Chapter 18. Chemical Kinetics

Summary

- rates of chemical reactions and rate laws
- integrated rate equations
- temperature dependence of reaction rates
- reaction mechanisms
- **sequential and parallel reactions**
- **numerical methods for chemical kinetic equations**
- **diffusion-controlled reactions**
- **measuring rates of ultra-fast reactions**

Sections 18.1 to 18.6: Reaction Rates and Rate Laws

(a review)

$$aA + bB + \ldots \rightarrow cC + dD + \ldots \qquad \Delta G_{T,p}$$

- a negative Gibbs energy change $\Delta G_{T,p}$ indicates **A**, **B**, … will spontaneously react to form products **C**, **D**, …

very useful, but:

- $\Delta G_{T,p}$ (and thermodynamics) provides no information about the rate of the reaction **(*why*?)**

- in general, there is no relation between the stoichiometric $aA + bB + \ldots \rightarrow cC + dD + \ldots$ equation and the rate equation for chemical reactions **(*why*?)**

Reaction Rates

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

Stoichiometry relates the changes in the mole numbers:

$$-\frac{1}{a}\frac{\mathrm{d}n_{\mathrm{A}}}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}n_{\mathrm{B}}}{\mathrm{d}t} \quad \cdots \quad = \frac{1}{c}\frac{\mathrm{d}n_{\mathrm{C}}}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}n_{\mathrm{D}}}{\mathrm{d}t} \quad \cdots$$

Dividing by the volume

$$n_i / V = [i]$$

gives the molar concentration changes of reactants and products:

$$-\frac{1}{a}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} \quad \cdots \quad = \frac{1}{c}\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} \quad \cdots$$

Example Use the equation for the decomposition of acetaldehyde to relate the reaction rate to the acetaldehye pressure.

$$\mathbf{CH_3COH(g) \rightarrow CH_4(g) + CO(g)}$$

Assuming ideal gas behavior:

$$p_{\mathrm{CH_3COH}} = \frac{n_{\mathrm{CH_3COH}}}{V}RT = [\mathrm{CH_3COH}]RT$$

$$[\mathrm{CH_3COH}] = p_{\mathrm{CH_3COH}} / RT$$

$$\text{reaction rate} = -\frac{\mathrm{d}[\mathrm{CH_3COH}]}{\mathrm{d}t} = -\frac{1}{RT}\frac{\mathrm{d}p_{\mathrm{CH_3COH}}}{\mathrm{d}t}$$

why the negative sign?

Rate Laws

The rates of chemical reactions depend on many factors:

the temperature, pressure, concentrations of the reactants, and the presence of a catalyst.

Reaction rates in homogenous (one-phase) systems are described by empirical **rate laws**, such as

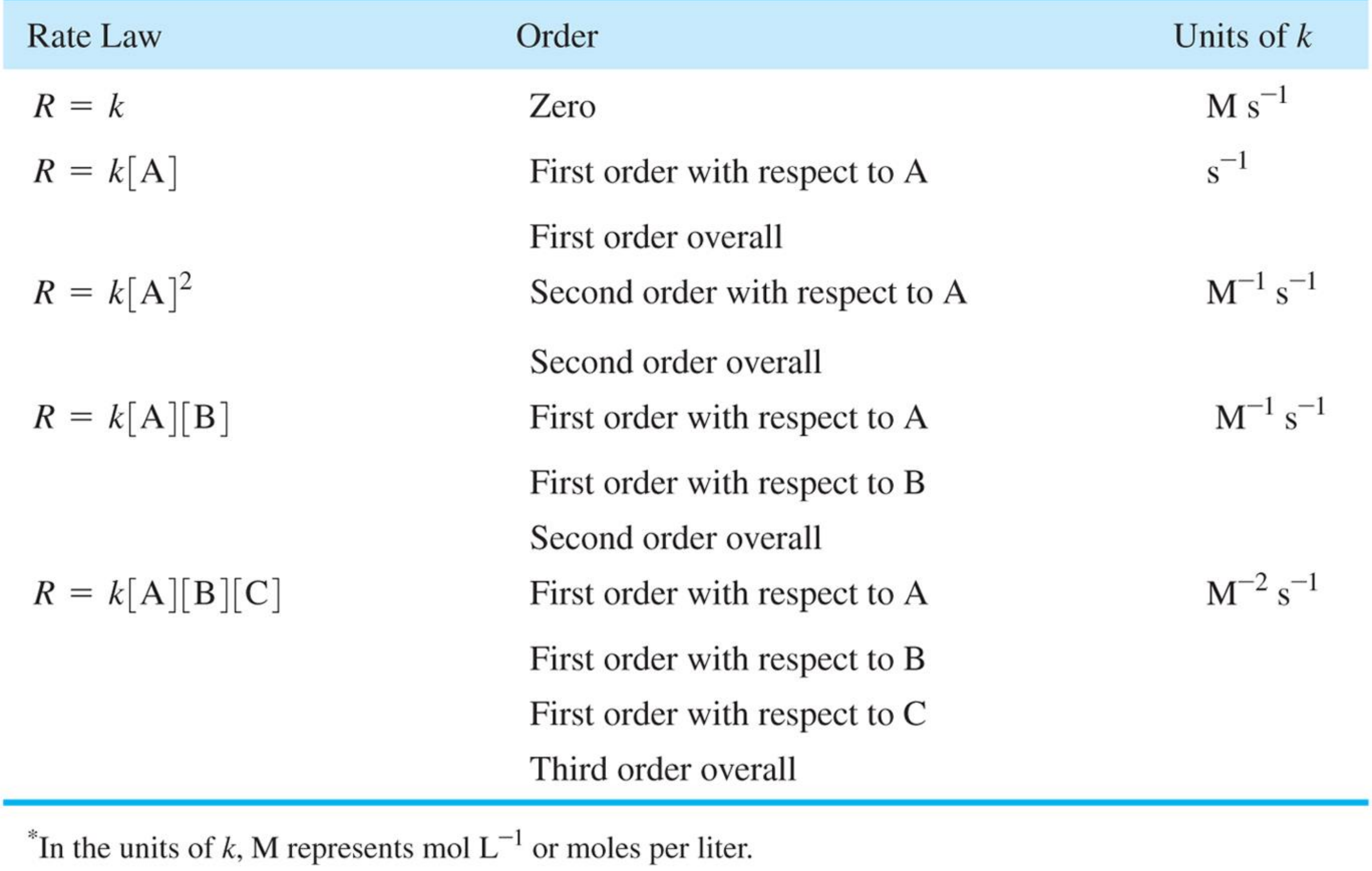
$$\boxed{\text{reaction rate} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}\cdots}$$

k = **rate constant**

[A] = concentration of chemical A, [B] = concentration of chemical B, …

α = **reaction order** for chemical A, β = reaction order for chemical B, …

Relationship between rate law, order and rate constant *k*



Rate Law	Order	Units of k
$R = k$	Zero	$M\ s^{-1}$
$R = k[A]$	First order with respect to A First order overall	s^{-1}
$R = k[A]^2$	Second order with respect to A Second order overall	$M^{-1}\ s^{-1}$
$R = k[A][B]$	First order with respect to A First order with respect to B Second order overall	$M^{-1}\ s^{-1}$
$R = k[A][B][C]$	First order with respect to A First order with respect to B First order with respect to C Third order overall	$M^{-2}\ s^{-1}$

*In the units of k, M represents mol L^{-1} or moles per liter.

Temperature Dependence of Rate Constants

Significant !

Rate constants depend **exponentially** on the temperature.

$$\boxed{k(T) \;=\; A\mathrm{e}^{-E_{\mathrm{act}}/RT}}$$

Arrhenius equations

$$\boxed{\ln k(T_2) \;=\; \ln k(T_1) \;-\; \frac{E_{\mathrm{act}}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

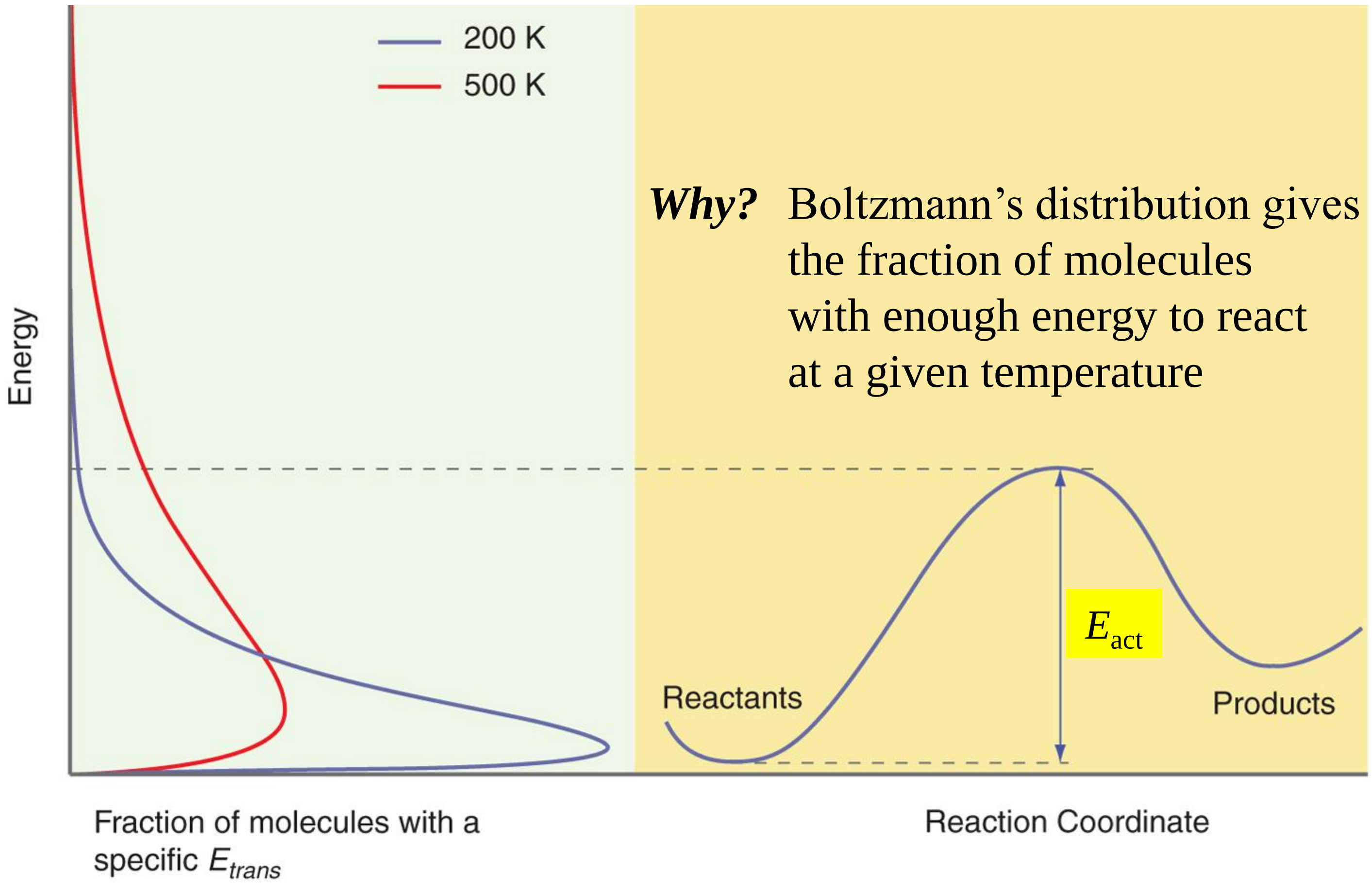
$k(T)$ = rate constant at temperature T

A = rate constant in the limit $T \to \infty$

E_{act} = molar activation energy

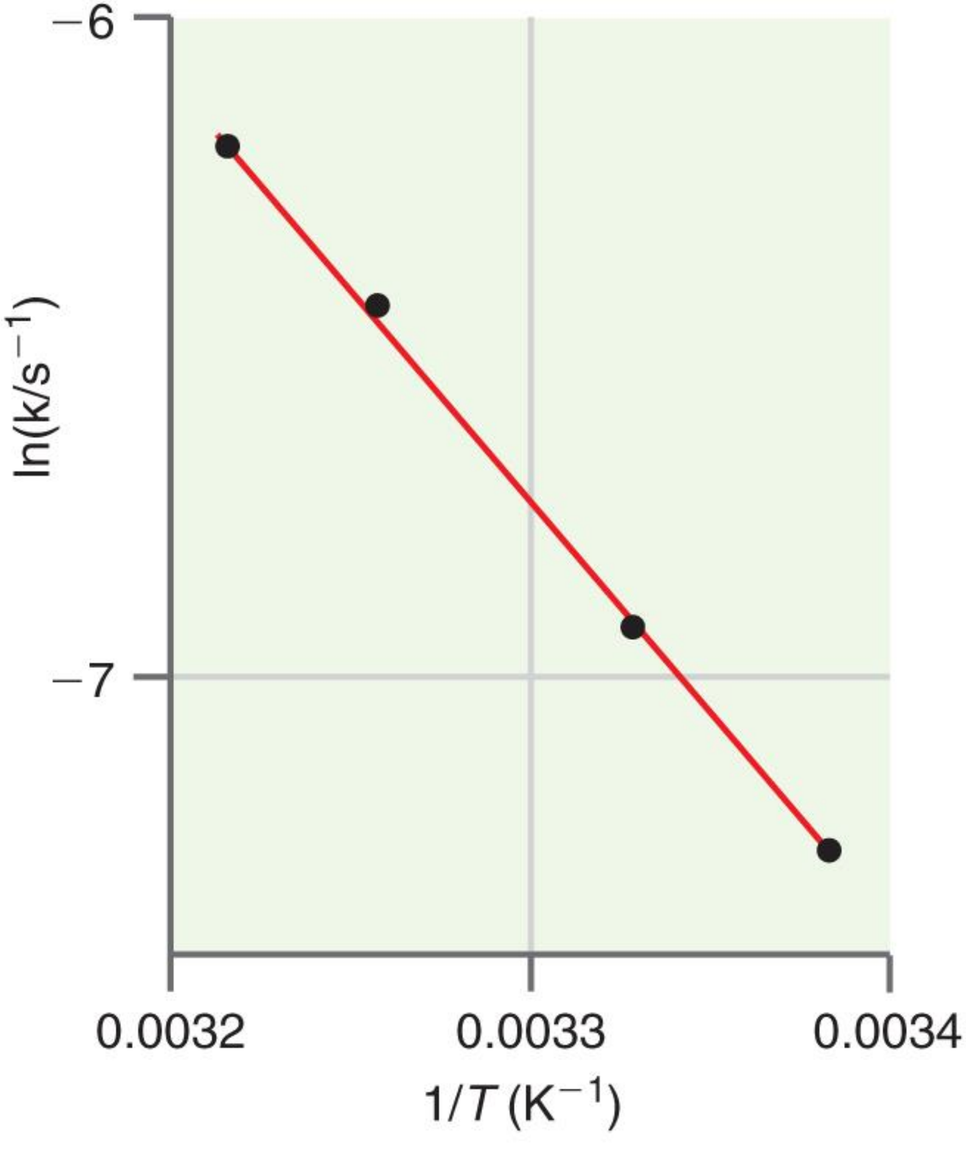
Temperature Dependence of Rate Constants

$$\boxed{k(T) \; = \; A\mathrm{e}^{-E_{\mathrm{act}}/RT}}$$



Why? Boltzmann’s distribution gives the fraction of molecules with enough energy to react at a given temperature

Arrhenius Plot: ln*k* against 1/*T*



slope = $-E_{act}/R$

Example The rate constant for a chemical reaction doubles for every 20 degree temperature increase near room temperature. Estimate the activation energy.

