Lecture 8

- Ch. 22 The Rate of Chemical Reactions

1. Experimental Techniques
2. The Rate of Reactions
3. Integrated Rate Laws — Lecture 8
4. Reactions Approaching Equilibrium
5. The Temperature Dependence of Reaction Rates
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The Determination of the Rate Law

• The determination of a rate law is simplified by the **isolation method** in which the concentrations of all the reactants except one are in large excess.

• For a reaction between A and B, if B is in large excess, then to a good approximation the [B] is constant throughout the reaction.

• Although the true rate law might be v = k[A][B], we can approximate [B] by $[B]_o$,

$$v = k'[A] \qquad \text{where } k' = k[B]_o$$

which is called a pseudo-first-order rate law.

• The dependence of the rate on the concentration of each reactants may be found by isolating them in turn.

• Therefore, a picture of the overall rate law can be constructed.

The Determination of the Rate Law

- In the **method of initial rates**, which is often used in conjunction with the isolation method, the rate is measured at the beginning of the reaction for several different initial concentrations of reactants.

- For example, supposing that the rate law for a reaction with A isolated (i.e., excess B) is $v = k[A]^a$.

  Then its initial rate (v_o) is given by: $v_0 = k[A]_0^a$

  Taking logarithms gives: $\log v_0 = \log k + a \log[A]_0$

- For a series of initial concentrations, a plot of log v_0 against log $[A]_0$ should be a straight line with slope a.

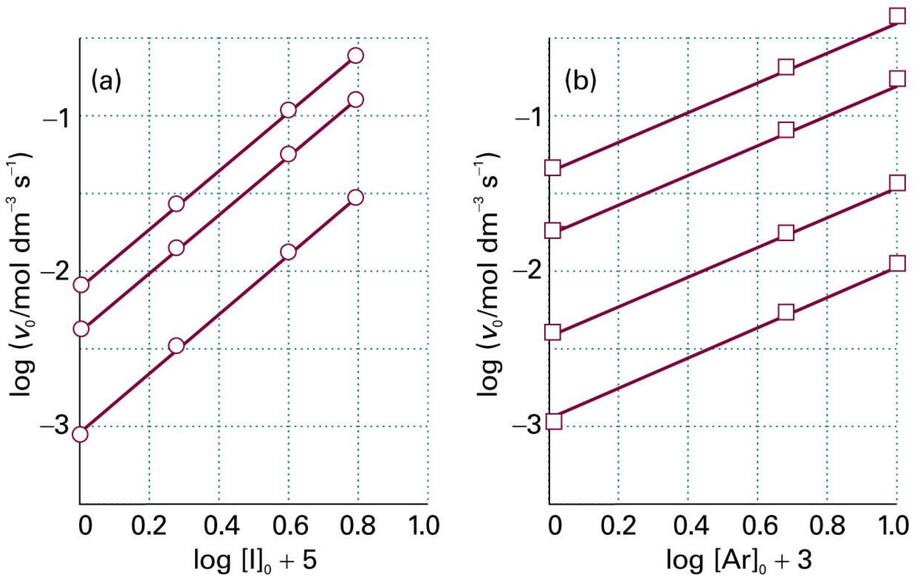
Example 22.2 Using the Method of Initial Rates

- For the reaction, $2\,\mathrm{I(g)} + \mathrm{Ar(g)} \rightarrow \mathrm{I_2(g)} + \mathrm{Ar(g)}$

The initial rates of reaction were measured at different initial concentrations. (See textbook for the given data)

Determine the orders of reaction with respect to the I and Ar concentrations and the rate constant.

$$\log v_0 = \log k + a \log[A]_0$$



Slope: a
Intercept: log k

$$v_0 = k[I]_0^2[Ar]_0$$

$$k = 9\times10^9\ \mathrm{mol^{-2}dm^6s^{-1}}$$

The Determination of the Rate Law

$$2\,I(g) + Ar(g) \rightarrow I_2(g) + Ar(g) \qquad v_0 = k[I]_0^2[Ar]_0$$

- The recombination of iodine atoms obeys the above rate law at the beginning of the reaction.

- However,….

- The method of initial rates might not reveal the full rate law.

- Sometimes, the products might participate in the reaction and affect its rate.

Ex) $$v = \frac{k[H_2][Br_2]^{3/2}}{[Br_2] + k'\,\boxed{}}$$

- To confirm the rate law obtained by the method of initial rates, the rate law should be fitted to the data *throughout* the reaction.

- Or the rate law should be tested by adding the product.

