Chemical Kinetics (Chapter 9)

Thermodynamics: Does reaction occur spontaneously?

Kinetics: How fast?

Consider reaction R \rightarrow P.

\([R]_1 = \text{concentration of } R \text{ at time } t_1.\)

\([R]_2 = \ldots \text{ of } R \text{ at time } t_2.\)

Reaction rate = \(- \frac{[R]_2 - [R]_1}{t_2 - t_1} = - \frac{\Delta [R]}{\Delta t} = - \frac{d[R]}{dt} \quad (\Delta t = t_2 - t_1 \rightarrow 0)\)

Convention: We use ‘-’ sign since \([R]_2 < [R]_1\), so rate is > 0.

Alternatively: rate = \(\frac{[P]_2 - [P]_1}{t_2 - t_1} = \frac{d[P]}{dt}\)
Chemical Kinetics (Chapter 9)

Consider reaction $R \rightarrow P$.

\[
\text{rate} = -\frac{d[R]}{dt} = \frac{d[P]}{dt} \quad \text{units often } M \text{ s}^{-1}
\]

Stoichiometry can complicate things:

If $2R \rightarrow P$

\[
\text{rate} = -\frac{1}{2} \frac{d[R]}{dt} = \frac{d[P]}{dt}
\]

In general, for reaction: $aA + bB \rightarrow cC + dD$

\[
-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}
\]
Chemical Kinetics (Chapter 9)

Rate Laws

Rate empirically found to depend on concentrations of species present, often in complicated way.

If A and B are reactants, one may find,

\[ \text{Rate} \propto [A]^x[B]^y = k [A]^x[B]^y. \]

Since concentrations change with time so does rate.

\( k = \text{rate constant}; \) does not depend on concentration, but depends on temperature: \( k = k(T). \)

Reaction order: Sum of \( x + y. \) Reaction is of order \( x \) in \([A]\) and \( y \) in \([B]\). Often unrelated to stoichiometry:

Example: \( 2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g) \quad \text{rate} = k[\text{N}_2\text{O}_5(g)] \)
Reaction order is an integer

**Zero-order reaction:** \[ A \rightarrow \text{Products} \]

If zero order: \[ \text{rate} = -\frac{d[A]}{dt} = k[A]^0 = k \]

Rate constant, \( k \), has units \( \text{M s}^{-1} \). Rate independent of \([A]\).

How does \([A]\) vary with time? \[ d[A] = -kdt \]

Integrate: \[ \int_{[A]_0}^{[A]} d[A] = -\int_{t=0}^{t} k \, dt, \quad [A]_0 = \text{concentration at } t = 0. \]

\[ [A] = [A]_0 - kt \]

Examples of zero-order reaction: Catalytic reactions when reactant concentration is high; catalyst covered, rate does not change if more reactant is added.
Reaction order is an integer

Half-life of reaction: The time, $t_{1/2}$, for concentration of reactant to reach half its original value, $[A] = [A]_0/2$.

For zero-order reaction:

$[A] = [A]_0/2 = [A]_0 - kt_{1/2} \quad \rightarrow \quad t_{1/2} = [A]_0/2k.$
Reaction order is an integer

First-order reaction: \( A \rightarrow \text{Products} \)

If first order:

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

Rate constant, \( k \), has units \( \text{s}^{-1} \).

How does \([A]\) vary with time? \( \rightarrow \)

\[
\frac{d[A]}{[A]} = -kdt
\]

Integrate:

\[
\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -\int_{t=0}^{t} k \, dt \rightarrow \ln \frac{[A]}{[A]_0} = -kt
\]

\[
[A] = [A]_0 e^{-kt}
\]
Reaction order is an integer

First-order reaction: \[ A \rightarrow \text{Products} \]

If first order: \[ \text{rate} = -\frac{d[A]}{dt} = k[A] \]

Rate constant, \( k \), has units \( \text{s}^{-1} \).

\[ \ln \frac{[A]}{[A]_0} = -kt \]

\[ [A] = [A]_0 e^{-kt} \]
Reaction order is an integer

First-order reaction: \[ A \rightarrow \text{Products} \]

Half-life? Time, \( t_{1/2} \), at which \([A] = [A]_0/2\).

\[
\ln \left( \frac{[A]_0/2}{[A]_0} \right) = -kt_{1/2} \quad \rightarrow \quad \ln \frac{1}{2} = -kt_{1/2}
\]

\( t_{1/2} = \ln2/k = 0.693/k \) independent of initial concentration.

