-k_1 t})$$

- Now consider the third differential equation:

$$\frac{d[C]}{dt} = k_1'[B]$$

  which becomes

$$\frac{dy_2}{dt} = k_1'(y_1 - y_2)$$

- Substitute for y_1:

$$\frac{dy_2}{dt} = k_1'([A]_0(1 - e^{-k_1 t}) - y_2)$$

  and rearrange to:

$$\frac{dy_2}{dt} + k_1' y_2 = k_1'([A]_0(1 - e^{-k_1 t})$$

- **Assume** that y_2 has the form:

$$y_2 = u(t)e^{-k_1' t}$$

  - Therefore:

$$\frac{dy_2}{dt} = \frac{du}{dt}e^{-k_1' t} - k_1' u e^{-k_1' t}$$

- Thus:

$$\frac{dy_2}{dt} + k_1' y_2 = k_1'([A]_0(1 - e^{-k_1 t})$$

  becomes:

$$\frac{du}{dt} e^{-k_1' t} - k_1' u e^{-k_1' t} + k_1' u e^{-k_1' t} = k_1'([A]_0(1 - e^{-k_1 t})$$

or

$$\frac{du}{dt} e^{-k_1' t} = k_1'([A]_0(1 - e^{-k_1 t})$$

- This may rearranged to:

$$\frac{du}{dt} = k_1'([A]_0(1 - e^{-k_1 t}) e^{k_1' t}$$

  or:

$$\frac{du}{dt} = k_1'[A]_0 e^{k_1' t} - k_1'[A]_0 e^{(k_1' - k_1)t}$$

  which upon integration yields:

$$u = [A]_0 e^{k_1' t} - \frac{k_1'[A]_0}{k_1' - k_1} e^{(k_1' - k_1)t} + C$$

- Substituting with:

$$y_2 = u(t) e^{-k_1' t}$$

  yields:

$$y_2 = [A]_0 - \frac{k_1'[A]_0}{k_1' - k_1} e^{-k_1 t} + C e^{-k_1' t}$$

- The value of the integration constant C is found from the initial conditions.
  - At $t = 0$, $y_2 = 0$. Therefore:

$$0 = [A]_0 - \frac{k_1'[A]_0}{k_1' - k_1} + C$$

$$C = \frac{k_1[A]_0}{k_1' - k_1}$$

- Thus:

$$y_2 = [A]_0 \left[1 - \frac{k_1 k_1'}{k_1' - k_1} \left(\frac{e^{-k_1 t}}{k_1} - \frac{e^{-k_1' t}}{k_1'} \right) \right]$$

- From this expressions for $[A]$, $[B]$, and $[C]$ may be derived.

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1[A]_0}{k_1' - k_1} \left(e^{-k_1 t} - e^{-k_1' t} \right)$$

$$[C] = [A]_0 \left(1 + \frac{k_1' e^{-k_1 t} - k_1 e^{-k_1' t}}{k_1 - k_1'} \right)$$

- Often k_1 and k_1' differ by one or more orders of magnitude and the steady-state approximation may be invoked.
  - The slower reaction is regarded as the rate determining step.

- Consider the case where $k_1 << k_1'$
  - Then as soon as A is converted to B, B quickly converts to C
- The concentrations as a function of time become:

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{k_1'} e^{-k_1 t}$$

$$[C] = [A]_0 \left(1 - e^{-k_1 t}\right)$$

The Steady-State Approximation

- This approximation assumes:
  - That the intermediate is consumed as soon as it is formed (i.e. [B] is small relative to [A]+[C])
  - That [B] is relatively constant with respect to time.
- This approximation is valid when $k_1 << k_1'$.

$$\frac{d[B]}{dt} = k_1[A] - k_1'[B] = 0$$

$$[B] = \frac{k_1}{k_1'}[A]$$

  - Since:

$$[A] = [A]_0 e^{-k_1 t}$$

  then

$$[B] = \frac{k_1}{k_1'} e^{-k_1 t}$$

  - Since [B] is so small relative to [A]+[C]:

$$[C] = [A]_0 \left(1 - e^{-k_1 t}\right)$$

  Which is the same result as obtained from the exact solution in the limit of $k_1 << k_1'$

Branching Reactions

- Branching reactions occur when one reactant can go to more than one product.

