The Steady-State Approximation

- This approximation assumes that for a reasonable time portion of the reaction the concentration of some intermediate $X$ remains roughly constant (and low):
  \[ \frac{d[X]}{dt} = 0 \]
  This assumption allows us to estimate $[X]$, which in turn helps determine the rate law.

- Example: Consider the sequence of first-order reactions $A \rightarrow B \rightarrow C$. The mechanism is
  \[
  \begin{align*}
  A &\rightarrow B & (k_1) \\
  B &\rightarrow C & (k_2)
  \end{align*}
  \]
  Assume $k_1 \ll k_2$

- Here the intermediate is $B$, so we set
  \[ \frac{d[B]}{dt} = k_1[A] - k_2[B] = 0 \]
  and determine $[B] = (k_1/k_2)[A]$.

- The reaction rate (for product formation) is
  \[ \frac{d[C]}{dt} = k_2[B] \approx k_1[A] \]
  (In this case the first reaction is rate-limiting)
Application of the steady-state approximation to Lindemann’s mechanism

- Recall that the steady-state approximation assumes that the concentration of some intermediate is constant (and low) for a significant time during the reaction.

- Consider the proposed mechanism:

\[
\begin{align*}
A + M & \rightarrow A^* + M \quad (k_1) \\
A^* + M & \rightarrow A + M \quad (k_2) \\
A^* & \rightarrow P \quad (k_3)
\end{align*}
\]

- Here we consider the intermediate \( A^* \), and set \( d[A^*]/dt = 0 \):

\[
d[A^*]/dt = k_1[A][M] - k_2[A^*][M] - k_3[A^*] = 0
\]

- Solving for \([A^*]\) gives

\[
[A^*] = \frac{k_1[A][M]}{(k_3 + k_2[M])}
\]

- Since the rate of product formation is \( d[P]/dt = k_3[A^*] \),

\[
\text{Rate} = k_3[A^*] = k_3k_1[A][M]/(k_3 + k_2[M])
\]
Lindemann's Mechanism

- Unimolecular gas-phase reactions were a puzzle in the 1920s. These included dissociations and isomerizations. Jean Perrin said that they were due to absorption of radiation.

- In 1921 F. A. Lindemann showed that Perrin's idea was unreasonable. A different mechanism was put forward:

\[
\begin{align*}
A + M &\rightarrow A^* + M \quad (k_1) \\
A^* + M &\rightarrow A + M \quad (k_2) \\
A^* &\rightarrow P \quad (k_3)
\end{align*}
\]

Using the steady-state approximation for \([A^*]\) and \(d[P]/dt = k_3[A^*]\),

\[
\frac{d[P]}{dt} = \frac{k_3 k_1 [A][M]}{k_3 + k_2[M]}
\]

- At high \([M]\) this reduces to

\[
d[P]/dt = (k_3 k_1 / k_2)[A] \quad \text{(first-order)}
\]

- At very low \([M]\) it reduces to

\[
d[P]/dt = k_1[M][A] \quad \text{(second-order)}
\]
LINDEMANN, Frederick Alexander, Viscount Cherwell (1886–1957), German-born British physicist, known as "the Prof." He became personal assistant to Winston Churchill, who appointed him paymaster-general in his wartime government. Some of his advice was good, some bad. As his colleague, Sir George Paget Thomson, said of him, "He was better as critic than as creator."

1 In 1931 Churchill was hit by a taxi on Fifth Avenue in New York and taken to a hospital. From there he sent a cable to Lindemann asking him to calculate the shock, to a stationary body weighing two hundred pounds, of a car weighing 2,400 pounds traveling between thirty and thirty-five miles an hour. He also asked the professor to bear in mind that the brakes did not operate before he was hit by the car and that he had been "carried forward on the cowcatcher" until he dropped off, adding that the information "must be impressive." Lindemann soon sent the following reply, "Collision equivalent falling thirty feet on pavement. Equal six thousand foot pounds energy. Equivalent stopping ten-pound brick dropped six hundred feet or two charges buck-shot pointblank range. Rate inversely proportional thickness cushion surrounding skeleton and give of frame. If assume average one inch your body transferred during impact at rate eight thousand horsepower. Congratulations on preparing suitable cushion and skill in bump."
Frederick A. Lindemann,
Lord Cherwell
(1886-1967)

- Son of a wealthy Alsatian businessman and an American mother
- Born in Germany, educated in Scotland and Germany.
- Ph.D with Walther Nernst in Berlin in 1910.
- Early work on quantum theory of solids.
- An avid tennis player who played in a long-sleeved shirt buttoned at the neck and wrists, with thick black socks and white boots.
- He went to Oxford Univ., built up the Physics Dept. to world-class status.
- In the early part of World War I pilots of aircraft that went into spins always crashed. Lindemann came up with formulas to show how a pilot should react. He learned to fly in three weeks, then tested his ideas in a dangerous dive. The ideas worked.
F. A. Lindemann (cont.)