Example of 1\(^{st}\) order reaction: Radioactive decay

Carbon-14: \[ ^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^0_{-1}\beta \] \( t_{1/2} = 5730 \) years
First-order reaction:

Example:

\[
\begin{array}{c}
\text{N} = \text{C} - \text{C} - \text{N} = \text{N} - \text{C} - \text{C} = \text{N} \xrightarrow{\Delta} 2\text{N} = \text{C} - \text{C} + \text{N}_2
\end{array}
\]

\[k = ?\quad \text{AIBN} \quad \rightarrow \quad \text{products}\]

Measure optical absorbance, \(A\), of AIBN at 350 nm.

We have following data:

<table>
<thead>
<tr>
<th>(t (s))</th>
<th>(A)</th>
<th>(t (s))</th>
<th>(\ln[(A-A_\infty)/(A_0-A_\infty)])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4000</td>
<td>1.07</td>
<td>4000</td>
<td>-0.496</td>
</tr>
<tr>
<td>8000</td>
<td>0.81</td>
<td>8000</td>
<td>-0.987</td>
</tr>
<tr>
<td>12,000</td>
<td>0.65</td>
<td>12,000</td>
<td>-1.482</td>
</tr>
<tr>
<td>(\infty)</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Slope = $-k$

$k = 1.24 \times 10^{-4} \text{ s}^{-1}$
Reaction order is an integer

Second-order reaction: \[ A \rightarrow \text{Products} \] \hspace{1cm} (1)
OR: \[ A + B \rightarrow \text{Products} \] \hspace{1cm} (2)

Consider (1): \[ \text{rate} = -\frac{d[A]}{dt} = k[A]^2 \]

Rate constant, \( k \), has units \( \text{M}^{-1} \text{s}^{-1} \).

How does \([A]\) vary with time? \[ \frac{d[A]}{[A]^2} = -kd\]

Integrate:

\[ \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -\int_t^{t=0} k \, dt \quad \text{-->} \quad \frac{1}{[A]} - \frac{1}{[A]_0} = -kt \]

\[ \text{-->} \quad \frac{1}{[A]} = \frac{1}{[A]_0} + kt \]

\( \frac{1}{[A]} \) vs. \( t \) graph with \( Slope = k \).

---

**Diagram:**

- Graph showing \( \frac{1}{[A]} \) vs. \( t \)
- Linear relationship with slope \( k \)
Reaction order is an integer

Second-order reaction: \( A \rightarrow \text{Products} \) \hspace{1cm} (1)

OR: \( A + B \rightarrow \text{Products} \) \hspace{1cm} (2)

Consider (2):

\[
\text{rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]
\]

If \([A]_0 = [B]_0\) then \([A] = [B]\) at all times, so we have again:

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

Then again:

\[
\frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad \text{(same for [B].)}
\]
2nd order reaction: Example of DNA renaturation

DNA

↓ Sonication

↓ Heat

↓ Renaturation
Kinetic analysis of renaturation

Second-order reaction: \( A + B \rightarrow AB \)

Since \([A] = [B]\), \( \text{rate} = k[A][B] = k[A]^2 \)

We found: \( \frac{1}{[A]} = \frac{1}{[A]_0} + kt \quad \rightarrow \quad [A] = \frac{[A]_0}{1 + [A]_0 kt} \)

At time, \( t \), fraction, \( f \), of \( A \) strands that remain dissociated:

\[
f = \frac{[A]}{[A]_0} = \frac{1}{1 + [A]_0 kt}
\]

\([A] = \text{concentration of a particular single strand at time, } t.\)
\([A]_0 = \text{initial concentration of a particular strand } A.\)

Define \( C_0 = \text{total concentration of all single strands before renaturation, regardless of their identity.} \)

\([A]_0 = C_0/2N\)

\(N = \text{smallest repeating sequence of nucleotide ("complexity")}\)
Kinetic analysis of renaturation

\([A]_0 = \) initial concentration of a particular strand A.

Define \(C_0 = \) total concentration of all single strands before renaturation, regardless of their identity.