$$A^{***} \begin{cases} \longrightarrow A^{**} + h\nu; & k_1 \\ \longrightarrow A^{*} + h\nu; & k_1' \\ \longrightarrow A + h\nu; & k_1'' \end{cases}$$

The rate expression becomes:

$$\frac{d[A^{***}]}{dt} = -k_1[A^{***}] - k_1'[A^{***}] - k_1''[A^{***}]$$

$$= -\left(k_1 + k_1' + k_1''\right)[A^{***}] = -k_{net}[A^{***}]$$

and

$$[A^{***}] = [A^{***}]_0 \; e^{-k_{net}t}$$

  - Thus the radiative "lifetime" is:

$$\tau_{rad} = \frac{1}{k_{net}}$$

- The rate of production of $[A^{**}]$ is:

$$\frac{d[A^{**}]}{dt} = k_1[A^{***}] = k_1[A^{***}]_0 \; e^{-k_{net}t}$$

with the assumptions:

  - That A^{**} is absent at $t = 0$
  - That A^{**} does not subsequently decay to one of the other products. This is often **not** the case for real spontaneous emission.

- Upon integration this becomes:

$$[A^{**}] = \frac{k_1[A^{***}]_0}{k_{net}} \left(1 - e^{-k_{net}t}\right)$$

- Similarly:

$$[A^{*}] = \frac{k_1'[A^{***}]_0}{k_{net}} \left(1 - e^{-k_{net}t}\right)$$

$$[A] = \frac{k_1''[A^{***}]_0}{k_{net}} \left(1 - e^{-k_{net}t}\right)$$

- Thus the rate of appearance is controlled by k_{net} while the proportions of the products are governed by the relative values of the rate coefficients.

Chain Reactions

- Consider $H_2 + X_2$ where X is a halogen.
  - If the HX bonds are formed as the H_2 and X_2 bonds break, then there is a *four-center* intermediate H_2X_2 intermediate.
- Until the late 1960's, experimental evidence indicated that the

$$H_2 + I_2 \rightarrow HI + HI$$

proceeded by a four-center intermediate.

  - The phenomenological rate law was:

$$\frac{d[HI]}{dt} = k[H_2][I_2]$$

  - The work of J. H. Sullivan on the temperature dependence of the reaction rate, showed that the reaction proceeded by the dissociation of I_2 then reaction of I with H_2.

- Consider the dissociation of the reactant molecules:

$$H_2 \longrightarrow H + H \qquad \Delta\text{H} = 4.48 \text{ eV}$$

$$I_2 \longrightarrow I + I \qquad \Delta\text{H} = 1.54 \text{ eV}$$

- Energetic considerations indicate that I_2 will dissociated with a lower input of energy than will H_2
- Experimental evidence is consistent with the following mechanism:

$$I_2 \longrightarrow I + I$$

$$H_2 + 2I \longrightarrow 2HI$$

- Evidence is mounting in favour of the following:

$$I_2 \longrightarrow I + I$$

$$H_2 + I \longrightarrow H_2I$$

$$H_2I + I \longrightarrow 2HI$$

The $H_2 + Br_2$ chain reaction

- The observed rate law is:

$$\Re = \frac{1}{2}\frac{d[HBr]}{dt} = \frac{k_{exp}[H_2][Br_2]^{1/2}}{1 + \alpha[HBr]/[Br_2]}$$

  - The form of the rate law is evidence that the reaction is not elementary.
  - The presence of the product $[HBr]$ inhibits the reaction.

- A mechanism consistent with this rate law is:
  - Initiation

$$Br_2 \longrightarrow 2Br \qquad k_a$$

  - Propagation

$$Br + H_2 \longrightarrow HBr + H \qquad k_b$$

$$H + Br_2 \longrightarrow HBr + Br \qquad k_c$$

  - Inhibition

$$H + HBr \longrightarrow Br + H_2 \qquad k_d$$

  - Termination

$$2Br \longrightarrow Br_2 \qquad k_e$$

- The derivation of the rate law starts with applying the steady-state approximation to the intermediate species $[H]$ and $[Br]$:

$$\frac{d[H]}{dt} = k_b[Br][H_2] - k_c[H][Br_2] - k_d[H][HBr] = 0$$

$$\frac{d[Br]}{dt} = 2k_a[Br_2] - k_b[Br][H_2] + k_c[H][Br_2]$$

$$+k_d[H][HBr] - 2k_e[Br]^2 = 0$$

  - Adding these two equations gives:

$$0 = 2k_a[Br_2] - 2k_e[Br]^2$$

or

$$[Br] = \left(\frac{k_a}{k_e}[Br_2]\right)^{1/2}$$

  - Isolating $[H]$ from the first equation:

$$[H] = \frac{k_b[Br][H_2]}{k_c[Br_2] + k_d[HBr]}$$

  - Substituting for $[Br]$ yields:

$$[H] = \frac{k_b\left(\frac{k_a}{k_e}[Br_2]\right)^{1/2}[H_2]}{k_c[Br_2] + k_d[HBr]}$$