Use: $T_A = 290\ \text{K}$ $\qquad k_A$

$k_B/k_A = 2$

$T_B = 310\ \text{K}$ $\qquad k_B$

$$\ln k(T_B) - \ln k(T_A) = \ln\left(\frac{k_B}{k_A}\right) = -\frac{E_{act}}{R}\left(\frac{1}{T_B} - \frac{1}{T_A}\right)$$

$$\ln 2 = -\frac{E_{act}}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{310\ \text{K}} - \frac{1}{290\ \text{K}}\right)$$

activation energy $\boldsymbol{E_{act} = 25{,}900\ \textbf{J mol}^{-1}}$

Zero-Order Reactions

$$\mathbf{A} \xrightarrow{k_0} \mathbf{B}$$

$$\boxed{\text{reaction rate} = k_0[\text{A}]^0 = k_0(1) = k_0 \quad \text{(a constant)}}$$

Rare for homogenous systems! Can occur for reactions limited by a fixed number of catalytic sites or light intensity (photochemical reactions). Integrating this rate law gives [A] as a function of time:

$$\frac{\mathrm{d}[\text{A}]}{\mathrm{d}t} = -k_0 \quad \Rightarrow \quad \mathrm{d}[\text{A}] = -k_0\mathrm{d}t$$

$$\int_{[\text{A}]_0}^{[\text{A}]_t} \mathrm{d}[\text{A}] = -k_0 \int_0^t \mathrm{d}t \quad \Rightarrow \quad \boxed{[\text{A}]_t - [\text{A}]_0 = -k_0 t}$$

$$(\text{ show } \; [\text{B}]_t = [\text{B}]_0 + k_0 t \;)$$

First-Order Reactions

$$\mathbf{A} \xrightarrow{k_1} \mathbf{B}$$

$$\boxed{\text{reaction rate} = k_1[\mathrm{A}]^1 = k_1[\mathrm{A}]}$$

Very important! One of the most common types of chemical kinetics. Integrating the first-order rate law gives:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_1[\mathrm{A}] \quad \Rightarrow \quad \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]} = \mathrm{d}\ln[\mathrm{A}] = -k_1\mathrm{d}t$$

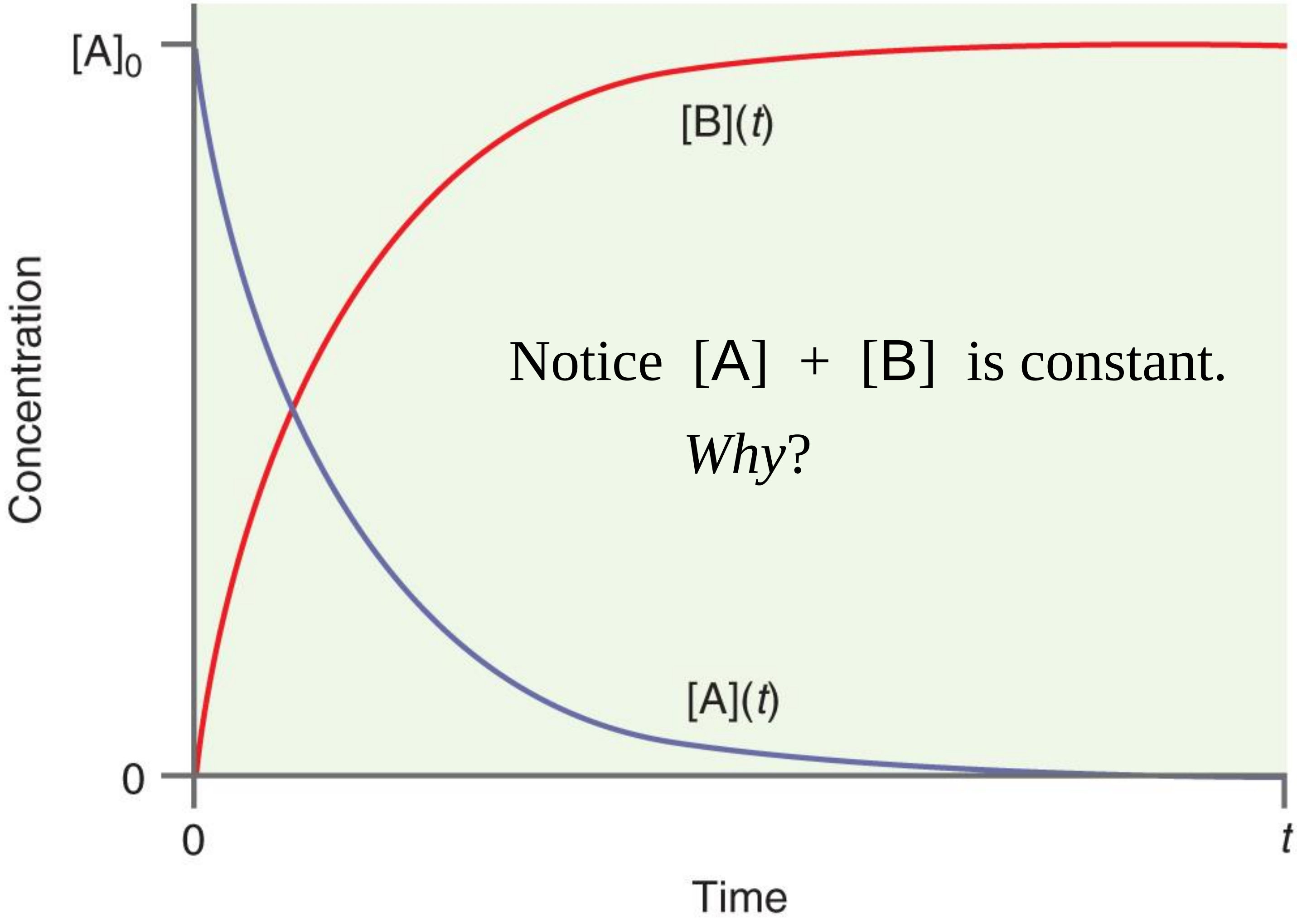
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \mathrm{d}\ln[\mathrm{A}] = -k_1\int_0^t \mathrm{d}t \quad \Rightarrow \quad \ln[\mathrm{A}]_t - \ln[\mathrm{A}]_0 = -k_1 t$$

$$\ln\left([\mathrm{A}]_t/[\mathrm{A}]_0\right) = -k_1 t \quad \Rightarrow \quad \boxed{[\mathrm{A}]_t = [\mathrm{A}]_0 \mathrm{e}^{-k_1 t}}$$

($[\mathrm{B}]_t$?)

First-Order Reaction Kinetics

$$A \xrightarrow{k_1} B$$



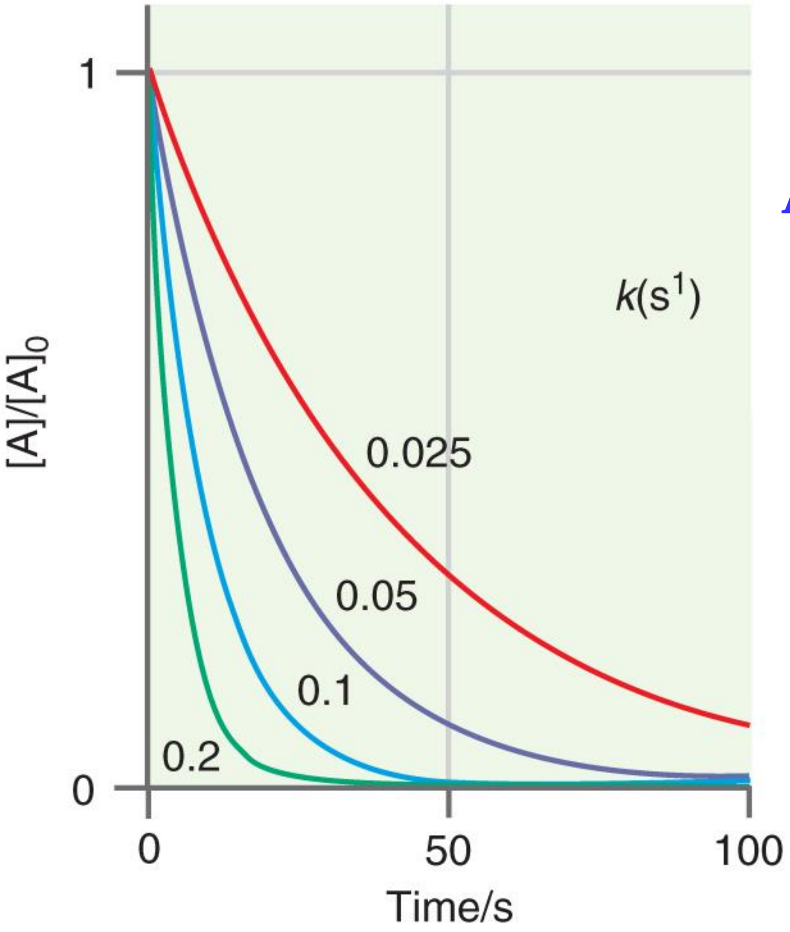
Notice [A] + [B] is constant.

Why?

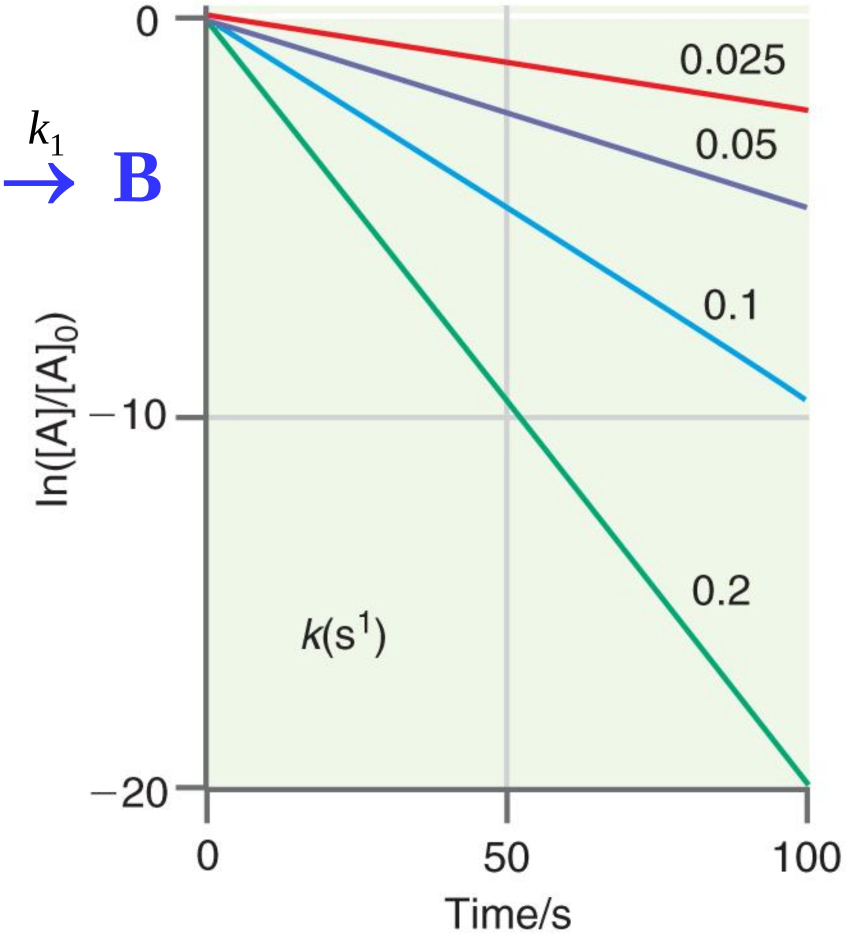
First-Order Reaction Kinetics

$[A]/[A]_0$ *vs.* time t
(curved plots)

$\ln([A]/[A]_0)$ *vs.* time t
(linear plots, slope $-k_1$)



$$\mathbf{A} \xrightarrow{k_1} \mathbf{B}$$



Second-Order Reactions

$$\mathbf{A + A \xrightarrow{k_2} B} \qquad \textbf{(Type I)}$$

$$\boxed{\text{reaction rate} = k_2[\mathrm{A}]^2}$$

Bimolecular reaction of A. Also very important!