\([A]_0 = C_0/2N\)

\(N = \) smallest repeating sequence of nucleotide ("complexity")

Examples:

(a) If DNA is \(\text{A-A-} \ldots \text{A} \quad \text{T-T-} \ldots \text{T}\) then \(N = 1\). Then \([A]_0 = C_0/2\), or half concentration of total fragments. (\([A]_0 \) is initial concentration of either adenine or thymine fragment.)

(b) If DNA has no repeating sequence, \(N \approx \# \) of base pairs. Then \([A]_0 \) is very small; each fragment has unique sequence.
Kinetic analysis of renaturation

Recall: fraction of A-strands dissociated at time, $t$:

$$f = \frac{[A]}{[A]_0} = \frac{1}{1 + [A]_0 kt} = \frac{1}{1 + C_0 kt / 2N} = \frac{1}{1 + C_0 k' t / N}$$

($k' = k/2 \text{ } \rightarrow \text{ just to remove factor of 2.}$)

Half life: $t_{1/2} = \text{time for half of strands to renature (} f = 1/2\text{).}$

$$f = \frac{1}{2} = \frac{1}{1 + C_0 k' t_{1/2} / N} \quad \rightarrow \quad C_0 t_{1/2} = N / k'$$

Measure: $C_0$ and $t_{1/2}$ (time for $f$ to reach 1/2) $\rightarrow \text{ } N / k'$. Start with $N=1$ to find $k'$, then measure $C_0$, $t_{1/2}$ to find other $N$ once $k'$ is known.

Expect: $f$

N small

N large

$C_0 t$
Kinetic analysis of renaturation

Half life: $t_{1/2} = \text{time for half of strands to renature (f = 1/2)}$.

$C_0 t_{1/2} = N/k'$
Mechanism and Molecularity of Reaction

Reaction typically occurs by sequence of elementary steps. The order of each step is called molecularity.

Consider decomposition of $H_2O_2$:

$$2H_2O_2(g) \rightarrow 2H_2O(g) + O_2(g) \quad \text{rate} = k[H_2O_2(g)]$$

Elementary steps of reaction mechanism:

1. $H_2O_2 \xrightarrow{k_1} 2OH \quad k_1 = \text{rate constant for step 1.}$
2. $H_2O_2 + OH \xrightarrow{k_2} H_2O + HO_2$
3. $HO_2 + OH \xrightarrow{k_3} H_2O + O_2$

$$2H_2O_2(g) \rightarrow 2H_2O(g) + O_2(g)$$

$OH, HO_2$ are intermediates, which are species that appear in mechanism but not in overall reaction.
Mechanism and Molecularity of Reaction

\[ 2\text{H}_2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + \text{O}_2(g) \quad \text{rate} = k[\text{H}_2\text{O}_2(g)] \]

Elementary steps of reaction mechanism:

1. \[ \text{H}_2\text{O}_2 \xrightarrow{k_1} 2\text{OH} \quad k_1 = \text{rate constant for step 1.} \]
2. \[ \text{H}_2\text{O}_2 + \text{OH} \xrightarrow{k_2} \text{H}_2\text{O} + \text{HO}_2 \]
3. \[ \text{HO}_2 + \text{OH} \xrightarrow{k_3} \text{H}_2\text{O} + \text{O}_2 \]

\[ 2\text{H}_2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + \text{O}_2(g) \]

\(\text{OH, HO}_2\) are **intermediates**, which are species that appear in mechanism but not in overall reaction.

If \(k_1 \ll k_2, k_3\): Step 1 is rate limiting \(\rightarrow \text{rate} = k_1[\text{H}_2\text{O}_2(g)]\).

Reaction order is molecularity of step 1: unimolecular.

Elementary steps are usually uni- or bimolecular, rarely termolecular.
Unimolecular Reactions

Elementary step: \( A \rightarrow \text{products} \)

Examples: 1. Isomerization (change of structure):

\[
\text{Cyclohexane: } \begin{array}{c}
\text{(chair)} \\
\text{(boat)}
\end{array}
\]

2. Thermal decomposition: \( \text{H}_2\text{O}_2 \rightarrow 2\text{OH} \)

Why is rate = \( k[A] \) for unimolecular reaction? Is this always the case?