- The rate expression for $[HBr]$ is:

$$\frac{d[HBr]}{dt} = k_b[Br][H_2] + k_c[H][Br_2] - k_d[H][HBr]$$

  - But from the expression for $d[H]/dt$:

$$k_b[Br][H_2] = k_c[H][Br_2] + k_d[H][HBr]$$

and

$$\frac{d[HBr]}{dt} = 2k_c[H][Br_2] = 2\Re$$

- Thus

$$\Re = \frac{1}{2}\frac{d[HBr]}{dt} = k_c[H][Br_2]$$

$$= k_c\left(\frac{k_b\left(\frac{k_a}{k_e}[Br_2]\right)^{1/2}[H_2]}{k_c[Br_2] + k_d[HBr]}\right)[Br_2]$$

$$= \frac{k_b(k_a/k_2)^{1/2}[H_2][Br_2]^{1/2}}{1 + (k_d/k_c)([HBr]/[Br_2])}$$

and

$$k_{exp} = k_b(k_a/k_e)^{1/2}$$

and

$$\alpha = k_d/k_c$$

Branching Chain Reactions-Explosions

- Explosions happen quickly:
  - In 1937 the Hindenberg disaster 2×10^5 m^3 of H_2 in burned in 45 s with 36 dead.
  - In the Challenger disaster an O-ring failed, rupturing H_2 and O_2 tanks. Seven died.
- In both cases the reaction was:

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

- Exothermic: $\Delta_r\overline{H}^\circ = -242$ kJ mol^{-1} at 298 K.
- H_2 and O_2 can be mixed at room temperature in any proportion with no reaction occurring.
- The reaction must be initiated by a spark, a flame, or a catalyst.
- The reaction proceeds by a free radical mechanism with branching.

- **Initiation:**

$$H_2 \longrightarrow H + H$$

$$O_2 \longrightarrow O + O$$

- **Branching:**

$$H + O_2 \longrightarrow OH + O$$

$$O + H_2 \longrightarrow OH + H$$

- **Propagation:**

$$OH + H_2 \longrightarrow H_2O + H$$

  - Note that the net of the propagation and branching reactions is:

$$3H_2 + O_2 \longrightarrow 2H_2O + 2H$$

- **Termination:**

$$H + H \longrightarrow H_2(\text{at walls of container})$$

$$H + O_2 + M \longrightarrow HO_2 + M$$

  - M may be any gas phase species able to act as a third body to stabilize the HO_2 product.
  - HO_2 is more stable and less reactive than H or O.
- The rate of the overall reaction depends on:
  - The total pressure of the system.
  - The temperature of the system.

Effects of Thermodynamic Variables on Reaction Rates

- The rate of a reaction may depend upon macroscopic conditions and constraints such as:
  - temperature
  - pressure
  - volume
  - isothermicity
  - adiabaticity
- These may affect:
  - Concentration
  - Rate Coefficient
- Concentration effects appear differently depending on the phases and stoichiometry involved.

  - If a gas phase reaction has a different number of moles as reactants and products, then the dependence on volume will be different from the dependence on pressure.
  - In the condensed phase, reactions are less sensitive to pressure and volume due to negligible compressibilities.

Temperature Dependence of Reaction Rates

- Temperature dependence can be large and is always due (at least in part) to the temperature dependence of the reaction rate coefficient.
- Some examples of temperature effects on reaction rate include:
  - Cooking or refrigerating food.
  - Insect activity such as chirping rates, flash rate of fireflies, crawling rate of ants.
  - Our metabolism.
- Temperature dependence is common to both complex and elementary reactions.
  - Observed long before it was understood.
- In 1889, Svante Arrhenius proposed an expression that has been shown to be correct, but not precisely for the reasons he proposed.
  - He built on the earlier work by van't Hoff on the temperature dependence of equilibrium:

$$\left(\frac{\partial \ln K_{eq}}{\partial (1/T)}\right)_P = -\frac{\Delta_r \overline{H}^\circ}{R}$$

  - He introduced the energy parameter called the activation energy, E_a:

$$E_a = -R\left(\frac{\partial \ln k}{\partial (1/T)}\right)_P$$

- Arrhenius interpreted this in terms of an equilibrium established between reactive and nonreactive molecules (without making a clear distinction between them) and explained the temperature effect as a shift in the equilibrium.
  - The current interpretation will be taken up in Chapter 27.