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_2[\mathrm{A}]^2 \quad \Rightarrow \quad \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]^2} = -\mathrm{d}\left(\frac{1}{[\mathrm{A}]}\right) = -k_2\mathrm{d}t$$

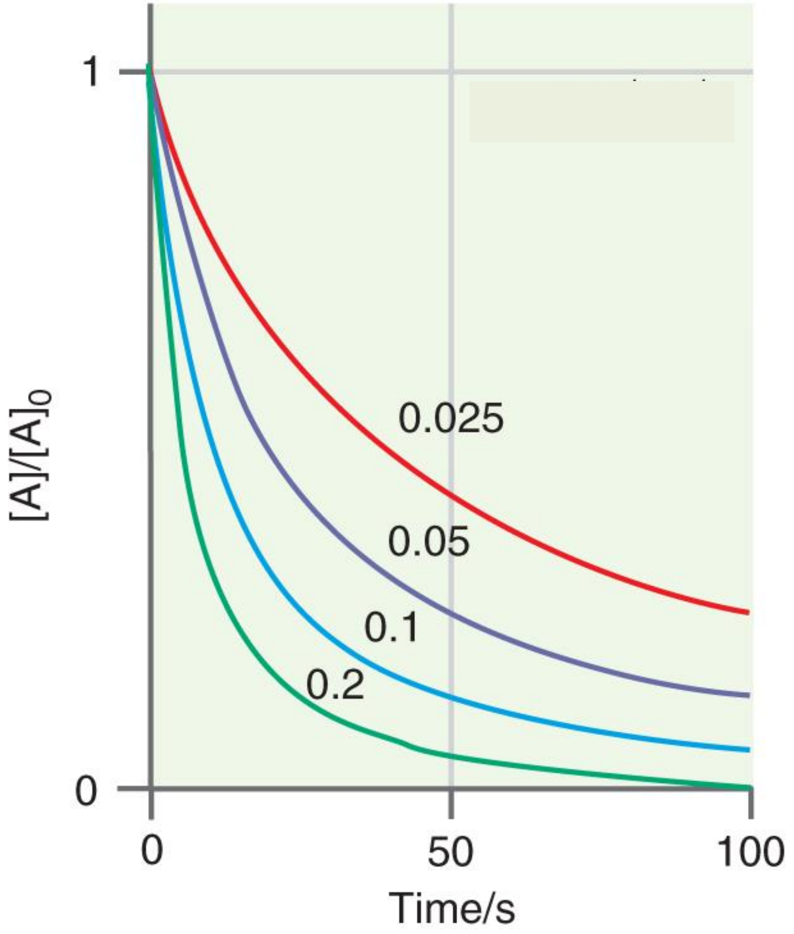
$$\int_{1/[\mathrm{A}]_0}^{1/[\mathrm{A}]_t} \mathrm{d}\left(\frac{1}{[\mathrm{A}]}\right) = k_2\int_0^t \mathrm{d}t \quad \Rightarrow \quad \boxed{\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = k_2 t}$$

($[\mathrm{B}]_t$?)

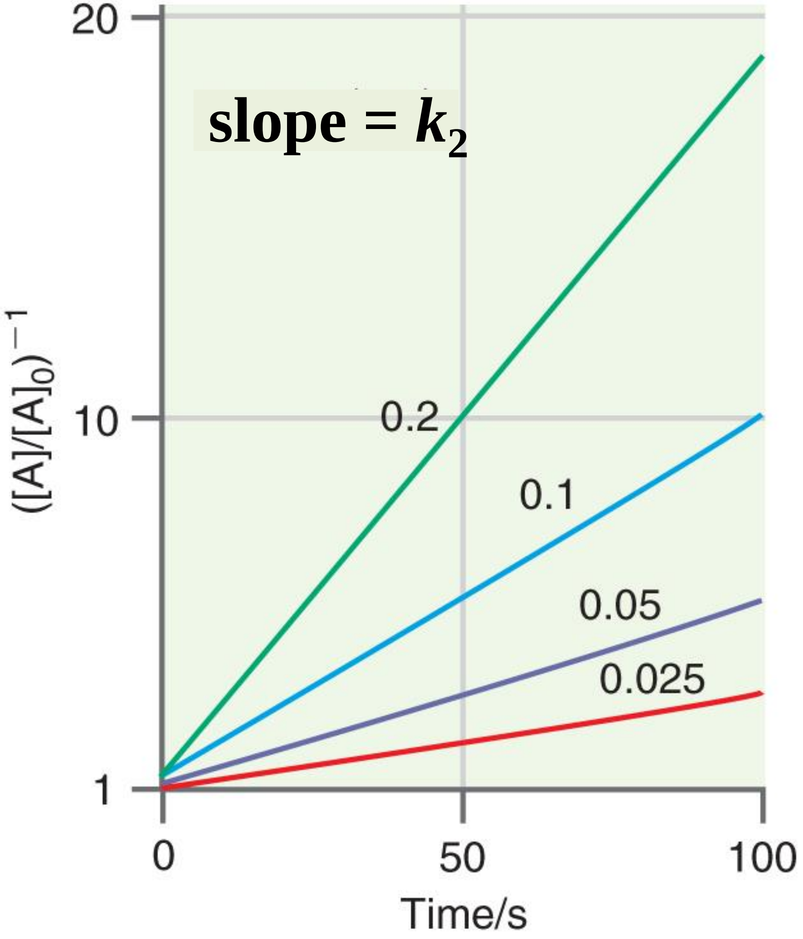
Second-Order Reactions

$$A + A \xrightarrow{k_2} B$$ **(Type I)**

$[A]/[A]_0$ *vs.* time *t* (curved)



$([A]/[A]_0)^{-1}$ *vs.* time *t* (linear)



slope = k_2

Second-Order Reactions

$$\mathbf{A} + \mathbf{B} \xrightarrow{k_2} \mathbf{P} \qquad \textbf{(Type II)}$$

$$\boxed{\text{reaction rate} = k_2[\mathrm{A}][\mathrm{B}]}$$

Bimolecular reaction of A and B. Math a bit trickier! From the reaction stoichiometry, notice: $[\mathrm{A}] - [\mathrm{A}]_0 = [\mathrm{B}] - [\mathrm{B}]_0$. Use the abbreviation $\boldsymbol{a} = \mathbf{[A]_0 - [B]_0}$ to give $[\mathrm{B}] = [\mathrm{A}] - a$ and

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_2[\mathrm{A}][\mathrm{B}] = -k_2[\mathrm{A}]([\mathrm{A}]-a)$$

$$\int_{1\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{\mathrm{d}[\mathrm{A}]}{[\mathrm{A}]([\mathrm{A}]-a)} = \frac{1}{a}\int \mathrm{d}\ln\left(\frac{[\mathrm{A}]-a}{[\mathrm{A}]}\right) = -k_2\int_0^t \mathrm{d}t$$

Derive (or look up!) this integral

$$\boxed{\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\ln\left(\frac{[\mathrm{B}]_t/[\mathrm{B}]_0}{[\mathrm{A}]_t/[\mathrm{A}]_0}\right) = k_2 t}$$

“Simple” Reaction Kinetics

$A \rightarrow P$

$A + A \rightarrow P$

$A + B \rightarrow P$

$A \rightarrow I \rightarrow P$

$$\begin{tikzcd}
 & P1 \\
A \arrow[ur] \arrow[dr] & \\
 & P2
\end{tikzcd}$$

The differential equations describing the reaction rates can be **solved analytically** (*i.e.*, integrated) to calculate concentrations of reactants and products as functions of time.

Nice, but what about *real-world* reactions?

Example Thermal "cracking" of ethane (from natural gas and petroleum) for the industrial production of ethylene, about 10^8 tonnes per year worth about \$$10^{11}$.
A **few** of the important reaction steps:

initiation $C_2H_6 \rightarrow 2\,CH_3^\bullet$

propagation $CH_3^\bullet + C_2H_6 \rightarrow CH_4 + C_2H_5^\bullet$

$C_2H_5^\bullet \rightarrow C_2H_4 + H^\bullet$

$H^\bullet + C_2H_6 \rightarrow C_2H_5^\bullet + H_2$

termination $H^\bullet + C_2H_5^\bullet \rightarrow C_2H_6$

Analytical solution of the rate equations: ***Mission Impossible***

Numerical Methods for Solving Reaction Rate Equations

Chemical reactions of practical significance frequently involve **many reactions with many different reactants and products**.

The differential equations describing these reactions are very complicated to solve analytically, or have no analytical solutions.

What to do? Give up?

Never !

Applied math and numerical methods ***to the rescue*** …

From first-year calculus:

$$\boxed{f(x+\mathrm{d}x) \;=\; f(x) \;+\; \frac{\mathrm{d}f}{\mathrm{d}x}\,\mathrm{d}x}$$

Practical application to chemical kinetics:

$$\boxed{[\mathrm{A}]_{t+\mathrm{d}t} \;=\; [\mathrm{A}]_t \;+\; \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}\,\mathrm{d}t}$$

Given the concentrations of reactants and products at time *t*, use the reaction equations to calculate the concentrations at time $t + \Delta t$, then repeat (iterate).

Numerical Methods for Chemical Kinetics

Example **A** reacts to form intermediate **I**
which reacts to form product **P**

$$\mathbf{A} \xrightarrow{k_\mathrm{I}} \mathbf{I} \xrightarrow{k_\mathbf{P}} \mathbf{P}$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_\mathrm{I}[\mathrm{A}]$$

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = k_\mathrm{I}[\mathrm{A}] - k_\mathrm{P}[\mathrm{I}]$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_\mathrm{I}[\mathrm{I}]$$

Solve these equations numerically …

Numerical Methods for Chemical Kinetics

Example **A** reacts to form intermediate **I**
which reacts to form product **P**

$$\mathbf{A} \xrightarrow{k_{\mathrm{I}}} \mathbf{I} \xrightarrow{k_{\mathbf{P}}} \mathbf{P}$$

$$[\mathrm{A}]_{t+\Delta t} = [\mathrm{A}]_t + \frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t}\Delta t = [\mathrm{A}]_t - k_{\mathrm{I}}[\mathrm{A}]_t\Delta t$$

$$[\mathrm{I}]_{t+\Delta t} = [\mathrm{I}]_t + \frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\Delta t = [\mathrm{I}]_t + k_{\mathrm{I}}[\mathrm{A}]_t\Delta t - k_{\mathrm{P}}[\mathrm{I}]_t\Delta t$$

$$[\mathrm{P}]_{t+\Delta t} = [\mathrm{P}]_t + \frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t}\Delta t = [\mathrm{P}]_t + k_{\mathrm{P}}[\mathrm{I}]_t\Delta t$$

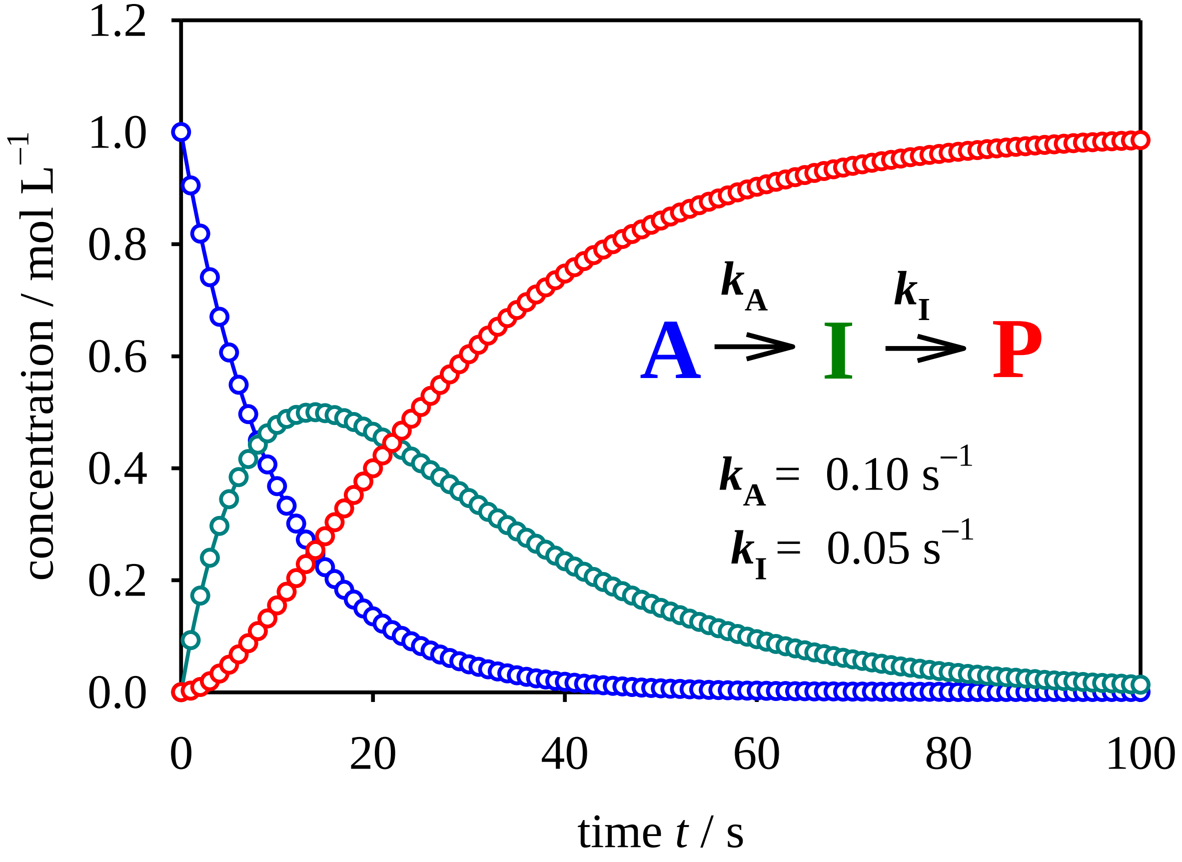
Numerical Methods for Chemical Kinetics

$$\mathbf{A} \xrightarrow{k_{\mathrm{I}}} \mathbf{I} \xrightarrow{k_{\mathbf{P}}} \mathbf{P}$$

```
KI = .10                          ! set rate constant KI
KP = .05                          ! set rate constant KP
T = .0
DT = .01                          ! set time increment DT
TMAX = 100.                       ! stop calculations at time TMAX
A = 1.                            ! set initial A concentration
I = .0                            ! set initial I concentrations
P = .0                            ! set initial P concentrations
JMAX = TMAX/DT
!
FOR J = 1 to JMAX                 ! take JMAX time steps DT
A = A – (KI*A*DT)
I = I + (KI*A*DT) - (KP*I*DT)
P = P + (KP*I*DT)
T = T + DT
PRINT “time, [A], [I], [P]: “, T, A, I, P
NEXT J
!
END
```

Comparison of analytical and numerical solutions of kinetic equations

$\Delta t \; = \; 0.01$ s



Reaction Mechanisms

A **sequence of single-step elementary reactions**, adding up to convert reactants to products in a stoichiometric reaction.