Reactant needs energy to react, and gets this from collisions with other molecules.
Unimolecular Reactions

Elementary step: \( A \rightarrow \text{products} \)

Lindemann Mechanism:

Let \( A = \text{reactant} \)

\( A^* = \text{reactant with enough energy to react} \)

Then:

1. \( A + A \rightarrow A + A^* \)  (activation step)

1'. \( A + A^* \rightarrow A + A \)  (deactivation)

2. \( A^* \rightarrow \text{products} \)

Rate of product formation: \( \frac{d[\text{product}]}{dt} = k_2[A^*] \)

We measure \([A]\), not \([A^*]\) --> need to relate \([A]\) to \([A^*]\).

If no step is rate limiting, use steady state approximation: assume \([A^*]\) does not change with time.
Unimolecular Reactions

Elementary step: \( A \rightarrow \) Products

Mechanism:
1. \( A + A \xrightarrow{k_1} A + A^* \) (activation step)
1’. \( A + A^* \xrightarrow{k_{-1}} A + A \) (deactivation)
2. \( A^* \xrightarrow{k_2} \) products (P)

\[
\frac{d[P]}{dt} = \frac{k_2 k_1 [A]^2}{k_2 + k_{-1} [A]}
\]

We found:
“High” Pressure (> 1 atm): \( k_{-1} \gg k_2 \) (fast deactivation)

Then:
\[
\frac{d[P]}{dt} = k[A], \quad k = \frac{k_2 k_1}{k_{-1}}
\]

usual case.

Low Pressure (<< 1 atm) \quad Then: \( k_2 \gg k_{-1} \rightarrow \quad \frac{d[P]}{dt} = k_1 [A]^2 \)
Bimolecular Reactions: Any elementary step involving 2 reactant molecules

Examples:
1. DNA renaturation: \( A + B \rightarrow AB \) (\( A, B = \) single strands)
2. \( \text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2 \)
3. \( \text{Fe}^{2+} + \text{Fe}^{3+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{2+} \) (electron transfer)

Termolecular Reactions: Elementary step involving simultaneous collision of 3 reactants: very rare, improbable.

Many known reactions involve NO(\( g \)) as reactant:

\[ 2\text{NO}(g) + X_2(g) \rightarrow 2\text{NOX}(g) \quad X = \text{Cl}, \text{Br}, \text{I} \]

Sometimes 3rd molecule is inert: removes energy to stabilize product.

Example: \( H + H + M \rightarrow H_2 + M \) \( M = \) inert molecule, such as \( \text{N}_2 \) or \( \text{Ar} \)
More complex reactions

Chain Reactions: Many elementary steps; order of reaction is often not integer.

Consider: \( H_2(g) + Br_2(g) \rightarrow 2HBr \) \hspace{1cm} \text{rate} = k[H_2][Br_2]^{1/2}

Plausible elementary steps:

1. \( Br_2 \xrightarrow{k_1} 2Br \) \hspace{1cm} (Chain initiation)
2. \( Br + H_2 \xrightarrow{k_2} HBr + H \) \hspace{1cm} (Chain propagation)
3. \( H + Br_2 \xrightarrow{k_3} HBr + Br \)
4. \( 2Br \xrightarrow{k_4} Br_2 \) \hspace{1cm} (Chain termination)

\( H_2(g) + Br_2(g) \rightarrow 2HBr \) \hspace{1cm} Why is rate = \( k[H_2][Br_2]^{1/2} \) ?

• If step 2 is slow and others fast, step 2 is rate limiting:

\[ \text{rate} = k_2[Br][H_2] \] \hspace{1cm} (Br is intermediate; we don’t know [Br])
More complex reactions

1. \[ \text{Br}_2 \xrightarrow{k_1} 2\text{Br} \] (Chain initiation)

2. \[ \text{Br} + \text{H}_2 \xrightarrow{k_2} \text{HBr} + \text{H} \] (Chain propagation)

3. \[ \text{H} + \text{Br}_2 \xrightarrow{k_3} \text{HBr} + \text{Br} \]

4. \[ 2\text{Br} \xrightarrow{k_4} \text{Br}_2 \] (Chain termination)

\[ \text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr} \]

Why is rate = \( k[\text{H}_2][\text{Br}_2]^{1/2} \)?