Applying the Arrhenius Expression

- Measure rates, establish rate laws, and determine rate coefficients at a range of temperatures.
  - Plot k against $(1/T)$ and interpret slope as E_a/R.
- Two experimental difficulties can make this difficult.
  - Difficulties in obtaining precise rate coefficients and errors propagated through computational manipulations to extract them from the experimental data.
  - Limited temperature span over which most reactions may be studied.
  - The result is noisy data over a brief span of $(1/T)$.
  - Therefore distinguishing between linear and non-linear plots was difficult.
- Implicit in this treatment is the assumption that E_a is independent of temperature.

  - When E_a is assumed independent of temperature, then

    $$E_a = -R\left(\frac{\partial \ln k}{\partial(1/T)}\right)_P$$

    can be rearranged and integrated:

    $$\int^k d\ln k = -\frac{E_a}{R}\int^{1/T} d\left(\frac{1}{T}\right)$$

    or

    $$\ln k = -\frac{E_a}{RT} + (\text{constant})$$

  - Exponentiating both sides give:

    $$k = Ae^{-E_a/RT}$$

    where A is the pre-exponential factor.

- A modified form of the Arrhenius expression may be used for a nonlinear Arrhenius plot.

  $$k = A'T^m e^{-E/RT}$$

  where m and E are constants.

  - Thus the slope of the Arrhenius plot will be:

    $$\left(\frac{\partial \ln k}{\partial(1/T)}\right)_P = -mT - \frac{E}{R}$$

  - This may be interpreted as the activation energy having a linear dependence on T.

- Most chemical reactions have a positive activation energy.
- Some chemical reactions have a negative activation energy.
  - This is usually a strong indicator that the reaction is not an elementary reaction and the mechanism must account for the apparent negative activation energy.

- Some reactions appear to have no activation energy.
  - Often these are free radical reactions.
- Other reactions cannot be described by either form of the Arrhenius expression.

A Closer Look at an Arrhenius Plots
Linearizing a non-linear equation

- In a laboratory experiment, measure k at various T.
  - Experimental uncertainties occur in both k and T
  - T is usually measured more precisely than k
- Since you wish to test your hypothesis that:

  $$k = Ae^{-E_a/RT}$$

  this is linearized to:

  $$\ln k = -\frac{E_a}{RT} + \ln A$$

  - Plot $\ln k$ against $1/T$
  - Fit a least-squares line with $x = 1/T$ and $y = \ln k$

- How do the errors in the experimental data affect the fit?

Assumptions in a Least-Squares Linear Fit

- The quantity that is minimized is:

$$SS = \sum_i \left(y_i - (a + bx_i)\right)^2$$

  - The least squares equations are derived by minimizing SS with respect to a and b.

- It is assumed that:
  - The errors in x are negligible.
  - The errors in y are from the same distribution and therefore all points have equal weight in the fit.
- Generally, the error in some function F of some measured quantity x that is subject to random experimental errors is:

$$[\epsilon(F)]^2 = \left(\frac{\partial F}{\partial x}\right)^2 [\epsilon(x)]^2$$

- How does the manipulation of the k and T data affect this.

- Consider first errors in T:

$$F(T) = \frac{1}{T}$$

$$\frac{dF}{dT} = -\frac{1}{T^2}$$

  - Therefore,:

$$[\Delta^2(1/T)] = \left(-\frac{1}{T^2}\right)^2 [\Delta(T)]^2 = \frac{[\Delta(T)]^2}{T^4}$$

  and uncertainty in $F(T)$ becomes:

$$[\Delta(1/T)] = \frac{[\Delta(T)]}{T^2}$$

- Now consider errors in k:

$$F(k) = \ln k$$

$$\frac{dF}{dk} = \frac{1}{k}$$

  - Therefore:

$$[\Delta(\ln k)]^2 = \frac{[\Delta(k)]^2}{k^2}$$

  and uncertainty in $F(k)$ becomes:

$$[\Delta(\ln k)] = \frac{[\Delta(k)]}{k}$$

- Therefore a conventional least-squares fit to the linearized data will be systematically biased.