The **molecularity** (unimolecular or bimolecular) is the number of molecules involved in an elementary reaction.

$A \rightarrow P$ **unimolecular**

$A + A \rightarrow P$ **bimolecular**

$A + B \rightarrow P$ **bimolecular**

(Trimolecular elementary reactions are rarely important. ***Why?***)

Reaction Mechanisms

In general, there is no relationship between a stoichiometric chemical reaction and the reaction rate law.

In contrast, the rate law for an elementary reaction is obtained directly from elementary reaction equation:

$\mathbf{A} \rightarrow \mathbf{P}$ $\quad$ $d[P]/dt = k_1[A]$

$\mathbf{A} + \mathbf{A} \rightarrow \mathbf{P}$ $\quad$ $d[P]/dt = k_2[A]^2$

$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{P}$ $\quad$ $d[P]/dt = k_2[A][B]$

Reaction Mechanisms

! Warning !

- determining reaction mechanisms can be very difficult (*but very interesting chemical detective work!*)

- many reaction intermediates are short-lived (< 1 ns), present only in trace amounts (< 1 ppb) and not easily detected

- a variety of experimental techniques may be required, such as uv, vis, IR, or mass spectroscopy or isotope substitution

- more than one mechanism can be consistent with kinetic data

Reaction Mechanisms

An **embarrassing** case study, the **hydrogen-iodine reaction:**

$$\mathbf{H_2(g) + I_2(g) \rightarrow 2HI(g)}$$

Experiments give the rate law

$$\frac{\mathrm{d[HI]}}{\mathrm{d}t} = k_2[\mathrm{H_2}][\mathrm{I_2}]$$

The mechanism is “obviously” the elementary bimolecular reaction step $\mathbf{H_2 + I_2 \rightarrow 2HI}$ to form hydrogen iodide.

This mechanism is found in hundreds of chemistry textbooks, even in an acceptance speech given by a Nobel Laureate.

Reaction Mechanisms

But wait! Another mechanism for the classic reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

was suggested by kineticist Max Bodenstein in 1898:

$I_2(g) \rightarrow 2I(g)$ fast

$H_2(g) + I(g) \rightarrow H_2I(g)$ fast

$H_2I(g) + I(g) \rightarrow 2HI(g)$ slow

Recent experiments using flash photolysis and other techniques (not available in 1898) showed Bodenstein's mechanism is correct!

(Show the bimolecular and Bodenstien mechanisms lead to the *same* rate law.)

Section 18.7 Sequential First-Order Reactions

$$\mathbf{A} \xrightarrow{k_\mathrm{A}} \mathbf{I} \xrightarrow{k_\mathrm{I}} \mathbf{P}$$

A reacts to form **intermediate** I which reacts to form **product** **P**.

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

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = k_\mathrm{A}[\mathrm{A}] - k_\mathrm{I}[\mathrm{I}]$$

$$\frac{\mathrm{d}[\mathrm{P}]}{\mathrm{d}t} = k_\mathrm{I}[\mathrm{I}]$$

Solving the differential equations for the sequential reactions

$$\mathbf{A} \xrightarrow{k_\mathrm{A}} \mathbf{I} \xrightarrow{k_\mathrm{I}} \mathbf{P}$$

with **initial conditions** $[\mathrm{A}]_0 > 0,\ [\mathrm{I}]_0 = 0,\ [\mathrm{P}]_0 = 0$ gives

$$[\mathrm{A}]_t = [\mathrm{A}]_0\,\mathrm{e}^{-k_\mathrm{A}t}$$

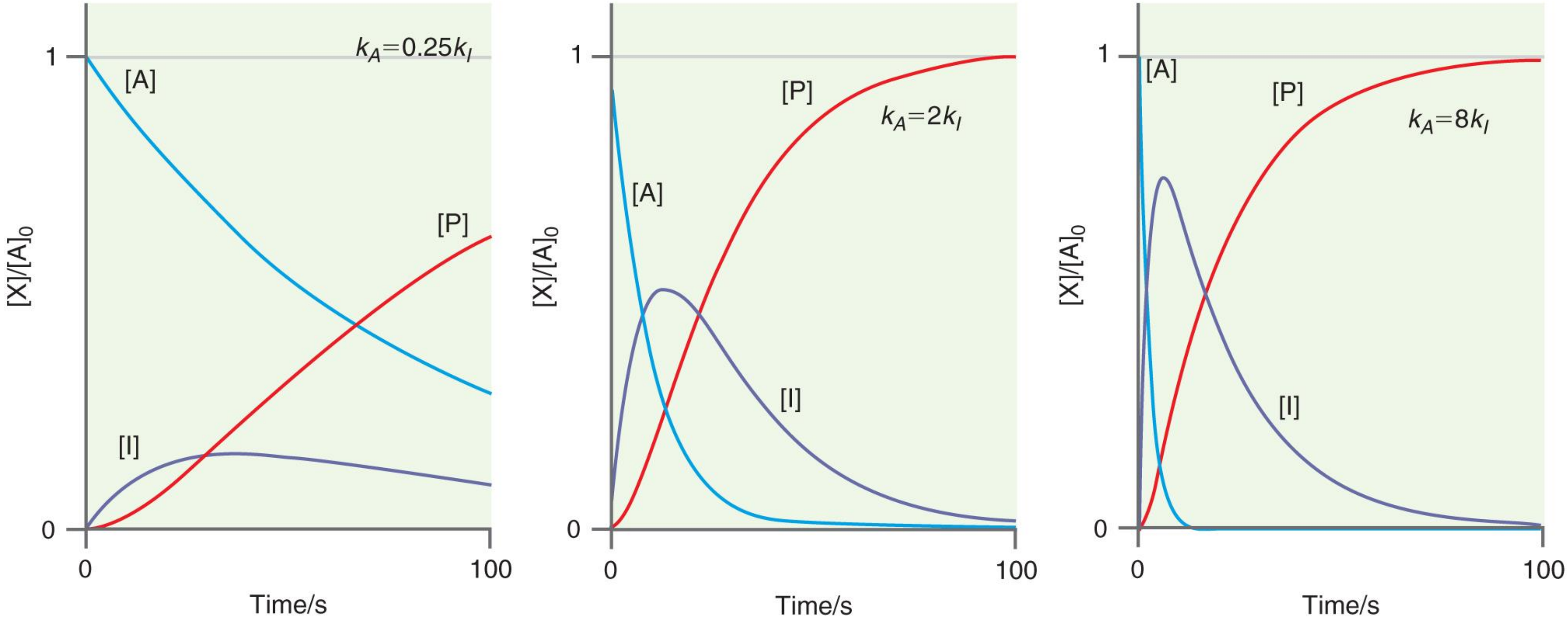
$$[\mathrm{I}]_t = [\mathrm{A}]_0\,\frac{k_\mathrm{A}}{k_\mathrm{I}-k_\mathrm{A}}\left(\mathrm{e}^{-k_\mathrm{A}t}-\mathrm{e}^{-k_\mathrm{I}t}\right)$$

$$[\mathrm{P}]_t = [\mathrm{A}]_0\left(1 + \frac{k_\mathrm{A}\mathrm{e}^{-k_\mathrm{I}t}-k_\mathrm{I}\mathrm{e}^{-k_\mathrm{A}t}}{k_\mathrm{I}-k_\mathrm{A}}\right)$$

Sequential reactions: $\mathbf{A} \xrightarrow{k_\mathrm{A}} \mathbf{I} \xrightarrow{k_\mathrm{I}} \mathbf{P}$

Notice $[\mathrm{A}]_t + [\mathrm{I}]_t + [\mathrm{P}]_t = [\mathrm{A}]_0$ ***why?***

Intermediate concentration [I] passes through a maximum value.



Sequential reactions: $\mathbf{A} \xrightarrow{k_\mathrm{A}} \mathbf{I} \xrightarrow{k_\mathrm{I}} \mathbf{P}$

Maximum concentration of intermediate I at t_{max}:

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = [\mathrm{A}]_0 \frac{k_\mathrm{A}}{k_\mathrm{I} - k_\mathrm{A}} \frac{\mathrm{d}}{\mathrm{d}t}\left(\mathrm{e}^{-k_\mathrm{A} t} - \mathrm{e}^{-k_\mathrm{I} t}\right) = 0$$

$$\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t} = [\mathrm{A}]_0 \frac{k_\mathrm{A}}{k_\mathrm{I} - k_\mathrm{A}} \left(-k_\mathrm{A} \mathrm{e}^{-k_\mathrm{A} t_{\mathrm{max}}} + k_\mathrm{I} \mathrm{e}^{-k_\mathrm{I} t_{\mathrm{max}}}\right) = 0$$

$$-k_\mathrm{A} \mathrm{e}^{-k_\mathrm{A} t_{\mathrm{max}}} + k_\mathrm{I} \mathrm{e}^{-k_\mathrm{I} t_{\mathrm{max}}} = 0$$

$$\boxed{t_{\mathrm{max}} = \frac{1}{k_\mathrm{A} - k_\mathrm{I}} \ln\left(\frac{k_\mathrm{A}}{k_\mathrm{I}}\right)}$$

Rate-Determining Step 1

$$\mathbf{A} \xrightarrow[\textbf{slow}]{k_{\mathrm{A}}} \mathbf{I} \xrightarrow[\textbf{fast}]{k_{\mathrm{I}}} \mathbf{P}$$

$$\boxed{k_{\mathrm{A}} << k_{\mathrm{I}}} \qquad \mathbf{A} \xrightarrow{k_{\mathrm{A}}} \mathbf{I}$$

$$\left[[\mathrm{I}]_t = [\mathrm{A}]_0 \frac{k_{\mathrm{A}}}{k_{\mathrm{I}} - k_{\mathrm{A}}} \left(\mathrm{e}^{-k_{\mathrm{A}} t} - \mathrm{e}^{-k_{\mathrm{I}} t} \right) \right]_{\substack{\textbf{limit} \\ k_{\mathrm{A}}/k_{\mathrm{I}} \to 0}} = [\mathrm{A}]_0 \frac{k_{\mathrm{A}}}{k_{\mathrm{I}}}$$

$$\left[[\mathrm{P}]_t = [\mathrm{A}]_0 \left(1 + \frac{k_{\mathrm{A}} \mathrm{e}^{-k_{\mathrm{I}} t} - k_{\mathrm{I}} \mathrm{e}^{-k_{\mathrm{A}} t}}{k_{\mathrm{I}} - k_{\mathrm{A}}} \right) \right]_{\substack{\textbf{limit} \\ k_{\mathrm{A}}/k_{\mathrm{I}} \to 0}} = [\mathrm{A}]_0 \left(1 - \mathrm{e}^{-k_{\mathrm{A}} t} \right)$$