- If step 2 is slow and others fast, step 2 is rate limiting:
  
  \[
  \text{rate} = k_2[\text{Br}][\text{H}_2] \quad \text{(Br is intermediate; we don’t know [Br])}
  \]

- If steps 1 & 4 are in equilibrium:

  Rate of loss of \( \text{Br}_2 \) (step 1) = rate of gain of \( \text{Br}_2 \) (step 4)
  
  \[
  k_1[\text{Br}_2] = k_4[\text{Br}]^2 \quad \Rightarrow \quad [\text{Br}] = (k_1/k_4)^{1/2}[\text{Br}_2]^{1/2}
  \]

  Then: \( \text{rate} = k[\text{H}_2][\text{Br}_2]^{1/2} \quad k = k_2(k_1/k_4)^{1/2} \)
Rate Constants

Reaction rate depends on concentration of reactions & products, also on rate constant, \( k = k(T) \).

Arrhenius equation for rate constant:

\[
k = Ae^{-E_a / RT}
\]

\( R = \) gas constant \quad \( T = \) temperature \quad \( A = \) frequency factor

\( E_a = \) activation energy (kJ/mol)

\( A \approx \) collision frequency between reactants; \( T \) dependence is small and we assume \( A \) is constant.

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

To find \( E_a \), plot \( \ln k \) vs. \( 1/T \):

Slope = \(-E_a/R\)
Rate Constants

\[ \ln k = \ln A - \frac{E_a}{RT} \]

To find \( E_a \), plot \( \ln k \) vs. \( \frac{1}{T} \):

\[ \text{Slope} = -\frac{E_a}{R} \]

If we know \( k_1 \) at \( T_1 \), what is \( k_2 \) at \( T_2 \)?

\[
\ln k_2 = \ln A - \frac{E_a}{RT_2}
\]

\[
-\left( \ln k_1 = \ln A - \frac{E_a}{RT_1} \right)
\]

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

Looks like van’t Hoff equation: do not confuse!

What is the meaning of \( E_a \)?
What is the meaning of $E_a$?

**Reaction path:** minimum energy path for reactants $\rightarrow$ products.

**Activation energy ($E_a$)** = lowest possible barrier to go from reactants to products.

**Catalyst:**
- lowers $E_a$
- Appears at beginning and end of reaction.

**Example:** $\text{Cl}^\cdot$ catalyzes decomposition of $O_3$:

$$\text{Cl} + O_3 + O \rightarrow \text{Cl} + 2O_2$$

Effect of Cl is to lower $E_a$ for $O_3 + O \rightarrow 2O_2$. 
Reaction Rates Near Equilibrium

If system is approaching equilibrium, rate constants can be determined by observing rate of relaxation to equilibrium.

Consider protein in native state, N, & denatured state, D:

\[ N \underset{k_r}{\overset{k_f}{\rightleftharpoons}} D \]

\([N], [D]\) measured by spectroscopy

At equilibrium: forward reaction rate = reverse reaction rate

\[ k_f [N] = k_r [D] \quad \text{--->} \quad \frac{k_f}{k_r} = \frac{[D]}{[N]} = K = \text{equilibrium constant} \]

By measuring \([N] \& [D]\) at equilibrium we find ratio \(k_f/k_r\). We need one more equation to find \(k_f \& k_r\).
Reaction Rates Near Equilibrium

\[ \text{N} \xrightarrow{k_f} \text{D} \quad \xleftarrow{k_r} \]

\[ k_f [N] = k_r [D] \quad \Rightarrow \quad \frac{k_f}{k_r} = \frac{[D]}{[N]} = K = \text{equilibrium constant} \]

By measuring \([N]\) & \([D]\) at equilibrium we find ratio \(k_f/k_r\).
We need one more equation to find \(k_f\) & \(k_r\).

Start with rate equation:

\[ -\frac{d[N]}{dt} = k_f [N] - k_r [D] \]

Rapidly increase \(T\): “Temperature jump”: \( T \rightarrow T' = T + \Delta T \)

After changing \(T\) --> \(T'\):

\[ [N] = [N]_e + \Delta [N] \]
\[ [D] = [D]_e + \Delta [D] \]

\([N]_e, [D]_e\) are equilibrium concentrations at new temp., \(T'\)
\(\Delta [N], \Delta [D]\) are deviations from new equilibrium concentrations
Reaction Rates Near Equilibrium

\[
N \xrightleftharpoons[{k_f}]{{k_r}} D
\]

[N], [D] measured by spectroscopy

Rapidly increase T: “Temperature jump”: \( T \rightarrow T' = T + \Delta T \)

\[
[N] = [N]_e + \Delta [N]
\]

After changing \( T \rightarrow T' \):

\[
[D] = [D]_e + \Delta [D]
\]

