

Experimentally determined rate law:

$$R = k[\text{NO}_2]^2[\text{O}_2]$$

The reaction is second wrt  $\text{NO}_2$  and first order wrt  $\text{O}_2$  and third order overall. So, it is an elementary reaction.

Notice the unit of  $k$  depends on the overall order of reaction.

(See [Table 35.1](#))

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

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

$$R [=] \text{M/s} = (\text{moles/volume})/\text{s}$$

$$k [=] \frac{R}{[\text{M}]^n} = \frac{\frac{\text{M}}{\text{s}}}{[\text{M}]^n} \quad n = \text{overall order of reaction}$$

$$\text{For } n = 0 \quad k [=] \text{M s}^{-1} \quad \left(-\frac{d\text{M}}{dt} = k\text{M}^0 = k\right)$$

$$n = 1 \quad k [=] \text{s}^{-1}$$

$$n = 2 \quad k [=] \text{M}^{-1} \text{s}^{-1}$$

### 35.3.1 Measuring Reaction Rates

How can one measure the rate of reaction?

Consider reaction (10).



< Monomer  $\rightarrow$  Polymer (Homopolymerization):  $M \rightarrow$  Polymer >

The rate of this reaction in terms of [A] is given

$$R = -\frac{d[A]}{dt} \quad (11)$$

- ▶ -(Slope of [A] vs t) > 0 (R > 0)
- ▶ Rate of consumption of A in terms of (mole/vol)/time.
- ▶ So, [A] and R decrease with time
- ▶ @ t=0, R=initial rate (Rate means initial rate hereafter)

Suppose the reaction is known to be first order reaction with rate constant  $k=40\text{s}^{-1}$  (See the unit above). Then

$$R = k[A] = (40\text{s}^{-1})[A] \quad (12)$$

Figure 2 shows how [A] and  $d[A]/dt$  decrease with reaction time.

Note:  $k$  is independent of time.

With  $k$  and order of reaction known  $\rightarrow$  R is determined at any time.

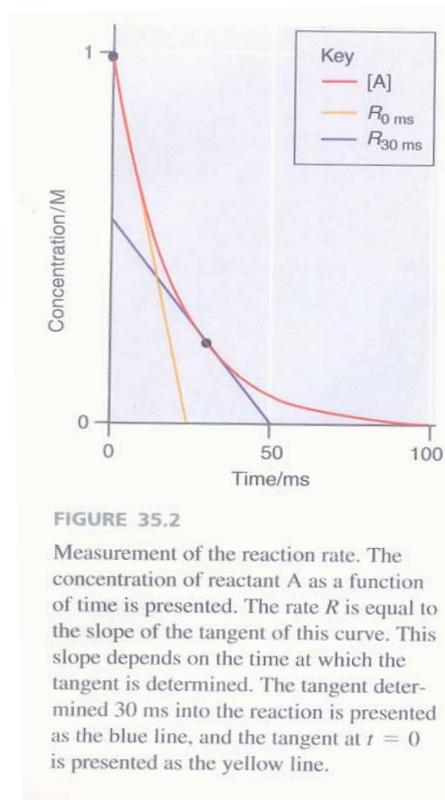


Figure 2

### 35.3.2 Determining Reaction Order

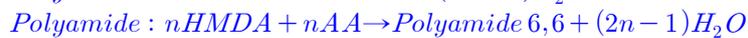
Consider the following reaction:



$$R = k[A]^\alpha [B]^\beta \quad (14)$$

*Examples in polymer chemistry*

– *Condensation polymerizations*



– *Radical Copolymerization*



# of variables=2 ( $\alpha$  and  $\beta$ )

# of equation=1

F=M-N=1 (One degree of freedom)

So,  $\alpha$  and  $\beta$  (and thus  $R$ ) can not be determined by measuring  $[A]$  and  $[B]$  as a function of time.

How can then we determine the order of reaction ( $\alpha$ ,  $\beta$ )?

**i) Isolation method**

$[A]_0 = 1.0M$  (One reactant is provided in excess)

$[B]_0 = 0.01M$

When all of B is reacted, the reaction is stopped.