Rate-Determining Step 2 $\mathbf{A} \xrightarrow[\text{fast}]{k_\mathrm{A}} \mathbf{I} \xrightarrow[\text{slow}]{k_\mathrm{I}} \mathbf{P}$

$$\boxed{k_\mathrm{A} \;>>\; k_\mathrm{I}} \qquad \mathbf{I} \xrightarrow{k_\mathrm{I}} \mathbf{P}$$

$$\left[[\mathrm{I}]_t \;=\; [\mathrm{A}]_0 \frac{k_\mathrm{A}}{k_\mathrm{I} - k_\mathrm{A}} \left(\mathrm{e}^{-k_\mathrm{A} t} - \mathrm{e}^{-k_\mathrm{I} t} \right) \right] \;=\; [\mathrm{A}]_0 \mathrm{e}^{-k_\mathrm{I} t}$$

limit

$\boldsymbol{k_\mathrm{A}/k_\mathrm{I} \to \infty}$

$$\left[[\mathrm{P}]_t \;=\; [\mathrm{A}]_0 \left(1 \;+\; \frac{k_\mathrm{A} \mathrm{e}^{-k_\mathrm{I} t} - k_\mathrm{I} \mathrm{e}^{-k_\mathrm{A} t}}{k_\mathrm{I} - k_\mathrm{A}} \right) \right] \;=\; [\mathrm{A}]_0 \left(1 - \mathrm{e}^{-k_\mathrm{I} t} \right)$$

limit

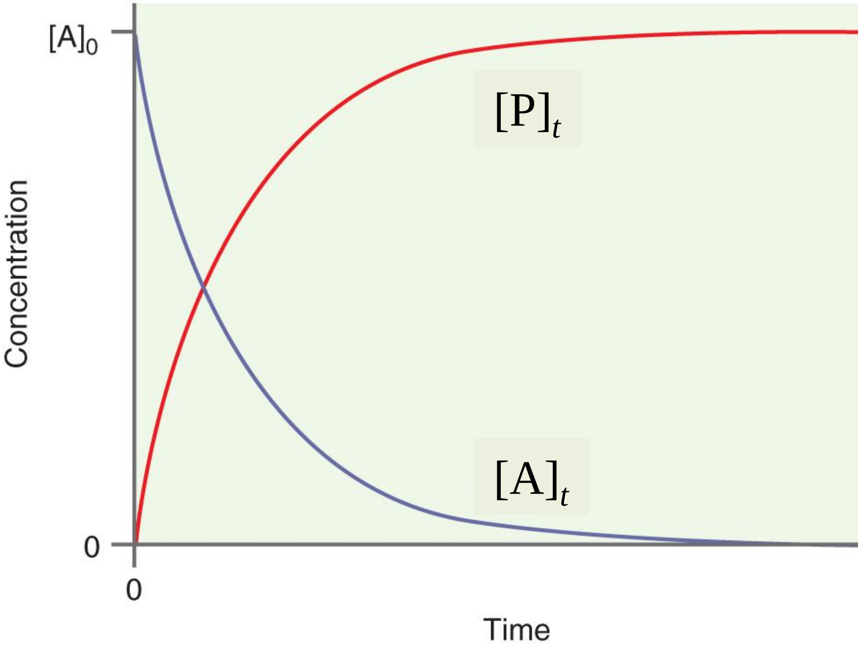
$\boldsymbol{k_\mathrm{A}/k_\mathrm{I} \to \infty}$

Limiting Cases

$\boxed{k_A \ll k_I}$

$$A \xrightarrow{\text{slow}} I \xrightarrow{\text{fast}} P$$

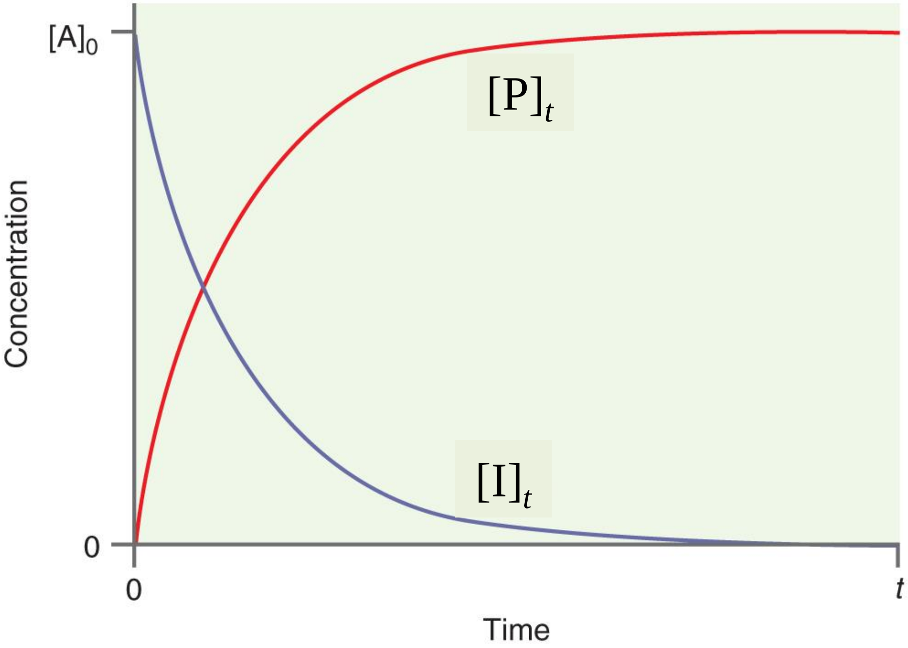
(only traces of intermediate I present)



$\boxed{k_A \gg k_I}$

$$A \xrightarrow{\text{fast}} I \xrightarrow{\text{slow}} P$$

(reactant A used up very quickly)



<u>**Steady-State**</u>

$$\mathbf{A} \xrightarrow{k_\mathrm{A}} \mathbf{I} \xrightarrow{k_\mathrm{I}} \mathbf{P}$$

Intermediate **I** is produced from **A** as rapidly as it decomposes to **P**.

at steady state:

$$\boxed{\frac{\mathrm{d[I]}}{\mathrm{d}t} = k_\mathrm{A}[\mathrm{A}] - k_\mathrm{I}[\mathrm{I}]_\mathrm{SS} = 0}$$

$$\boxed{[\mathrm{I}]_\mathrm{SS} = \frac{k_\mathrm{A}}{k_\mathrm{I}}[\mathrm{A}]_t}$$

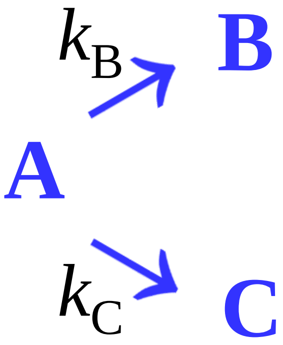
Product formation using the steady-state approximation:

$$\frac{\mathrm{d[P]}}{\mathrm{d}t} = k_\mathrm{I}[\mathrm{I}]_\mathrm{SS} = k_\mathrm{I}\frac{k_\mathrm{A}}{k_\mathrm{I}}[\mathrm{A}]_t = k_\mathrm{A}[\mathrm{A}]_0\mathrm{e}^{-k_\mathrm{A}t}$$

$$[\mathrm{P}]_t = [\mathrm{A}]_0(1 - \mathrm{e}^{-k_\mathrm{A}t})$$

(same result for $k_\mathrm{A} >> k_\mathrm{I}$)

Section 18.8 Parallel First-Order Reactions



$$\frac{d[A]}{dt} = -k_B[A] - k_C[A] = -(k_B + k_C)[A]$$

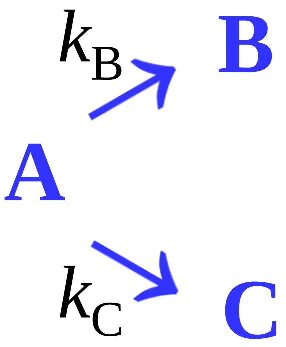
$$\frac{d[B]}{dt} = k_B[A]$$

$$\frac{d[C]}{dt} = k_C[A]$$

initial conditions
(at $t = 0$):

$[A]_0 > 0$
$[B] = 0$
$[C] = 0$

Parallel First-Order Reactions



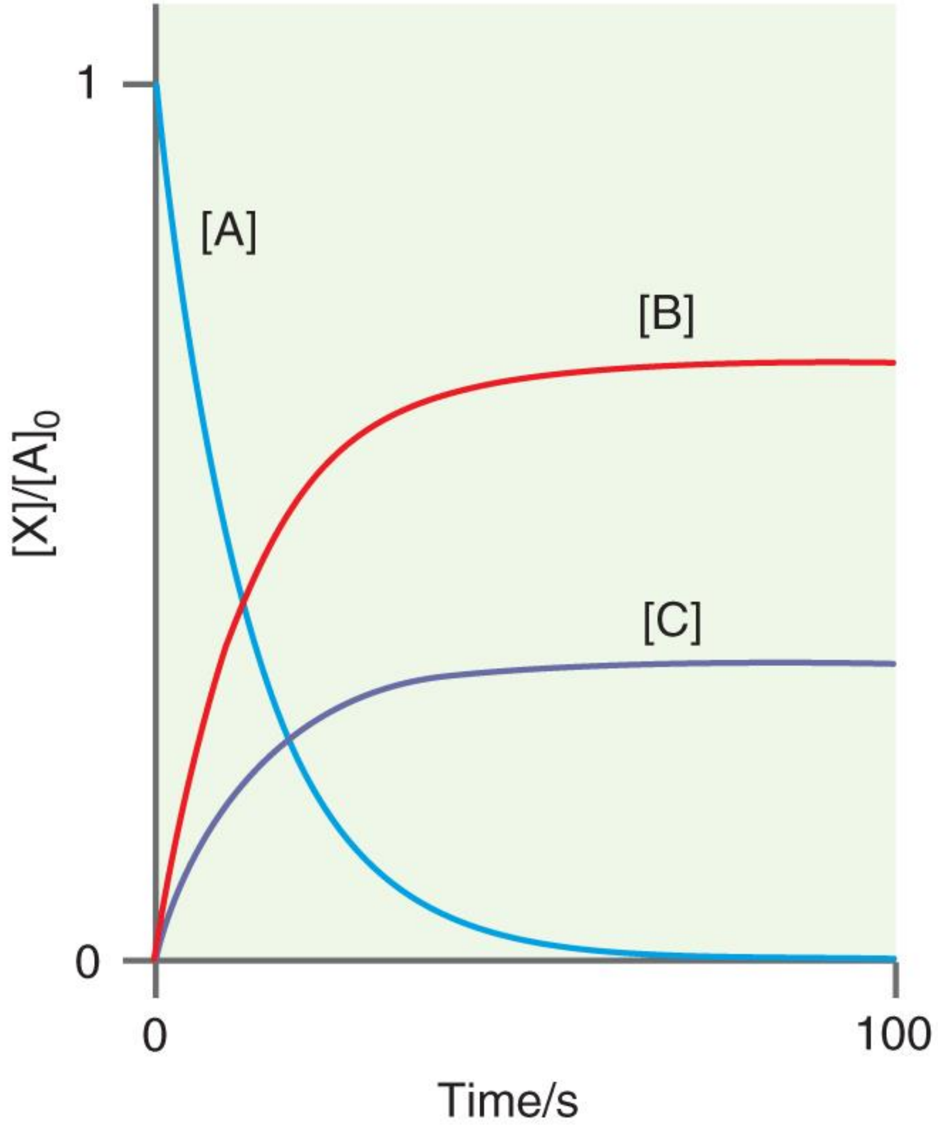
$$\begin{tikzcd} & \mathbf{B} \\ \mathbf{A} \arrow[ur, "k_{\mathrm{B}}"] \arrow[dr, "k_{\mathrm{C}}"'] & \\ & \mathbf{C} \end{tikzcd}$$

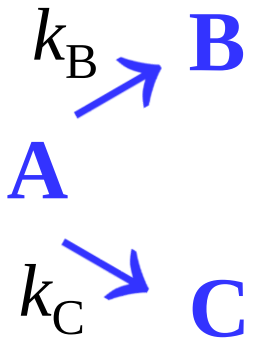
$$[\mathrm{A}]_t = [\mathrm{A}]_0\, \mathrm{e}^{-(k_{\mathrm{B}}+k_{\mathrm{C}})t}$$

$$[\mathrm{B}]_t = \frac{k_{\mathrm{B}}}{k_{\mathrm{B}}+k_C}[\mathrm{A}]_0\left(1 - \mathrm{e}^{-(k_{\mathrm{B}}+k_{\mathrm{C}})t}\right)$$

$$[\mathrm{C}]_t = \frac{k_C}{k_{\mathrm{B}}+k_C}[\mathrm{A}]_0\left(1 - \mathrm{e}^{-(k_{\mathrm{B}}+k_{\mathrm{C}})t}\right)$$

Parallel First-Order Reactions



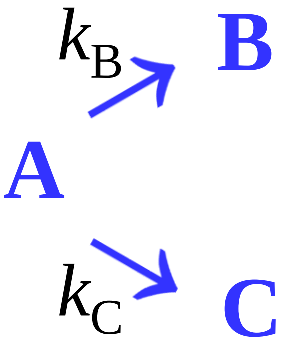


$$\begin{tikzcd} & B \\ A \arrow[ur, "k_B"] \arrow[dr, "k_C"'] & \\ & C \end{tikzcd}$$