Integrated Rate Laws: First-Order Reactions

- Because rate laws are differential equations, if we want to find the concentrations as a function of time, the rate law should be integrated. → **Integrated rate law**

- For **first-order reactions**, the rate law is:

$$\frac{d[A]}{dt} = -k[A] \longrightarrow \frac{d[A]}{[A]} = -kdt$$

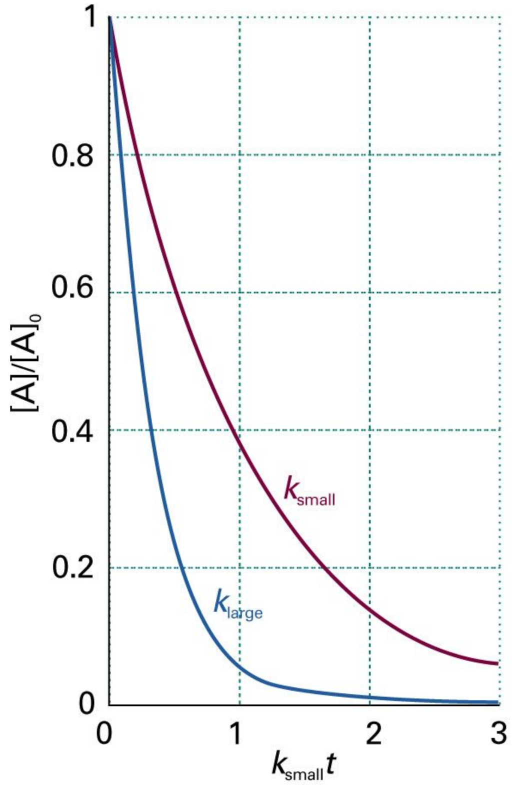
Because k is independent of time,

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k\int_0^t dt \longrightarrow \boxed{\ln\left(\frac{[A]}{[A]_0}\right) = -kt}$$

$$\boxed{[A] = [A]_0 e^{-kt}}$$

where $[A]_0$ is the initial concentration of A at t = 0.

Integrated Rate Laws: First-Order Reactions



$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$$\boxed{[A] = [A]_0 e^{-kt}}$$

- For first-order reactions, the plot of $\ln([A]/[A]_0)$ against time will give a straight line.
- The [A] decreases exponentially with time with a rate determined by k.

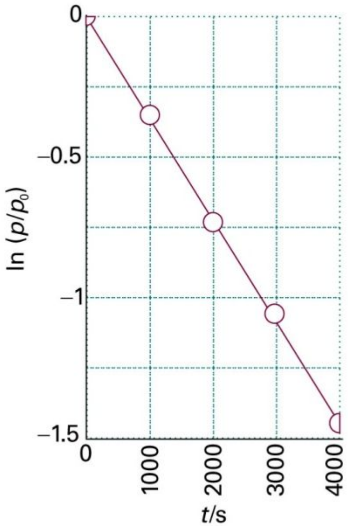
Example 22.3 Analyzing a First-Order Reaction

$$CH_3N_2CH_3(g) \rightarrow CH_3CH_3(g) + N_2(g)$$

• The variation in the partial pressure of azomethane with time at 600 K was followed with the results given below.

t / s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Confirm that the decomposition is first-order in azomethane, and find the rate constant at 600 K.



• For the first-order reaction, the plot of ln (p/p_0) against t must be straight line.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt \xrightarrow{p_A = RT[A]} \ln\left(\frac{p}{p_0}\right) = -kt$$

• The slope gives $k = 3.6\times10^{-4}\ s^{-1}$.

Half-Lives of First-Order Reactions

- The Half-life ($t_{1/2}$) of a substance is the time taken for the concentration of a reactant to fall to half its initial value.

- For first-order reactions,

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

During the half-life, [A] decreases from $[A]_0$ to $\frac{1}{2}[A]_0$.

$$\ln\left(\frac{(1/2)\cancel{[A]_0}}{\cancel{[A]_0}}\right) = -kt_{1/2} \longrightarrow \boxed{t_{1/2} = \frac{\ln 2}{k}}$$

- For the first-order reactions, the half-life of a reactant is independent of its initial concentration.

- Therefore, at an arbitrary stage of the reaction, [A] will decrease to ½[A] after a further interval of (ln2)/k.

Time Constants of First-Order Reactions

• The time constant (τ) is the time required for the concentration of a reactant to fall to 1/e of its initial value

• For first-order reactions,

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

During the time constant, [A] decreases from $[A]_0$ to $(1/e)[A]_0$.

$$\ln\left(\frac{(1/e)[A]_0}{[A]_0}\right) = -k\tau \longrightarrow \boxed{\tau = \frac{1}{k}} \qquad [A] = [A]_0 e^{\frac{-t}{1/k}}$$

• Therefore, the time constant is another indication of the rate of a first-order reaction.

Second-Order Reactions

- For **second-order reactions**, if the rate law is $\frac{d[A]}{dt} = -k[A]^2$.

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

Because k is independent of time,

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k\int_0^t dt \longrightarrow \boxed{\frac{1}{[A]} - \frac{1}{[A]_0} = kt}$$