  - This bias may be corrected by weighting each point by $(\ln k)^2$.

Thermal Runaway

- Temperature control of a reaction is very important.
  - Rate coefficients can be strongly temperature dependent.
  - Heat transfer has a time scale that must be considered in experimental design.
- If the rate of heat transfer is comparable to heat production then isothermal conditions may be approached.
- If the rate of heat transfer is much less than the rate of heat production, then adiabatic conditions may be approached.
  - Heat is produced by an exothermal reaction.
  - T increases
  - The rate of reaction increases

  - The rate of heat production increases.
  - Thermal explosion may result.

The Bhopal Disaster

- Accidental water contamination led to thermal runaway and caused the Bhopal disaster, which killed over 2000 and permanently injured the respiratory systems of over 200,000.
- A Union Carbide plant manufactured pesticides from methyl isocyanate ($CH_3N{=}C{=}O$)
- Methyl isocyanate reacts with water to produce a cyclic trimer (trimethyl isocyanurate) or a gummy, resinous polymer.
  - These reactions are vigorously exothermic.
- The boiling point of methyl isocyanate is 39°C.
  - The vapour is about twice as heavy as air.
  - A concentration of 2 ppm has been reported toxic in humans.
  - Methyl isocyanate attacks the respiratory system, eyes and skin.
  - It can injure the lungs and bronchial airways, cause permanent eye damage, and death.

Thermal Runaway and Isomerization

- Isomerizations are usually unimolecular.
- Entropy changes are typically small with the result that the Gibb's Free Energy is comparable to the enthalphy of reaction.
  - The greater the exothermicity the greater the likelihood that there may be a spontaneous reaction.
- The rate of a spontaneous reaction is affected by the Arrhenius activation energy.
- Consider
$$\mathrm{CH_3NC} \longrightarrow \mathrm{CH_3CN} \qquad \Delta_r\overline{H}^\circ = -100 \text{ kJ mol}^{-1}$$
- The Arrhenius parameters are:
$$A = 3.98 \times 10^{13} \text{ s}^{-1}$$

$$E_a = 161 \text{ kJ mol}^{-1}$$

- If the reaction is carried out adiabatically at constant volume, then it starts slowly, but heats up.
- When the system achieves thermal runaway, the temperature rises rapidly and equilbrium is reached very quickly after that. (See Fig. 26.6)

The Attainment of Chemical Equilibrium

- Equilbrium is dynamic, not static.
  - At equilibrium, the forward rate is equal to the reverse rate.
  - There exists a relationship between the reaction equilibrium coefficient and the forward and reverse rate coefficients.
- Consider the first-order isomerization of methyl isocyanide:

$$\text{CH}_3\text{NC} \longrightarrow \text{CH}_3\text{CN}$$

  and its reverse reaction:

$$\text{CH}_3\text{CN} \longrightarrow \text{CH}_3\text{NC}$$

  - Both the forward and reverse reaction are first order.
  - The corresponding reaction coefficients are k_f and k_r.
  - Thus:

$$\frac{d[CH_3NC]}{dt} = -k_f[CH_3NC] + k_r[CH_3CN]$$

  - At equilibrium:

$$\frac{d[CH_3NC]}{dt} = 0$$

$$-k_f[CH_3NC]_{eq} + k_r[CH_3CN]_{eq} = 0$$

$$\frac{k_f}{k_r} = \frac{[CH_3CN]_{eq}}{[CH_3NC]_{eq}} = K_{eq}$$

- This is a statement of the principle of detailed balance.
- One of the implications of the principle of detailed balance is that, for an elementary process, only two of the three quantities k_f, k_r, and K_{eq} need to be determined with the third found from the other two.
- For a multi-step mechanism, detailed balance holds for each individual step in the mechanism.
- Consider the following:

$$C \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

  which describes the overall equilibrium

$$C \rightleftharpoons B$$

  - If the reaction was started with pure C, then the study of initial rates could establish k_{-2}.
  - If the reaction was started with pure B, then the study of initial rates could establish k_{-1}.
  - However, $K_{eq} \neq k_{-2}/k_{-1}$
  - Instead, from detailed balance:

$$\frac{[A]_{eq}}{[C]_{eq}} = \frac{k_{-2}}{k_2}$$

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{k_1}{k_{-1}}$$

and

$$K_{eq} = \frac{[B]_{eq}}{[C]_{eq}} = \frac{k_1 k_{-2}}{k_{-1} k_2}$$

- Consider a study of the reaction starting with pure A.
  - The relative rates of production of B and C will indicate the relative rate coefficients.
- Consider the case where:

$$k_1 = 10k_2 = 100k_{-1} = 2000k_{-2}$$

  - Thus:

$$K_{eq} = 0.5$$

  - The relative rate coefficients indicate that B is produced 10 times as fast as C.
  - The equilibrium coefficient indicates that the equilibrium concentration of C is twice that of B.
  - Early in the reaction the ratio of $[B]$ to $[C]$ is controlled by the kinetics and is approximately k_1/k_2.
  - The time scale for true equilibrium is much longer.

Chemical Relaxation

- Chemical relaxation techniques are based on rapid perturbation of equilibrium systems which are then allowed to reach or relax to a new equilibrium.
  - Detailed balance is used in the interpretation of the data.
- The perturbation must be fast compared to the relaxation time.

- Such perturbations may be:
  - Pressure jump
  - Temperature jump
  - pH jump
  - Flash photolysis
- The effect of the perturbation is to change the position of the equilibrium.
  - Recall ξ, the extent of reaction.
  - The conditions before perturbation, led to an extent of reaction ξ.
  - The conditions after perturbation require an extent of reaction ξ_{eq}.
- If the perturbation is sufficiently small, i.e.

$$\left(\frac{\partial G}{\partial \xi}\right) \ll RT$$

then

$$\frac{\partial \xi}{\partial t} \propto \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{eq} (\xi - \xi_{eq})$$

where ξ_{eq} is the point where $(\partial G/\partial \xi) = 0$

- This means that the relaxation process is exponential in time.
- The characteristic time is τ, the relaxation time.

Autoionization of Water

- Consider an acid-base titration with an indicator.
  - Transient colour change observed which disappears quickly.
  - Acid-base neutralization is rapid.
- The reaction:

$$\mathrm{H^+(aq) + OH^-(aq) \longrightarrow H_2O}$$

is second order with rate coefficient

$$k_f \;=\; 1.12 \;\times\; 10^{11}\ \mathrm{M^{-1}\ s^{-1}}.$$

- The equilibrium coefficient is:

$$K_{eq} = \frac{a_{H_2O}}{a_{H^+}a_{OH^-}} = 1.01 \times 10^{14}$$

- Detailed balance requires that at equilibrium the forward and reverse rates are balanced.

$$\Re = 0 = k_f[\mathrm{H^+}][\mathrm{OH^-}] - k_r[H_2O]$$

- Note that the equilibrium coefficient is defined in terms of activities and the rates are defined in terms of concentrations.
  - For pure water: $[\mathrm{H_2O}]$=55.51 M and $a_{H_2O} = 1$.
  - For $\mathrm{H^+(aq)}$ and $\mathrm{OH^-(aq)}$, the concentrations are sufficiently dilute that the activities are equivalent to the concentrations.
- Therefore:

$$[\mathrm{H^+}][\mathrm{OH^-}] = \frac{1}{K_{eq}} = K_w = 9.9 \times 10^{-15}$$

- From this k_r can be determined:

$$k_r = \frac{k_f[\mathrm{H^+}][\mathrm{OH^-}]}{[H_2O]}$$

$$= \frac{(1.12 \;\times\; 10^{11}\ \mathrm{M^{-1}\ s^{-1}})(9.9 \times 10^{-15})}{55.51\ \mathrm{M}}$$

$$= 2 \times 10^{-5}\ \mathrm{s^{-1}}$$

- This is one example of a reaction with the stoichiometry:

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C$$

- The rate law in general form is:

$$\Re = k_f[A][B] - k_r[C]$$

- Consider a slight perturbation from equilibrium at time $t = 0$.
- The concentrations at this time are $[\mathrm{A}]_0$, $[\mathrm{B}]_0$, and $[\mathrm{C}]_0$.