$k_B = 0.10\ s^{-1}$

$k_C = 0.05\ s^{-1}$

Parallel First-Order Reaction Yields Φ_i



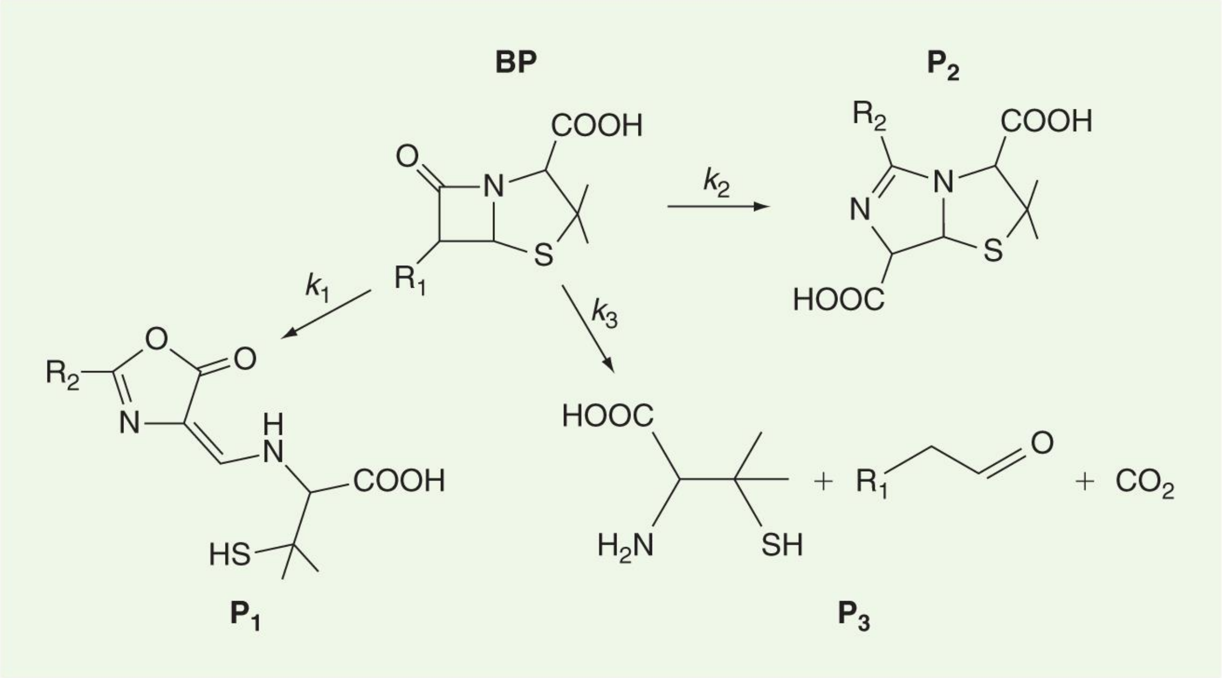
Φ_B is defined as the probability A reacts to form product B:

$$\Phi_B = \frac{[B]}{[B]+[C]} = \frac{k_B}{k_B + k_C}$$

Φ_C for product C:

$$\Phi_C = \frac{[C]}{[B]+[C]} = \frac{k_C}{k_B + k_C}$$

Parallel First-Order Reaction Yields



Benzyl penicillin (BP) reacts to form products P_1, P_2 and P_3 with

$k_1 = 0.00070\ \mathrm{s}^{-1}$
$k_2 = 0.0041\ \mathrm{s}^{-1}$
$k_3 = 0.0057\ \mathrm{s}^{-1}$

yield for the formation of P_1:

$$\Phi_{\mathrm{P1}} = \frac{k_1}{k_1 + k_2 + k_3} = \frac{0.00070\ \mathrm{s}^{-1}}{0.00070\ \mathrm{s}^{-1} + 0.0041\ \mathrm{s}^{-1} + 0.0057\ \mathrm{s}^{-1}} = 0.067$$

(6.7 %)

Section 18.10 Reversible Reactions

$$\mathrm{A} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathrm{B}$$

Irreversible (“one-way” →) reactions have been studied up to now. Back reactions assumed to be negligible.

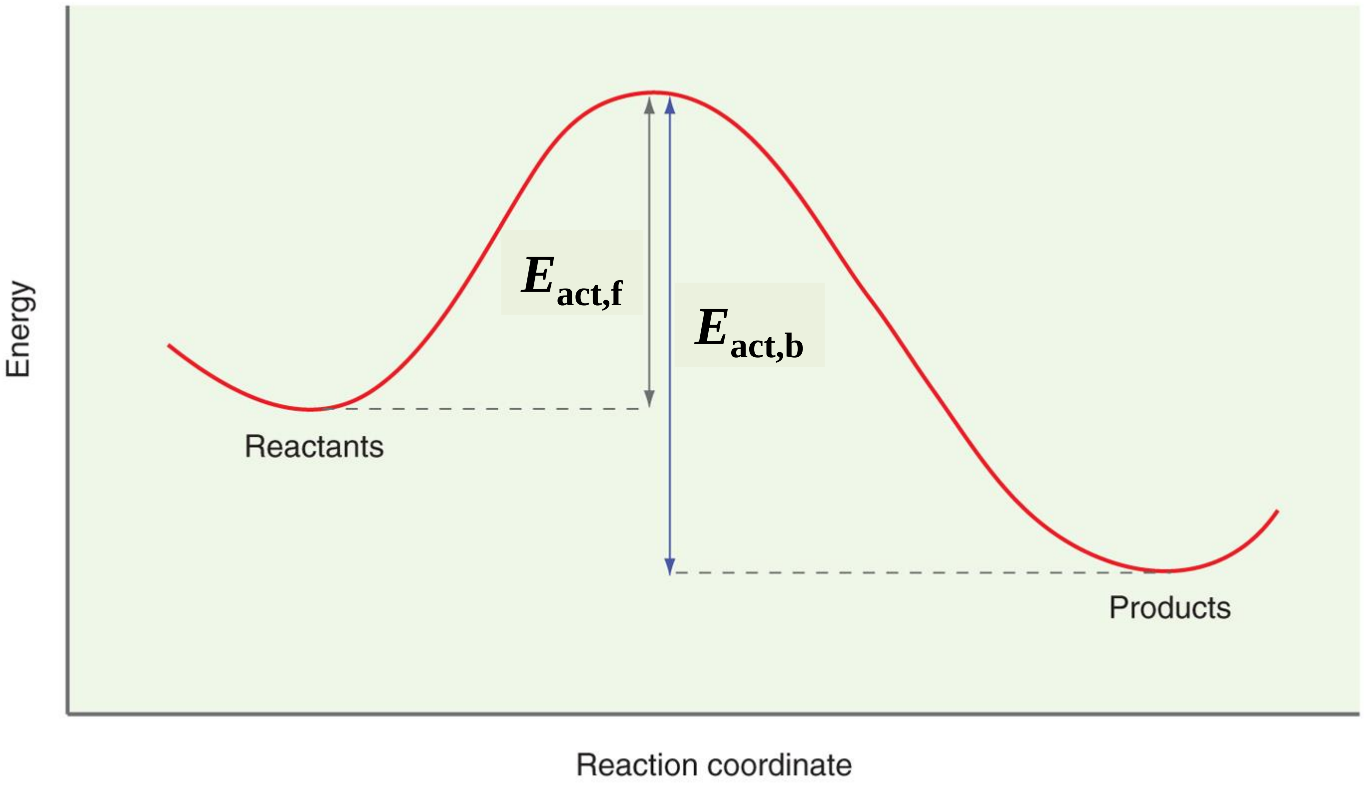
But for many systems, depending on the energetics, both forward and back reactions are significant.

Rate constants for **reversible** reactions are used to calculate equilibrium constants, **linking kinetics and thermodynamics**.

Reversible Reactions – *Why*?

$$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B$$

Forward and back reactions can both be important if their activation energies are similar.



Reversible Reaction, an Example

$$\mathbf{A} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathbf{B}$$

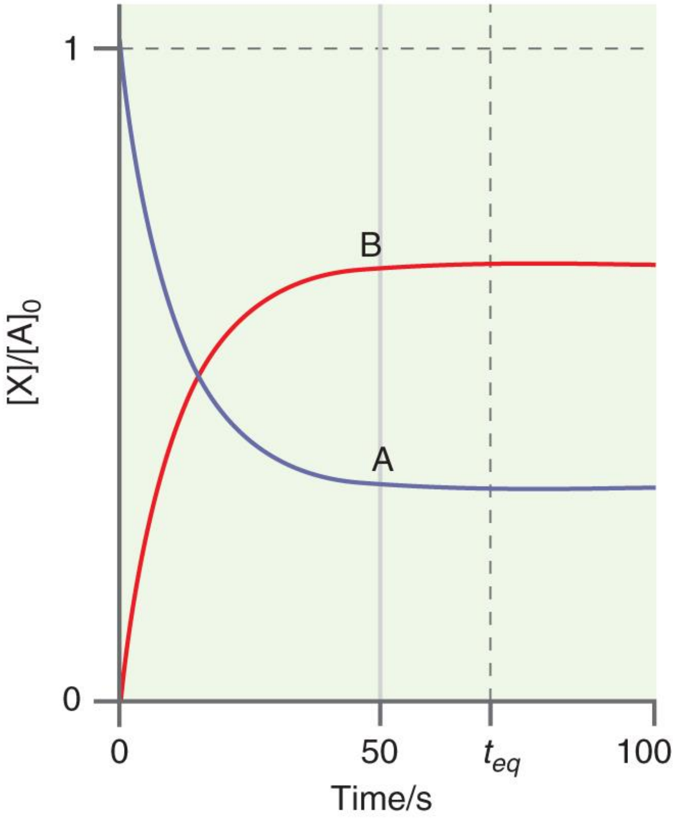
Including both forward and back reactions:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_\mathrm{f}[\mathrm{A}] + k_\mathrm{b}[\mathrm{B}]$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_\mathrm{f}[\mathrm{A}] - k_\mathrm{b}[\mathrm{B}]$$

Reversible Reaction

$$\mathbf{A} \underset{k_\mathrm{b}}{\overset{k_\mathrm{f}}{\rightleftarrows}} \mathbf{B}$$



A and B are loaded into a container and react to reach equilibrium.

The concentrations of A and B reach constant values as $t \to \infty$. ***Makes sense.***

Okay, but the equilibrium [B]/[A] ratio is constant, independent of the initial A and B concentrations. ***Why !***

Reversible Reactions

$$\mathbf{A} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathbf{B}$$

Forward and back reactions **at equilibrium**:

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_f[\mathrm{A}] + k_b[\mathrm{B}] \mathbf{= 0}$$

$$\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = k_f[\mathrm{A}] - k_b[\mathrm{B}] \mathbf{= 0}$$

(**no changes in the concentrations** of A or B)

Reversible Reactions

$$\mathbf{A} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathbf{B}$$

Forward and back reaction rates equal at equilibrium:

$$-k_f[A]_{eq} + k_b[B]_{eq} \quad \mathbf{= \ 0}$$

$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{k_f}{k_b} = K_{\text{equilibrium}}$$

Significance:

- Rate constants for chemical reactions can be used to calculate thermodynamic equilibrium constants
- Chemical equilibrium is **dynamic**

Example The rate constants for the reversible dissociation of water

$$H_2O(l) \underset{k_b}{\overset{k_f}{\rightleftarrows}} H^+(aq) + OH^-(aq)$$

are $k_f = 2.5 \times 10^{-5}\ s^{-1}$ and $k_b = 1.4 \times 10^{11}\ L\ mol^{-1}\ s^{-1}$ at 25 °C. Calculate the equilibrium constant.

At equilibrium:

$$\frac{d[H_2O]}{dt} = -k_f[H_2O] + k_b[H^+][OH^-] = 0$$

Equilibrium constant:

$$K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} = \frac{k_f}{k_b} = \frac{2.5\times10^{-5}s^{-1}}{1.4\times10^{11}\ L\ mol^{-1}\ s^{-1}} = 1.8\times10^{-16}\,mol\,L^{-1}$$

The equilibrium constant for the dissociation of water

$$\mathbf{H_2O(\mathit{l})\ \underset{\boldsymbol{k_b}}{\overset{\boldsymbol{k_f}}{\rightleftarrows}}\ H^+(aq)\ +\ OH^-(aq)}$$

at 25 °C is $K_{eq} = \dfrac{[H^+][OH^-]}{[H_2O]} = 1.8\times10^{-16}\,\mathrm{mol\,L^{-1}}$ **from kinetics**.

But wait! Everyone knows $K_w = 1.0 \times 10^{-14}\ \mathrm{mol\ L^{-1}}$ at 25 °C!
What's the difference? **Thermodynamic equilibrium constant K_w** uses Raoult's law for H_2O and Henry's law for H^+ and OH^- ions:

$$K_W = \frac{a_{H^+}\,a_{OH^-}}{a_{H_2O}} = \frac{\gamma_+[H^+]\ \gamma_-[OH^-]}{\gamma_{H_2O}\ x_{H_2O}} \approx \frac{(1)[H^+]\,(1)[OH^-]}{(1)\,(1)} = [H^+][OH^-]$$

$$\boxed{K_{eq} = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_W}{[H_2O]} = \frac{1.0\times10^{-14}\,\mathrm{mol^2\ L^{-2}}}{55\ \mathrm{mol\,L^{-1}}} = 1.8\times10^{-16}\,\mathrm{mol\,L^{-1}}}$$

Example $H^+(aq) + OH^-(aq) \xrightarrow{k_b} H_2O(l)$

Use $k_b = 1.4 \times 10^{11}$ L mol $^{-1}$ s^{-1} at 25 °C to calculate the half life of the reaction for initial conditions $[H^+]_0 = [OH^-]_0 = 0.50$ mol L^{-1}.

In this case $[H^+]_t = [OH^-]_t$ and $\dfrac{d[H^+]}{dt} = -k_b[H^+][OH^-] = -k_b[H^+]^2$

Second-Order Kinetics $$\boxed{\frac{1}{[H^+]_t} = \frac{1}{[H^+]_0} + k_b t}$$

At $t = t_{1/2}$: $$\frac{[H^+]_0}{[H^+]_{t1/2}} = \frac{[H^+]_0}{[H^+]_0/2} = 2 = [H^+]_0\left(\frac{1}{[H^+]_0} + k_b t_{1/2}\right)$$

The half life is $$t_{1/2} = \frac{1}{k_b[H^+]_0} = \frac{1}{(1.4\times10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1})(0.50\ \text{mol L}^{-1})} = 1.4\times10^{-11}\ \text{s}$$

14 trillionths of a second! This is a *fast reaction* !

Another example of fast forward and backward reactions:

Nitric Acid Production

Step 1 $4\ NH_3 + 5\ O_2 = 4\ NO + 6\ H_2O$

Step 2 $2\ NO + O_2 = 2\ NO_2$ **(interesting kinetics!)**

Step 3 $3\ NO_2 + H_2O = 2\ HNO_3 + NO$

Step 2 $2\,NO + O_2 = 2\,NO_2$

Experiments give the **empirical rate equation**:

$$\frac{d[NO_2]}{dt} = k[NO]^2[O_2]$$

A *tri-molecular* elementary reaction ?

