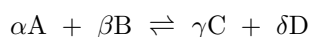


The Phenomenology of Chemical Reaction Rates

- 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:



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 \mathfrak{R} is:

$$\begin{aligned}\mathfrak{R} &= \frac{1}{V} \frac{d\xi}{dt} = -\frac{1}{\alpha V} \frac{dn_A}{dt} = -\frac{1}{\beta V} \frac{dn_B}{dt} \\ &= \frac{1}{\gamma V} \frac{dn_C}{dt} = \frac{1}{\delta V} \frac{dn_D}{dt}\end{aligned}$$

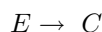
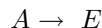
or

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

- 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:



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. its initial rate).
- The phenomenological 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*:

$$\mathfrak{R} = f([A], [B], [C], [D], [E], [F], \dots)$$

- 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:

$$\mathfrak{R} = k \prod_i A_i^{\alpha_i}$$

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 \mathfrak{R} 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 $\text{concentration}^{-1} \text{time}^{-1}$
- For a third order reaction, k has units of $\text{concentration}^{-2} \text{time}^{-1}$
- For a n th order reaction, k has units of $\text{concentration}^{-n+1} \text{time}^{-1}$

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 a first order reaction of the general form:



- 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.

$$N(t) = N^0 e^{-t/\tau_{rad}}$$

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:

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

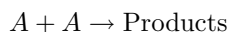
or

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

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

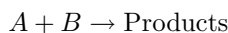
Second-Order Reactions

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



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

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



$$\Re = -\frac{d[A]}{dt} = k'_2 [A][B]$$

- 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

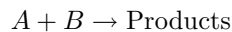
$$\frac{1}{[A]} = \frac{1}{[A]_0} + 2k_2 t$$

- 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:



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

- 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 hand 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:

$$\begin{aligned} a[B]_0 + b[A]_0 &= 1 \\ -ax - bx &= 0 \end{aligned}$$

and

$$\begin{aligned} a &= -b \\ a &= \frac{1}{[B]_0 - [A]_0} \\ b &= \frac{1}{[A]_0 - [B]_0} \end{aligned}$$

- 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 $[A]_0 \gg [B]_0$.

- 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.

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

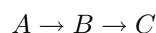
where

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

- 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 complicated 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:



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.

$$\begin{aligned}\frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[B]}{dt} &= k_1[A] - k'_1[B] \\ \frac{d[C]}{dt} &= k'_1[B]\end{aligned}$$

- It will be assumed that $[B]_0 = [C]_0 = 0$

- Therefore at all times:

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

- Solve the first differential equation:

$$\begin{aligned}\frac{d[A]}{[A]} &= -k_1 t \\ [A] &= [A]_0 e^{-k_1 t}\end{aligned}$$

- 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.

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

$$[B] = \frac{k_1 [A]_0}{k'_1 - k_1} (e^{-k_1 t} - e^{-k'_1 t})$$

$$[C] = [A]_0 \left(1 + \frac{k'_1 e^{-k_1 t} - k_1 e^{-k'_1 t}}{k_1 - k'_1} \right)$$

- 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 $k_1 \ll k'_1$
 - Then as soon as A is converted to B , B quickly converts to C
- The concentrations as a function of time become:

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

$$[B] = \frac{k_1 [A]_0}{k'_1} e^{-k_1 t}$$

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

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 $k_1 \ll k'_1$.

$$\frac{d[B]}{dt} = k_1[A] - k'_1[B] = 0$$

$$[B] = \frac{k_1}{k'_1} [A]$$

- 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 $[A] + [C]$:

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

Which is the same result as obtained from the exact solution in the limit of $k_1 \ll k'_1$

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:

$$\begin{aligned} \frac{d[A^{***}]}{dt} &= -k_1[A^{***}] - k'_1[A^{***}] - k''_1[A^{***}] \\ &= -(k_1 + k'_1 + k''_1) [A^{***}] = -k_{net}[A^{***}] \end{aligned}$$

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:

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

- Similarly:

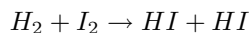
$$[A^*] = \frac{k'_1[A^{***}]_0}{k_{net}} (1 - e^{-k_{net}t})$$

$$[A] = \frac{k''_1[A^{***}]_0}{k_{net}} (1 - e^{-k_{net}t})$$

- 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

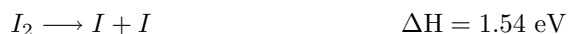


proceeded by a four-center intermediate.