- The new equilibrium concentrations will be [A]$_{eq}$, [B]$_{eq}$, and [C]$_{eq}$.
- Therefore at any time:

  $$[A]_{eq} = [A] - x$$

  $$[B]_{eq} = [B] - x$$

  and

  $$[C]_{eq} = [C] + x$$

  where x is a function of time and is the reaction progess variable in concentration units.

  - The sign of x depends on the direction of the equilibrium shift.
- The rate law may be written in terms of x:

$$\Re = -\frac{dx}{dt} = k_f([A]_{eq} + x)([B]_{eq} + x) - k_r([C]_{eq} - x)$$

which can be expanded as:

$$-\frac{dx}{dt} = k_f[A]_{eq}[B]_{eq} - k_r[C]_{eq}$$

$$+[k_f[A]_{eq} + k_f[B]_{eq} + k_r]x + k_f x^2$$

  - Because the perturbation is small, the $k_f x^2$ term is ignored.
  - $k_f[A]_{eq}[B]_{eq} - k_r[C]_{eq} = 0$ by the definition of equilibrium.
- Thus the equation becomes:

  $$\frac{dx}{dt} = -[k_f[A]_{eq} + k_f[B]_{eq} + k_r]x = -\frac{x}{\tau}$$

  where τ, the relaxation time constant becomes:

  $$\tau = \frac{1}{k_f[A]_{eq} + k_f[B]_{eq} + k_r}$$

- Separating variables and integrating from $x = [A]_0 - [A]_{eq}$ at $t = 0$ to $x = [A] - [A]_{eq}$ at time t:

  $$\frac{dx}{x} = -\frac{dt}{\tau}$$

  $$[A] = [A]_{eq}(1 - e^{-t/\tau}) + [A]_0 e^{-t/\tau}$$

Determination of k$_f$ and k$_r$

- Kinetic measurements of $[A]$ and t yield τ.
- Equilibrium measurements give K_{eq}.
- This data yields two simultaneous equations which can be solved for k_f and k_r.

Chemical Oscillations

- Not all systems relax linearly to equilibrium.
- Reactions may oscillate in time or concentration through and around the equilibrium point.
  - Frequency is often constant.
  - Implicated in many biological processes.
  - Living systems are not a equilibrium.

Lotka-Volterra mechanism

- One of the most studied oscillating reactions is:

$$A + X \xrightarrow{k_a} 2X$$

$$X + Y \xrightarrow{k_b} 2Y$$

$$Y \xrightarrow{k_c} C$$

- This may be considered a “prey-predator”cycle, where:
  - A is the food source
  - X is the herbivore
  - Y is the predator of X
  - B is the dead predator.
  - Both X and Y are able to reproduce
  - The net process is:

$$\text{food source} \rightarrow \text{dead predator}$$

- In the prey-predator cycle:
  - The food source is available at a steady rate .
  - The herbivore consumes the food source and reproduces. In the absence of predators, the population of the herbivore increases to the capacity of the food supply.
  - But the herbivore population is a food supply for the predator population. As the herbivore population increases, the predator population increases.
  - As the predator population increases, the herbivore population starts to decrease, which eventually leads to a decrease in the predator population.
- Note that the reactions are written in terms of elementary processes, not in terms of stoichiometry.
  - For the first reaction:

$$A + X \xrightarrow{k_a} 2X$$

    the stoichiometry is:

$$A \longrightarrow X$$

    but the rate is:

$$\frac{d[X]}{dt} = k_a[A][X]$$

  - The rate of production of the product depends on the concentration of the product. Such a process is *autocatalytic.*

  - An autocatalytic process represents a positive feedback mechanism.
  - Positive feedback mechanisms are widely found in *in vivo* biochemical systems.

Belusov-Zhabotinskii Reactions

- The best studied system of oscillatory reactions.
- It was discovered in 1951 and published in 1958.
- Involves the Ce^{4+} catalyzed oxidation and bromination of citric acid by bromate ion.
  - Malonic acid (or other *easily* brominated organic acids) may be used instead of citric acid.
- Mechanism was deduced in 1972 and involves 18 elementary steps and 21 species.
- Behaviour of the mechanism may be modelled by the oregonator mechanism which involves 5 steps, 7 species, and f .

$$A + X \longrightarrow X$$

$$X + Y \longrightarrow P$$

$$B + X \longrightarrow 2X + Z$$

$$2X \longrightarrow Q$$

$$Z \longrightarrow fY$$

- Oscillating reactions can give rise to chemical waves.
  - In embryology chemical waves give rise to spots and stripes.