Experiments also show rate constant k decreases with temperature.

A *negative* activation energy ?

What's going on?

Step 2 $\quad 2\,\mathrm{NO} + \mathrm{O_2} = 2\,\mathrm{NO_2}$

First: $\mathrm{NO} + \mathrm{NO} \underset{k_{1b}}{\overset{k_{1f}}{\rightleftarrows}} \mathrm{N_2O_2}$ **fast and reversible**

forward rate = backward rate

$k_{1f}[\mathrm{NO}]^2 = k_{1b}[\mathrm{N_2O_2}]$ gives $[\mathrm{N_2O_2}] = \dfrac{k_{1f}}{k_{1b}}[\mathrm{NO}]^2$

Then: $\mathrm{N_2O_2} + \mathrm{O_2} \xrightarrow[\text{slow}]{k_2} 2\,\mathrm{NO_2}$ $\quad \dfrac{d[\mathrm{NO_2}]}{dt} = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$

Overall: $2\mathrm{NO} + \mathrm{O_2} \rightarrow 2\,\mathrm{NO_2}$

$$\frac{d[\mathrm{NO_2}]}{dt} = k_2 \frac{k_{1f}}{k_{1b}}[\mathrm{NO}]^2[\mathrm{O_2}]$$

$$= k\,[\mathrm{NO}]^2[\mathrm{O_2}]$$

Step 2 $2\,NO + O_2 = 2\,NO_2$

experimental rate law:

$$\frac{d[NO_2]}{dt} = -k\,[NO]^2[O_2]$$

A ***tri*-molecular** $NO + NO + O_2 \rightarrow 2NO_2$ mechanism involving an impossible three-body collision?

NO! … Two bimolecular and one unimolecular elementary reactions with rate constants k_f, k_b, k_2 give

apparent rate constant $k = k_2 k_{1f} / k_{2b}$

Step 2 $2\,\mathrm{NO} \;+\; \mathrm{O_2} \;=\; 2\,\mathrm{NO_2}$

experimental rate law:

$$\frac{\mathrm{d}[\mathrm{NO_2}]}{\mathrm{d}t} = -k\,[\mathrm{NO}]^2[\mathrm{O_2}]$$

Rate constant *k* decreases with temperature.

A *negative* activation energy ?

$$k(T) \;=\; A\mathrm{e}^{-E_{\mathrm{act}}/RT}$$

$$\frac{\mathrm{d}k(T)}{\mathrm{d}T} \;=\; A\frac{E_{\mathrm{act}}}{RT^2}\mathrm{e}^{-E_{\mathrm{act}}/RT} \;=\; \frac{k}{RT^2}E_{\mathrm{act}} \quad < \quad 0 \;\; ?$$

Step 2 $2\,NO + O_2 = 2\,NO_2$

rate law with apparent rate constant *k* that **decreases with *T***

$$\frac{d[NO_2]}{dt} = -k\,[NO]^2[O_2]$$

Why? *k* is a composite of three “true” rate constants k_{1f}, k_{2f}, k_2.

$$NO + NO \underset{k_{1b}}{\overset{k_{1f}}{\rightleftarrows}} N_2O_2 \qquad N_2O_2 + O_2 \xrightarrow{k_2} 2\,NO_2$$

$$k = \frac{k_{1f}}{k_{1b}}k_2 = K_{eq}k_2$$

k drops as *T* is raised because *k* is proportional to k_{1f}/k_{2b}, the equilibrium constant K_{eq} for the exothermic (bond forming) NO + NO = N_2O_2 reaction. K_{eq} (and therefore *k*) decreases strongly with *T*. From thermodynamics, recall the **Van’t Hoff equation:**

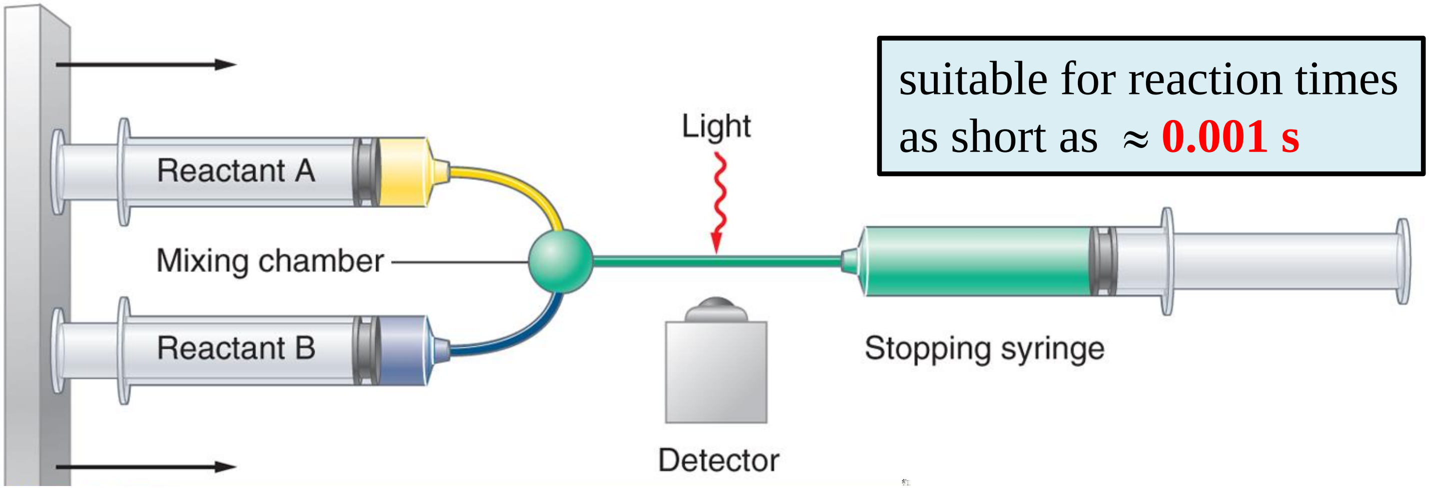
$$d\ln K_{eq} / dT = \Delta H / RT^2 \qquad \Delta H < 0$$

Fast Reactions – Require Special Measurement Techniques

(***Why?*** Fast reactions can occur before the reactants are completely mixed, producing reactant concentrations that are not well defined.)

Stopped-Flow Methods

Reactants A and B are held in solution syringes. Operating the syringes rapidly mixes the solutions in a T-junction. The reaction is monitored by measuring changes absorbance downstream from the mixing junction.



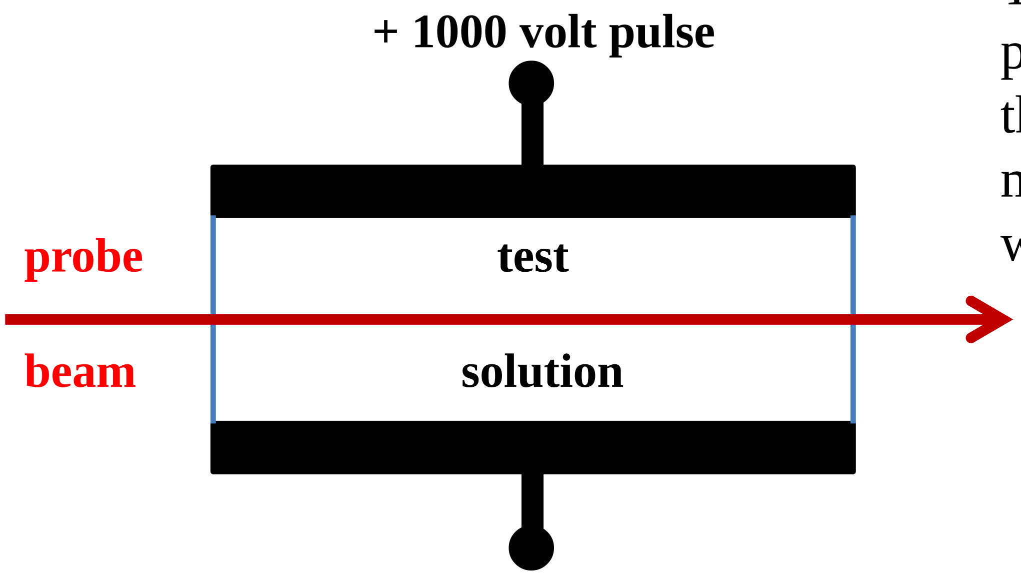
suitable for reaction times as short as ≈ **0.001 s**

Ok, but what about *really fast* reactions?

[*e.g.*, $H^+(aq) + OH^-(aq) \rightarrow H_2O(\mathit{l})$ in *trillionths* of a second]

Relaxation-Perturbation Methods*

Reactants and products are **suddenly** removed (“perturbed”) from equilibrium by a short laser pulse, optical flash, shock wave or electrical discharge.



The return of reactant and product concentrations to the new equilibrium values is measured by spectrophotometry with fast data acquisition.

suitable for reaction times as short as ≈ 10^{-15} s !

*1967 Chemistry Nobel Prize for Manfred Eigen for studies of fast reactions.

Relaxation-Perturbation Methods

Example 1

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{B}$$

A and B are initially in equilibrium, with equal forward back reaction rates:

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_\mathrm{f}[\mathrm{A}]_\mathrm{eq} + k_\mathrm{b}[\mathrm{B}]_\mathrm{eq} = 0$$

$$K_\mathrm{eq}(T) = \frac{k_\mathrm{f}}{k_\mathrm{b}} = \frac{[\mathrm{B}]_\mathrm{eq}}{[\mathrm{A}]_\mathrm{eq}}$$

Relaxation-Perturbation Method for A ↔ B

At time $t = 0$, the temperature jumps from T to $T + \Delta T$, changing the equilibrium constant from $K(T)$ to $K(T + \Delta T)$.

The concentrations of A and B are now displaced from their new equilibrium values, by $\xi(t)$ and $-\xi(t)$ respectively.

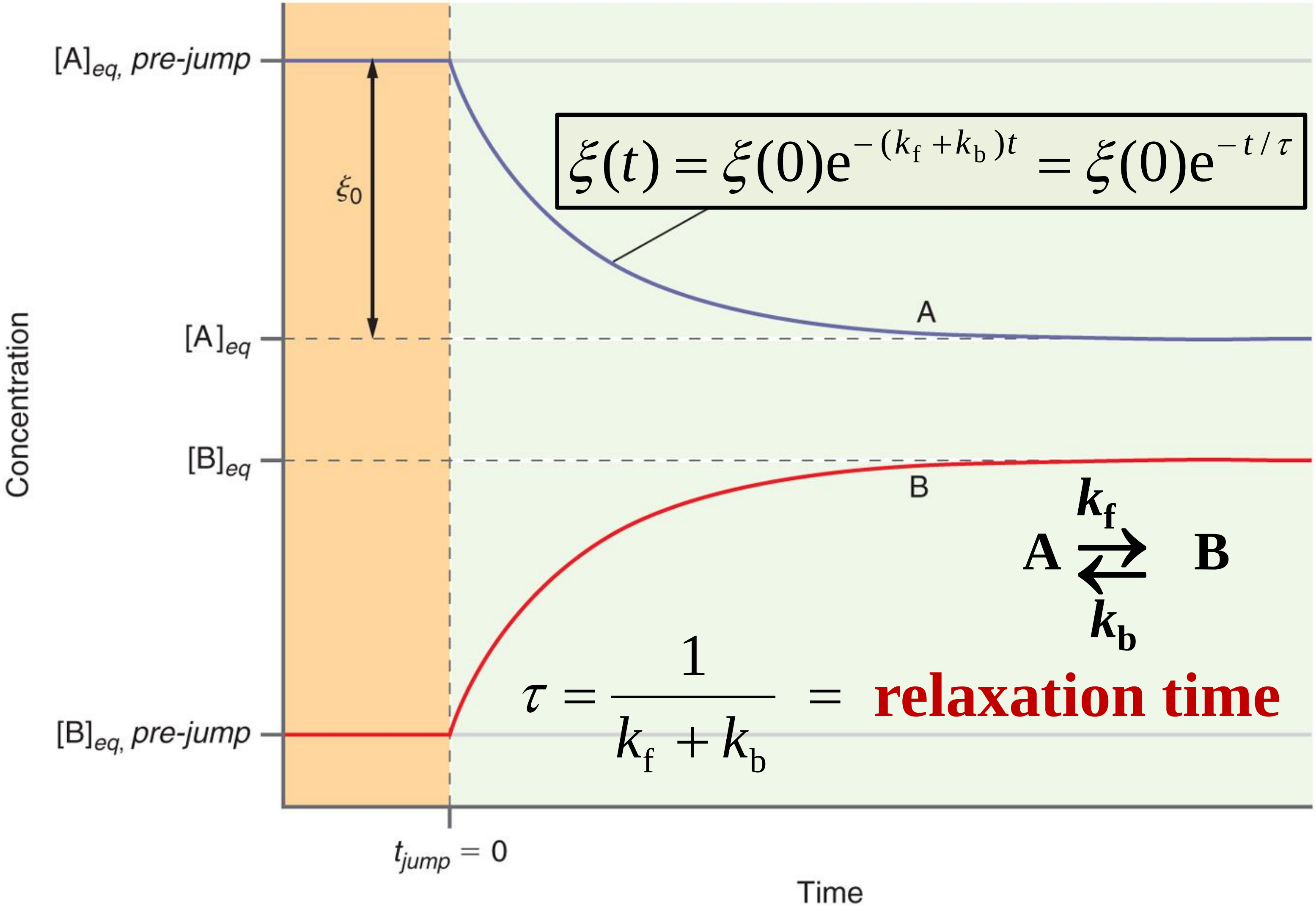
$$\frac{\mathrm{d}\left([\mathrm{A}]_{\mathrm{eq}} + \xi(t)\right)}{\mathrm{d}t} = -k_{\mathrm{f}}\left([\mathrm{A}]_{\mathrm{eq}} + \xi(t)\right) + k_{\mathrm{b}}\left([\mathrm{B}]_{\mathrm{eq}} - \xi(t)\right)$$

$$\cancelto{\text{cancel}}{\frac{\mathrm{d}[\mathrm{A}]_{\mathrm{eq}}}{\mathrm{d}t}} + \frac{\mathrm{d}\xi(t)}{\mathrm{d}t} = \cancelto{\text{cancel}}{-k_{\mathrm{f}}[\mathrm{A}]_{\mathrm{eq}} + k_{\mathrm{b}}[\mathrm{B}]_{\mathrm{eq}}} - (k_{\mathrm{f}} + k_{\mathrm{b}})\xi(t)$$

$$\boxed{\frac{\mathrm{d}\xi(t)}{\mathrm{d}t} = -(k_{\mathrm{f}} + k_{\mathrm{b}})\xi(t)}$$

$$\mathbf{A} \underset{\boldsymbol{k_{\mathrm{b}}}}{\overset{\boldsymbol{k_{\mathrm{f}}}}{\rightleftarrows}} \mathbf{B}$$