\([N]_e, [D]_e\) are equilibrium concentrations at new temp., \( T' \)

\(\Delta [N], \Delta [D]\) are deviations from new equilibrium concentrations

Schematically:

\[
[D]_e \quad [D](t) \quad \Delta [D]
\]

\(\Delta [D]\) changes with time until the new equilibrium concentration is reached.
Reaction Rates Near Equilibrium

\[ \text{Schematically:} \quad [D]_e, \Delta[D] \]

\[ [N] = [N]_e + \Delta[N] \]

\[ \Delta[N] = -\Delta[D] \quad \text{(mass conservation)} \]

\[ -\frac{d[N]}{dt} = \frac{d[N]_e}{dt} - \frac{d\Delta[N]}{dt} \]

\[ -\frac{d\Delta[N]}{dt} = (k_f + k_r)\Delta[N] = \frac{\Delta[N]}{\tau} \]

\[ \tau = \text{relaxation time} = (k_f + k_r)^{-1} \]
Reaction Rates Near Equilibrium

\[ N \xrightleftharpoons[k_f]{k_r} D \]

\([N], [D]\) measured by spectroscopy

\[
- \frac{d\Delta[N]}{dt} = (k_f + k_r)\Delta[N] = \frac{\Delta[N]}{\tau}
\]

\(\tau = \text{relaxation time}\)

\(\tau = (k_f + k_r)^{-1}\)

\[
\Delta[N] = \Delta[N]_0 e^{-t/\tau}
\]

\(\Delta[N]_0 = \text{deviation from } [N]_e \text{ at } t = 0.\)

Or:

\[
\ln \Delta[N] = \ln \Delta[N]_0 - t/\tau
\]

\[
\ln \Delta[N] \quad \text{Slope} = -1/\tau = -(k_r + k_f)
\]

2 equations for \(k_r, k_f\):

1. \(k_f/k_r = [D]_e/[N]_e\)

2. Slope of \(\ln \Delta[N] \) vs. \(t\)
Another Reaction: Enzyme-Substrate Binding

\[
E + S \xrightarrow{k_f} ES \xleftarrow{k_r} E
\]

At \( t = 0 \), increase \( T \): \( T \rightarrow T' = T + \Delta T \)

After changing \( T \rightarrow T' \):
- \([E] = [E]_e + \Delta[E] \)
- \([S] = [S]_e + \Delta[S] \)
- \([ES] = [ES]_e + \Delta[ES] \)

\([E]_e \) = equilibrium concentration of \( E \) at new temperature, \( T' \).

Rate Equation:
\[ -\frac{d[E]}{dt} = -\frac{d\Delta[E]}{dt} = k_f[E][S] - k_r[ES] \]

At equilibrium:
\[ k_f[E][S] = k_r[ES] \]

Mass conservation:
\[ \Delta[E] = \Delta[S] = -\Delta[ES] \]
Another Reaction: Enzyme-Substrate Binding

\[ E + S \overset{k_f}{\underset{k_r}{\rightleftharpoons}} ES \]

Rate Equation:

\[-\frac{d[E]}{dt} = -\frac{d[ES]}{dt} = k_f[E][S] - k_r[ES] \]

At equilibrium:

\[ k_f[E][S] = k_r[ES] \]

Mass conservation:

\[ \Delta[E] = \Delta[S] = -\Delta[ES] \]

Rearrange to:

\[-\frac{d[ES]}{dt} = \left(k_f([E]_e + [S]_e) + k_r\right)\Delta[E] = \frac{1}{\tau}\Delta[E] \]

Time constant:

\[ \tau = \left(k_f([E]_e + [S]_e) + k_r\right)^{-1} \]

\[ \ln\Delta[E] \quad \text{Slope} = -1/\tau \]

2 equations for \(k_r, k_f\):

1. \(k_f/k_r = [ES]_e/[E]_e [S]_e\)

2. Slope of \(\ln\Delta[E]\) vs. \(t\).
Another Reaction: Enzyme-Substrate Binding

Example: A sample of pure water was subjected to a temperature jump. The relaxation time for the system (as measured by pH) to reach new equilibrium at 25 °C was found to be 36 µs.

Find $k_f$, $k_r$ for $H^+ + OH^- \rightleftharpoons H_2O$

Time constant: $\tau = \left[ k_f ([E]_e + [S]_e) + k_r \right]^{-1}$