- He had an unusual personality—very formal, a teetotaler, he was an extreme vegetarian, who lived largely on egg whites, Port Salut cheese, and olive oil; he lived at Oxford, never married.

- He met Winston Churchill while playing tennis, became a trusted advisor and personal friend of the Churchills. He was known as "The Prof."

- Some of his wartime advice was good, some bad and highly controversial.

- During the 1930s he saw to it that many refugee scientists from Hitler's Germany found positions at Oxford and elsewhere in England. (Schrödinger, Max Born, Frisch, ...)
• **Historical notes:** In 1919 the French physicist Perrin proposed that molecules were activated by absorbing IR radiation from the walls of the container. Lindemann refuted this idea. A more detailed analysis was proposed at the same time (1921) and in greater detail by J. A. Christiansen (Ph.D thesis) in Denmark. Also, I. Langmuir in the USA published a refutation in 1920.

• The gas M may be anything, including the molecule A itself or a product molecule.

• Lindemann’s theory suggests that the rate should fall off in the low-pressure region. This is observed:

Lindemann’s theory predicts a steeper falloff in k than is observed and requires some modifications to be complete.

![Graph](image-url)

Apparent first-order rate constants for the isomerization of CH$_3$NC at 503.5 K. The curve shows the results of the RRKM (Rice, Ramsberger, Kassel, and Marcus) theory. At high pressure the first-order rate constant is independent of pressure and is designated as $k_e$. As the pressure is reduced, the rate constant decreases and is said to be in the falloff region. [Reprinted with permission from F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.* 84:4215 (1962). Copyright © 1962 American Chemical Society.]
Modifications of Lindemann's theory

• A key idea of the theory is that there is a lag between the time of excitation of $A \rightarrow A^*$ and the reaction (an isomerization or dissociation). In 1927 C. Hinshelwood modified the theory by including contributions from internal degrees of freedom.

• Rice and Ramsperger and (independently) Kassel examined the energy dependence of the rate constant. The energy must concentrate in a critical portion of the molecule for reaction to occur. The total energy is rapidly redistributed among the vibrational and other degrees of freedom of the activated molecule $A^*$. The RRK method (1927-8) takes this time into account and gives a better measure of the falloff in $k$.

• In 1939 N. B. Slater related the treatment to the vibrational modes of molecules, weighting them differently. His analysis is difficult in practice.

• The RRKM method: In 1951 Rice and Marcus modified the theory to conform to the transition state model. This is the most commonly used approach at the present time.
Diffusion-controlled reactions

- **Diffusion-controlled reactions:** These are reactions that are limited by the rate at which the reactants can diffuse and meet.

- Using the **Stokes-Einstein equation** the rate constant of a diffusion-controlled reaction is

\[
k = \frac{8RT}{3\eta}
\]

where \( R = \) gas constant and \( \eta = \) viscosity.

- **Example:** Quenching of the fluorescence or phosphorescence of organic compounds by \( O_2 \) is often diffusion-controlled.

- **Example:** The recombination of I atoms to form I\(_2\) in hexane (\( \eta = 0.326 \text{ cp} \)) at 298 K. The calculated value is \( k = 2.0 \times 10^{10} \text{ L/mol-s} \); the observed value is \( k = 1.3 \times 10^{10} \text{ L/mol-s} \).

- **Note:** Rates for \( H^+ \) and \( OH^- \) reactions in solution are greater than the normal diffusion-controlled rates. These ions are part of the solvent and can be transferred by a switching mechanism. (\( H^+ \) also tunnels.)
Atom-atom recombination

- Atom-atom recombination: The recombination rate $I + I \rightarrow I_2$ decreases with temperature and thus appears to have a negative activation energy.
  
  --The rate depends on the concentration of foreign gases $M$

- Two proposed models--energy transfer and complex formation:

  --Energy transfer

  (1) $I + I \xrightarrow{k_1} I_2^*$
  (2) $I_2^* \xrightarrow{k_2} I + I$
  (3) $I_2^* + M \xrightarrow{k_3} I_2 + M^*$

  --Complex formation

  (1) $I + M \xrightarrow{k_1} I \cdots M$
  (2) $I \cdots M \xrightarrow{k_2} I + M$
  (3) $I \cdots M + I \xrightarrow{k_3} I_2 + M^*$

  --Steady-state approximation for $[I_2^*]$ gives a rate law with two limiting forms (high $[M]$ and low $[M]$)
  
  --Experiments show that heavy $M$'s favor complex formation whereas light $M$'s favor energy transfer