At time $t = 0$, A and B are slightly "perturbed" from their equilibrium concentrations, then react to regain equilibrium.



$$\boxed{\xi(t) = \xi(0)e^{-(k_f + k_b)t} = \xi(0)e^{-t/\tau}}$$

$$\mathbf{A} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathbf{B}$$

$$\tau = \frac{1}{k_f + k_b} =$$ **relaxation time**

Relaxation-Perturbation Methods

Example 2 Self-Ionization of Water (Section 18.12)

$$\mathrm{H_2O(liquid)} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{H^+(aq)} + \mathrm{OH^-(aq)}$$

initial equilibrium ($t < 0$):

$$\frac{\mathrm{d[H_2O]}}{\mathrm{d}t} = -k_\mathrm{f}[\mathrm{H_2O}]_\mathrm{eq} + k_\mathrm{b}[\mathrm{H^+}]_\mathrm{eq}[\mathrm{OH^-}]_\mathrm{eq} = 0$$

$$K_\mathrm{eq}(T) = \frac{k_\mathrm{f}}{k_\mathrm{b}} = \frac{[\mathrm{H^+}]_\mathrm{eq}[\mathrm{OH^-}]_\mathrm{eq}}{[\mathrm{H_2O}]_\mathrm{eq}}$$

Self-Ionization of Water

At time $t = 0$, the temperature jumps from T to $T + \Delta T$, changing the equilibrium constant from $K(T)$ to $K(T + \Delta T)$.

The concentration of H_2O and concentrations of H^+ and OH^- are displaced from equilibrium by $\xi(t)$ and $-\xi(t)$ respectively.

$$\frac{d\left([H_2O]_{eq} + \xi(t)\right)}{dt} = -k_f\left([H_2O]_{eq} + \xi(t)\right) + k_b\left([H^+]_{eq} - \xi(t)\right)\left([OH^-]_{eq} - \xi(t)\right)$$

cancel **cancel**

$$\cancel{\frac{d[H_2O]_{eq}}{dt}} + \frac{d\xi(t)}{dt} = \cancel{-k_f[H_2O]_{eq} + k_b[H^+]_{eq}[OH^-]_{eq}} - k_f\xi(t)$$

2nd order ≈ 0

$$- k_b[H^+]_{eq}\xi(t) - k_b[OH^-]_{eq}\xi(t) + \cancel{k_b\xi(t)}\xi(t)$$

$$\boxed{\frac{d\xi(t)}{dt} = -\left(k_f + k_b\{[H^+]_{eq} + [OH^-]_{eq}\}\right)\xi(t)}$$

$$\mathbf{H_2O} \underset{\boldsymbol{k_b}}{\overset{\boldsymbol{k_f}}{\rightleftarrows}} \mathbf{H^+ + OH^-}$$

Self-Ionization of Water

$$H_2O \underset{k_b}{\overset{k_f}{\rightleftarrows}} H^+ + OH^-$$

$$\frac{\mathrm{d}\xi(t)}{\mathrm{d}t} = -\tau^{-1}\xi(t)$$

$$\xi(t) = \xi(0)\mathrm{e}^{-t/\tau}$$

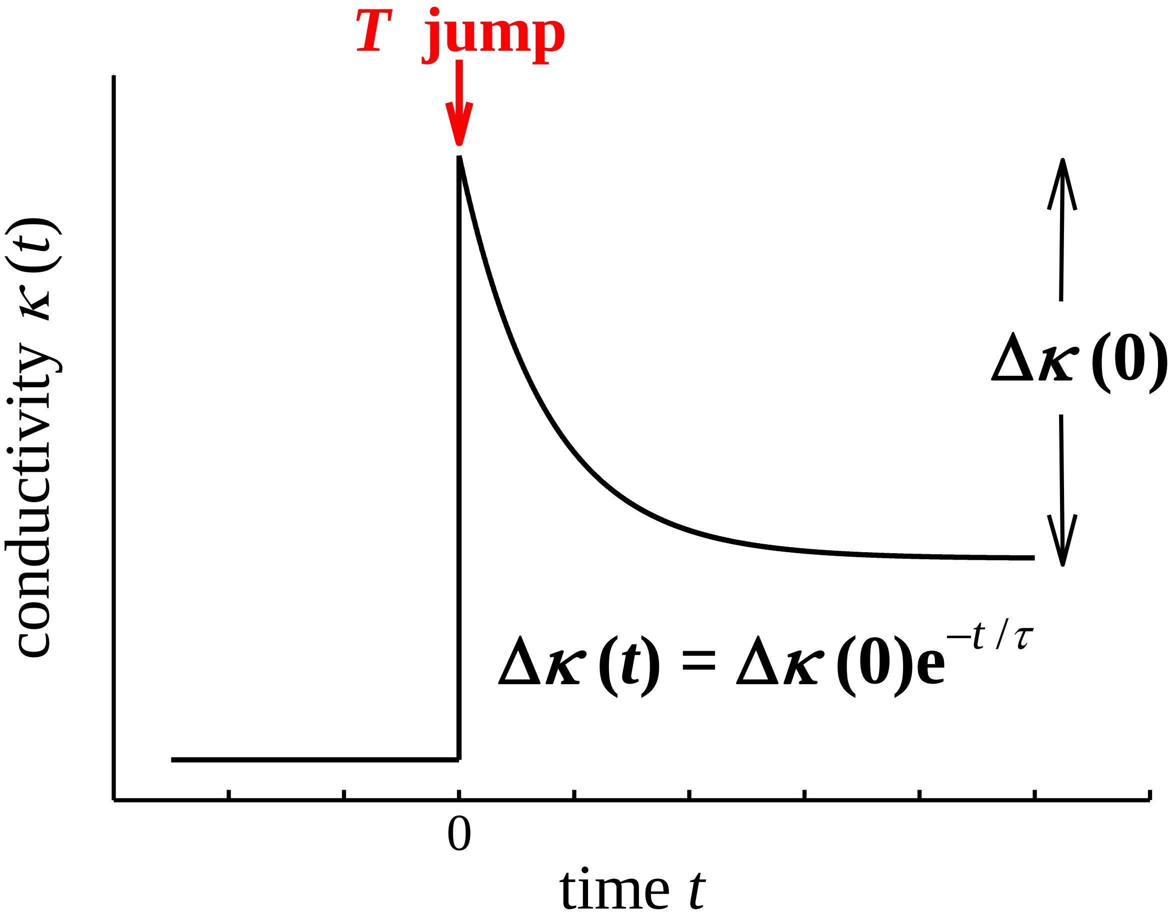
relaxation time:

$$\boxed{\tau = \frac{1}{k_\mathrm{f} + k_\mathrm{b}\{[\mathrm{H}^+]_\mathrm{eq} + [\mathrm{OH}^-]_\mathrm{eq}\}}}$$

Important: **Near equilibrium**, the first-order forward reaction and second-order back reaction simplify to give “psuedo-first-order” kinetics with rate constant $1/\tau$

Self-Ionization of Water

Calculate the **relaxation time τ** by measuring changes in the ionic conductivity after the temperature jump.



$$H_2O(\text{liquid}) \underset{k_b}{\overset{k_f}{\rightleftarrows}} H^+(aq) + OH^-(aq)$$

At 25 °C, thermodynamics gives the **equilibrium constant**

$$K_{eq}(T) = \frac{k_f}{k_b} = \frac{[H^+]_{eq}[OH^-]_{eq}}{[H_2O]_{eq}} = 1.8 \times 10^{-16}\ \text{mol L}^{-1}$$

and kinetic experiments give the **relaxation time**

$$\tau = \frac{1}{k_f + k_b\{[H^+]_{eq} + [OH^-]_{eq}\}} = 37 \times 10^{-6}\ \text{s}$$

Solve for

$$k_f = 2.5 \times 10^{-5}\ \text{s}^{-1}$$

$$k_b = 1.4 \times 10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

Diffusion-Controlled Reactions (Section 18.15)

Why are some reactions (such as $H^+ + OH^- \rightarrow H_2O$) so fast?

The molecules (or ions) react immediately as soon as they diffuse into contact.

Fick's law can be used to calculate rate constant k_2 for the **diffusion-controlled bimolecular reactions**.

$$\mathbf{A + B \xrightarrow{k_2} products}$$

In terms of the diffusion coefficients and sizes of the reactant molecules.

Diffusion-Controlled Reactions

The rate of the reaction

$$\mathbf{A + B \xrightarrow{k_2} products}$$

is controlled by the flux of B molecules into a sphere of radius *r* centered on molecule A. Using $4\pi r^2$ for the surface area of the sphere, the number of B molecules entering per unit time is

$$\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t} = -4\pi r^2 D_\mathrm{B} \frac{\mathrm{d}C_\mathrm{B}(r)}{\mathrm{d}r}$$

Integrating over *r* and using the bulk concentration [B] as $r \to \infty$:

$$C_\mathrm{B}(r) = \frac{\mathrm{d}N_\mathrm{B}/\mathrm{d}t}{4\pi r D_\mathrm{B}} + [\mathrm{B}]$$

Diffusion-Controlled Reactions

If the reaction

$$\mathbf{A} + \mathbf{B} \xrightarrow{\boldsymbol{k_2}} \textbf{products}$$

is diffusion-controlled, the concentration of B is zero at

$r = r_\mathrm{A} + r_\mathrm{B} = r_\mathrm{AB}$, the collision diameter of A and B molecules.

$$-\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t} = 4\pi D_\mathrm{B}\, r_\mathrm{AB}[\mathrm{B}]$$

This is the reaction rate <u>for one A molecule</u>. Multiplying by the number of A molecules $n_\mathrm{A} N_\mathrm{av}$ (moles of A times Avogadro's number) and dividing the volume gives the reaction rate per unit volume:

$$N_\mathrm{av}\frac{n_\mathrm{A}}{V}\left(-\frac{\mathrm{d}N_\mathrm{B}}{\mathrm{d}t}\right) = 4\pi N_\mathrm{av} D_\mathrm{B}\, r_\mathrm{AB}[\mathrm{A}][\mathrm{B}]$$

Diffusion-Controlled Reactions

So far, the rate of the reaction

$$\mathbf{A} + \mathbf{B} \xrightarrow{k_2} \mathbf{products}$$

has been analyzed in terms of B molecules diffusing toward A molecules. But A molecules are diffusing too! Including the diffusion coefficient of the A molecules gives the reaction rate

$$k_2[\mathrm{A}][\mathrm{B}] = 4\pi N_{\mathrm{av}}(D_{\mathrm{A}} + D_{\mathrm{B}})r_{\mathrm{AB}}[\mathrm{A}][\mathrm{B}]$$

The **predicted bimolecular rate constant** for diffusion-controlled reactions is

$$\boxed{k_2 = 4\pi N_{\mathrm{av}}(D_{\mathrm{A}} + D_{\mathrm{B}})r_{\mathrm{AB}}}$$

Diffusion-Controlled Reaction – an Example

$$\mathbf{H^+(aq) \;+\; OH^-(aq) \;\xrightarrow{k_2}\; H_2O(\mathit{l})}$$

Data at 25 °C:

$$D_{\mathrm{H+}} = 9.3 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$$

$$D_{\mathrm{OH-}} = 5.3 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$$

$$r_{\mathrm{HOH}} = 0.22 \times 10^{-9}\ \mathrm{m}$$

The **predicted bimolecular rate constant** is

$$\begin{aligned} k_2 &= 4\pi N_{\mathrm{av}}(D_{\mathrm{A}} + D_{\mathrm{B}})r_{\mathrm{AB}} \\ &= 4\pi\,(6.02 \times 10^{23}\ \mathrm{mol^{-1}})\ (9.3 + 5.3)\ (10^{-9}\ \mathrm{m^2\ s^{-1}})\ (0.22 \times 10^{-9}\ \mathrm{m}) \\ &= 2.4 \times 10^{7}\ \mathrm{m^3\ mol^{-1}\ s^{-1}} \end{aligned}$$

$$\boxed{k_2 = 2.4 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}}$$

Diffusion-Controlled Reaction – an Example

$$\mathrm{H^+(aq)} \;+\; \mathrm{OH^-(aq)} \;\xrightarrow{k_2}\; \mathrm{H_2O}(l)$$

The **predicted** bimolecular rate constant at 25 °C is

$$k_2 = 2.4 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

The **measured** bimolecular rate constant is

$$k_2 = 11.4 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

Why is the measured rate constant larger? What feature of H^+ and OH^- is not included in the model used used to predict k_2?