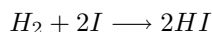
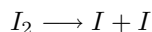
- The phenomenological rate law was:

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

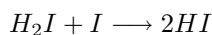
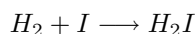
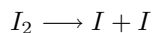
- The work of J. H. Sullivan on the temperature dependence of the reaction rate, showed that the reaction proceeded by the dissociation of I_2 then reaction of I with H_2 .
- Consider the dissociation of the reactant molecules:



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



- Evidence is mounting in favour of the following:



The $H_2 + Br_2$ chain reaction

- The observed rate law is:

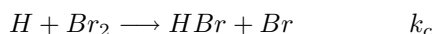
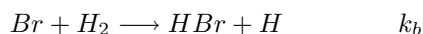
$$\Re = \frac{1}{2} \frac{d[HBr]}{dt} = \frac{k_{exp}[H_2][Br_2]^{1/2}}{1 + \alpha[HBr]/[Br_2]}$$

- 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:

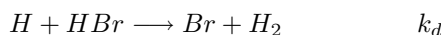
- Initiation



- Propagation



- Inhibition



- Termination



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

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

$$\begin{aligned} \frac{d[Br]}{dt} &= 2k_a[Br_2] - k_b[Br][H_2] + k_c[H][Br_2] \\ &\quad + k_d[H][HBr] - 2k_e[Br]^2 = 0 \end{aligned}$$

- 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

$$\begin{aligned} \Re &= \frac{1}{2} \frac{d[HBr]}{dt} = k_c [H] [Br_2] \\ &= k_c \left(\frac{k_b \left(\frac{k_a}{k_e} [Br_2] \right)^{1/2} [H_2]}{k_c [Br_2] + k_d [HBr]} \right) [Br_2] \\ &= \frac{k_b (k_a/k_e)^{1/2} [H_2] [Br_2]^{1/2}}{1 + (k_d/k_c) ([HBr]/[Br_2])} \end{aligned}$$

and

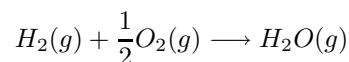
$$k_{exp} = k_b (k_a/k_e)^{1/2}$$

and

$$\alpha = k_d/k_c$$

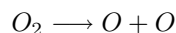
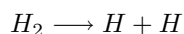
Branching Chain Reactions-Explosions

- Explosions happen quickly:
 - In 1937 the Hindenberg disaster $2 \times 10^5 \text{ m}^3$ 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:

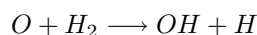
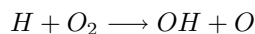


- Exothermic: $\Delta_r \overline{H}^\circ = -242 \text{ kJ mol}^{-1}$ at 298 K.
- H_2 and O_2 can be mixed at room temperature in any proportion with no reaction occurring.
- The reaction must be initiated by a spark, a flame, or a catalyst.
- The reaction proceeds by a free radical mechanism with branching.

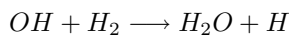
- **Initiation:**



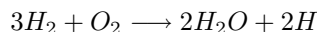
- **Branching:**



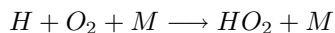
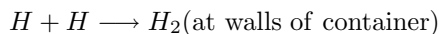
- **Propagation:**



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



- **Termination:**



- 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:

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

- 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 ($\text{CH}_3\text{N}=\text{C}=\text{O}$)
- 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 enthalpy 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



- The Arrhenius parameters are:

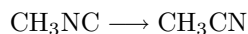
$$A = 3.98 \times 10^{13} \text{ s}^{-1}$$

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

- 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 equilibrium is reached very quickly after that. (See Fig. 26.6)