At that time  $[A] \approx 0.99M \approx [A]_0 \approx \text{Constant}$

Then

$$R = k[A]^\alpha [B]^\beta = k'[B]^\beta \quad \left( = -\frac{d[B]}{dt} = \text{Measured, See Fig 2} \right) \quad (15)$$

$\rightarrow \beta$  determined

where  $k' = k[A]^\alpha \approx \text{Constant}$

**ii) Method of initial rates**

Concentration of one reactant is changed.

$\rightarrow$  The initial rate of reaction is measured.

$\rightarrow$  The variation of initial rate as a function of concentration is analyzed to determine the order of reaction wrt that reactant.

For reaction (13)  $A + B \xrightarrow{k} C$  (13)

$[A]$  = Varied in two values

$[B]$  = Constant

Reaction rate at two different  $[A]$  is analyzed as:

$$\frac{R_1}{R_2} = \frac{k[A]_1^\alpha [B]_1^\beta}{k[A]_2^\alpha [B]_1^\beta} = \left( \frac{[A]_1}{[A]_2} \right)^\alpha \quad k \neq k(\text{Concentration})$$

$$\text{Ln} \frac{R_1}{R_2} = \alpha \text{Ln} \left( \frac{[A]_1}{[A]_2} \right) \quad (16)$$

The  $\alpha$  is determined from (16) by measuring  $R_1$  and  $R_2$ .

The  $\beta$  can be determined by the similar experiment.

**EXAMPLE 35.2**

Using the following data for the reaction illustrated in Equation (35.13), determine the order of the reaction wrt A and B, and the rate constant for the reaction:

[A](M)	[B](M)	Initial Rate (Ms <sup>-1</sup> )
2.30×10 <sup>-4</sup>	3.10×10 <sup>-5</sup>	5.25×10 <sup>-4</sup>
4.60×10 <sup>-4</sup>	6.20×10 <sup>-5</sup>	4.20×10 <sup>-3</sup>
9.20×10 <sup>-4</sup>	6.20×10 <sup>-5</sup>	1.68×10 <sup>-2</sup>

Solution

Using the last two entries in the table, the order of the reaction with respect to A is

$$\ln\left(\frac{R_1}{R_2}\right) = \alpha \ln\left(\frac{[A]_1}{[A]_2}\right)$$

$$\ln\left(\frac{4.20 \times 10^{-3}}{1.68 \times 10^{-2}}\right) = \alpha \ln\left(\frac{4.60 \times 10^{-4}}{9.20 \times 10^{-4}}\right)$$

$$-1.386 = \alpha(-0.693)$$

$$2 = \alpha$$

Using this result and the first two entries in the table, the order of the reaction with respect to B is given by

$$\frac{R_1}{R_2} = \frac{k[A]_1^2[B]_1^\beta}{k[A]_2^2[B]_2^\beta} = \frac{[A]_1^2[B]_1^\beta}{[A]_2^2[B]_2^\beta}$$

$$\left(\frac{5.25 \times 10^{-4}}{4.20 \times 10^{-3}}\right) = \left(\frac{2.30 \times 10^{-4}}{4.60 \times 10^{-4}}\right)^2 \left(\frac{3.10 \times 10^{-5}}{6.20 \times 10^{-5}}\right)^\beta$$

$$0.500 = (0.500)^\beta$$

$$1 = \beta$$

Therefore, the reaction is second order in A, first order in B, and third order overall. Using any row from the table, the rate constant is readily determined:

$$R = k[A]^2[B]$$

$$5.2 \times 10^{-4} \text{ Ms}^{-1} = k(2.3 \times 10^{-4} \text{ M})^2(3.1 \times 10^{-5} \text{ M})$$

$$3.17 \times 10^8 \text{ M}^{-2} \text{ s}^{-1} = k$$

Having determined k, the overall rate law is

$$R = (3.17 \times 10^8 \text{ M}^{-2} \text{ s}^{-1})[A]^2[B]$$