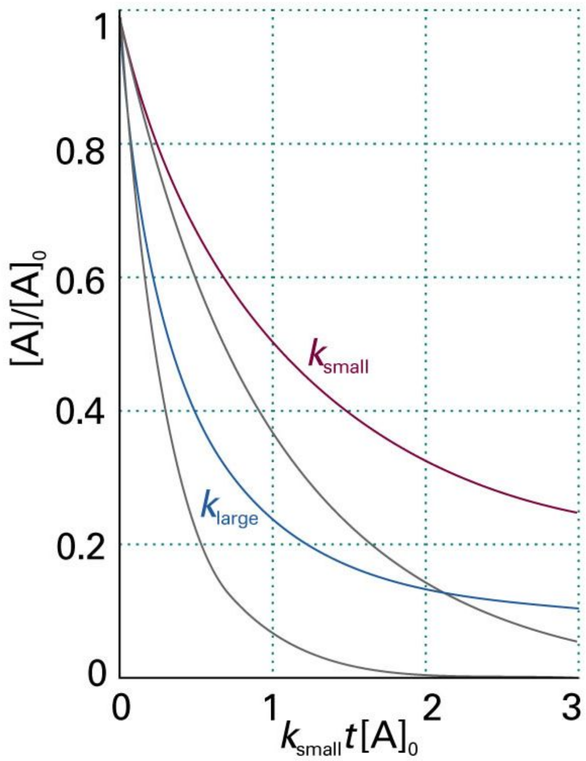
$$\boxed{[A] = \frac{[A]_0}{1 + kt[A]_0}}$$

where $[A]_0$ is the initial concentration of A at t = 0.

Second-Order Reactions

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

• To test for a **second-order reactions**, we should plot 1/[A] against t. → straight line with a slope k.



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

• The [A] in the second-order reaction approaches zero more slowly than that in a first-order reaction (gray lines).

• The [A] in the second-order reaction with a higher k approaches zero more rapidly.

Half-Lives of Second-Order Reactions

• By substututing $t = t_{1/2}$ and $[A] = ½[A]_0$, the half-life of a species A in a second-order reaction is:

$$\frac{1}{(1/2)[A]_0} - \frac{1}{[A]_0} = kt_{1/2} \longrightarrow \boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

• Unlike a first-order reaction, the half-life in a second-order reaction varies with the initial concentration.

• In general, for an nth-order reaction of the form A → products

the half-life is:

$$\boxed{t_{1/2} \propto \frac{1}{k[A]_o^{n-1}}}^{*}$$

*See Exercise 12.12a.

Second-Order Reactions

- If the rate law of a second-order reaction is $\frac{d[A]}{dt} = -k[A][B]$.

- To integrate the above equation, we should know how [B] is related to [A].

- For example, if the reaction is A + B → P, then [A] and [B] should be equally decreased during the course of the reaction.

- Therefore the integrated rate law is:*

$$\ln\left(\frac{[B]/[B]_0}{[A]/[A]_0}\right) = ([B]_0 - [A]_0)kt$$

The plot of the left side against t is a straight line

*See Justification 22.3.

Second-Order Reactions: Justification 22.3

- For the reaction $A + B \rightarrow P$, [A] and [B] should be equally decreased during the course of the reaction.

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

$$\frac{d[A]}{dt} = -k([A]_0 - x)([B]_0 - x) \qquad \frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)$$

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)} dx = \int_0^t k dt = kt$$

$$\frac{1}{(a-x)(b-x)} = \frac{1}{b-a}\left(\frac{1}{a-x} - \frac{1}{b-x}\right) \qquad \int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\left(\int \frac{dx}{a-x} - \int \frac{dx}{b-x}\right)$$

$$\int_0^x \frac{1}{([A]_0 - x)([B]_0 - x)} dx = \frac{1}{[B]_0 - [A]_0}\left[\int \frac{dx}{([A]_0 - x)} - \int \frac{dx}{([B]_0 - x)}\right]$$

$$= \frac{1}{[B]_0 - [A]_0}\left[\ln \frac{[A]_0}{([A]_0 - x)} - \ln \frac{[B]_0}{([B]_0 - x)}\right] = \frac{1}{[B]_0 - [A]_0}\left[\ln \frac{[A]_0}{[A]} - \ln \frac{[B]_0}{[B]}\right]$$

Integrated Rate Laws

Order	Reaction	Rate law*	$t_{1/2}$
0	A → P	$v = k$ $kt = x$ for $0 \le x \le [A]_0$	$[A]_0/2k$
1	A → P	$v = k[A]$ $kt = \ln \dfrac{[A]_0}{[A]_0 - x}$	$(\ln 2)/k$
2	A → P	$v = k[A]^2$ $kt = \dfrac{x}{[A]_0([A]_0 - x)}$	$1/k[A]_0$
	A + B → P	$v = k[A][B]$ $kt = \dfrac{1}{[B]_0 - [A]_0} \ln \dfrac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	A + 2 B → P	$v = k[A][B]$ $kt = \dfrac{1}{[B]_0 - 2[A]_0} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	A → P with autocatalysis	$v = k[A][P]$ $kt = \dfrac{1}{[A]_0 + [P]_0} \ln \dfrac{[A]_0([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	A + 2 B → P	$v = k[A][B]^2$ $kt = \dfrac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0} + \dfrac{1}{(2[A]_0 - [B]_0)^2} \ln \dfrac{[A]_0([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \ge 2$	A → P	$v = k[A]^n$ $kt = \dfrac{1}{n-1}\left\{\dfrac{1}{([A]_0 - x)^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right\}$	$\dfrac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}}$

Notice

- Next Reading:

8^{th} Ed: p.804 ~ 811

9^{th} Ed: p.796 ~ 803