The Attainment of Chemical Equilibrium

- Equilibrium 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:



and its reverse reaction:



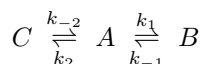
- Both the forward and reverse reaction are first order.
- The corresponding reaction coefficients are k_f and k_r .
- Thus:

$$\frac{d[\text{CH}_3\text{NC}]}{dt} = -k_f[\text{CH}_3\text{NC}] + k_r[\text{CH}_3\text{CN}]$$

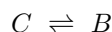
- At equilibrium:

$$\begin{aligned} \frac{d[\text{CH}_3\text{NC}]}{dt} &= 0 \\ -k_f[\text{CH}_3\text{NC}]_{eq} + k_r[\text{CH}_3\text{CN}]_{eq} &= 0 \\ \frac{k_f}{k_r} &= \frac{[\text{CH}_3\text{CN}]_{eq}}{[\text{CH}_3\text{NC}]_{eq}} = K_{eq} \end{aligned}$$

- 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:



which describes the overall equilibrium



- 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

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

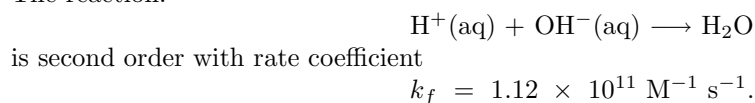
where ξ_{eq} is the point where $(\partial G / \partial \xi) = 0$

- 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:



- The equilibrium coefficient is:

$$K_{eq} = \frac{a_{\text{H}_2\text{O}}}{a_{\text{H}^+} a_{\text{OH}^-}} = 1.01 \times 10^{14}$$

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

$$\mathfrak{R} = 0 = k_f[\text{H}^+][\text{OH}^-] - k_r[\text{H}_2\text{O}]$$

- Note that the equilibrium coefficient is defined in terms of activities and the rates are defined in terms of concentrations.

- For pure water: $[\text{H}_2\text{O}] = 55.51 \text{ M}$ and $a_{\text{H}_2\text{O}} = 1$.
- For $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$, the concentrations are sufficiently dilute that the activities are equivalent to the concentrations.

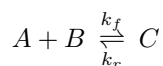
- Therefore:

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

- From this k_r can be determined:

$$\begin{aligned} k_r &= \frac{k_f[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \\ &= \frac{(1.12 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1})(9.9 \times 10^{-15})}{55.51 \text{ M}} \\ &= 2 \times 10^{-5} \text{ s}^{-1} \end{aligned}$$

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



- The rate law in general form is:

$$\mathfrak{R} = k_f[A][B] - k_r[C]$$

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

- 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 progress 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:

$$-\frac{dx}{dt} = k_f[A]_{eq}[B]_{eq} - k_r[C]_{eq} + [k_f[A]_{eq} + k_f[B]_{eq} + k_r]x + k_fx^2$$

- Because the perturbation is small, the k_fx^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

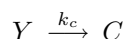
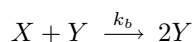
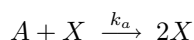
- Kinetic measurements of $[A]$ and t yield τ .
- Equilibrium measurements give K_{eq} .
- This data yields two simultaneous equations which can be solved for k_f and k_r .

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.

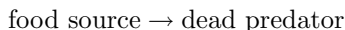
Lotka-Volterra mechanism

- One of the most studied oscillating reactions is:



- 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:

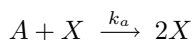


- In the prey-predator cycle:

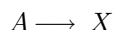
- The food source is available at a steady rate .
- The herbivore consumes the food source and reproduces. In the absence of predators, the population of the herbivore increases to the capacity of the food supply.
- But the herbivore population is a food supply for the predator population. As the herbivore 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:



the stoichiometry is:



but the rate is:

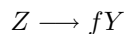
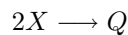
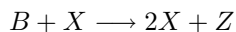
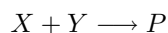
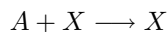
$$\frac{d[X]}{dt} = k_a[A][X]$$

- 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 .



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