Biophysical chemistry

Part A
Chapter: 3
Chemical kinetics
Lecture - 2

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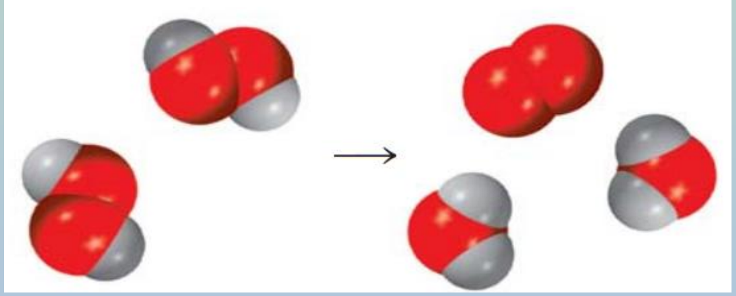
The Rate of a Reaction

If one of the products or reactants is a gas,
we can use a manometer to find the reaction rate.

Decomposition of Hydrogen Peroxide

$$2\,H_2O_2(aq) \rightarrow 2H_2O\ (l) + O_2(g)$$



The oxygen pressure can be readily converted to concentration by using the ideal gas equation:

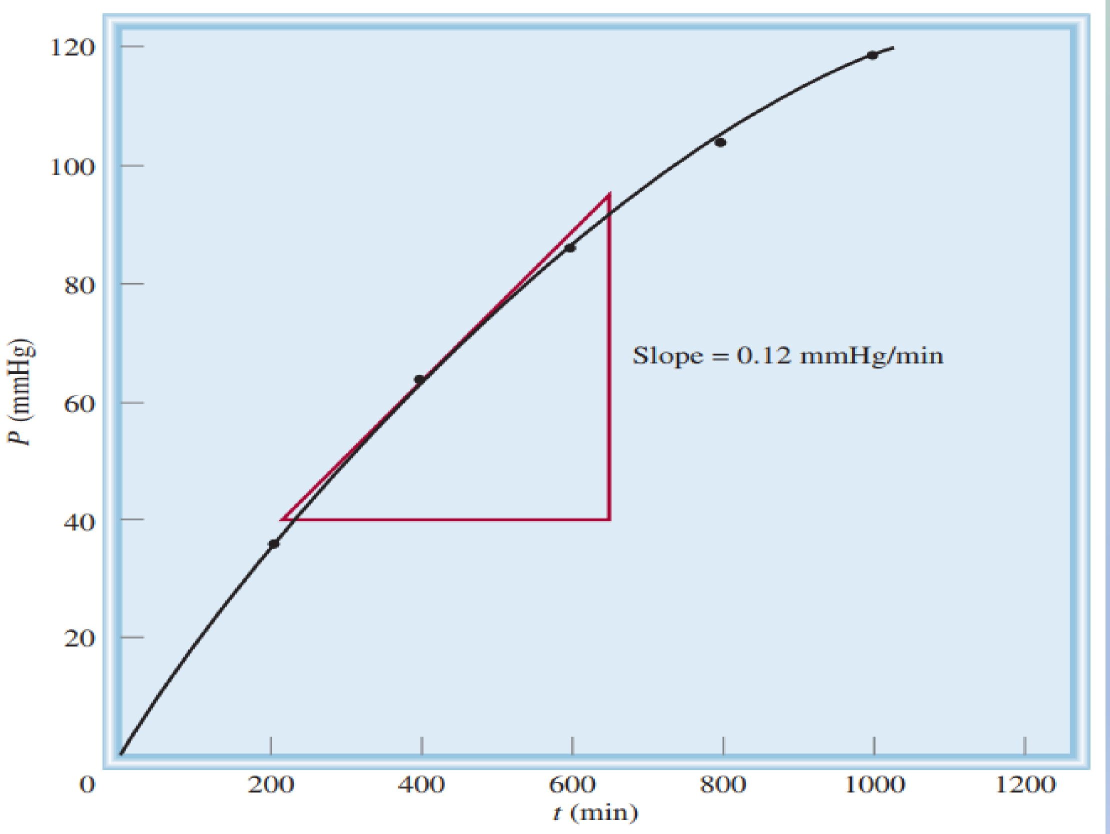
$$PV = nRT$$

Or $$P = \frac{n}{V}RT \text{ or } [O_2]RT$$

$$[O_2] = \frac{P}{RT}$$

The Rate of a Reaction

The reaction rate = $\frac{\Delta[O_2]}{\Delta t}$ or $\frac{1}{RT}\frac{\Delta P}{\Delta t}$



The instantaneous rate for the decomposition of hydrogen peroxide at 400 min is given by the slope of the tangent multiplied by 1/RT

Reaction Rates and Stoichiometry

Stoichiometry – is the measure of the quantitative relationship between the products and reactants of a given chemical reaction in terms of their relative ratios of mass or volume

$$2A \rightarrow B$$

Two moles of A disappear for each mole of B that forms

$$\text{Rate} = \frac{1}{2}\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad \frac{\Delta[B]}{\Delta t}$$

In general, for the reaction

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

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} \quad \text{or} \quad -\frac{1}{b}\frac{\Delta[B]}{\Delta t} \quad \text{or} \quad \frac{1}{c}\frac{\Delta[C]}{\Delta t} \quad \text{or} \quad \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Reaction Rates and Stoichiometry

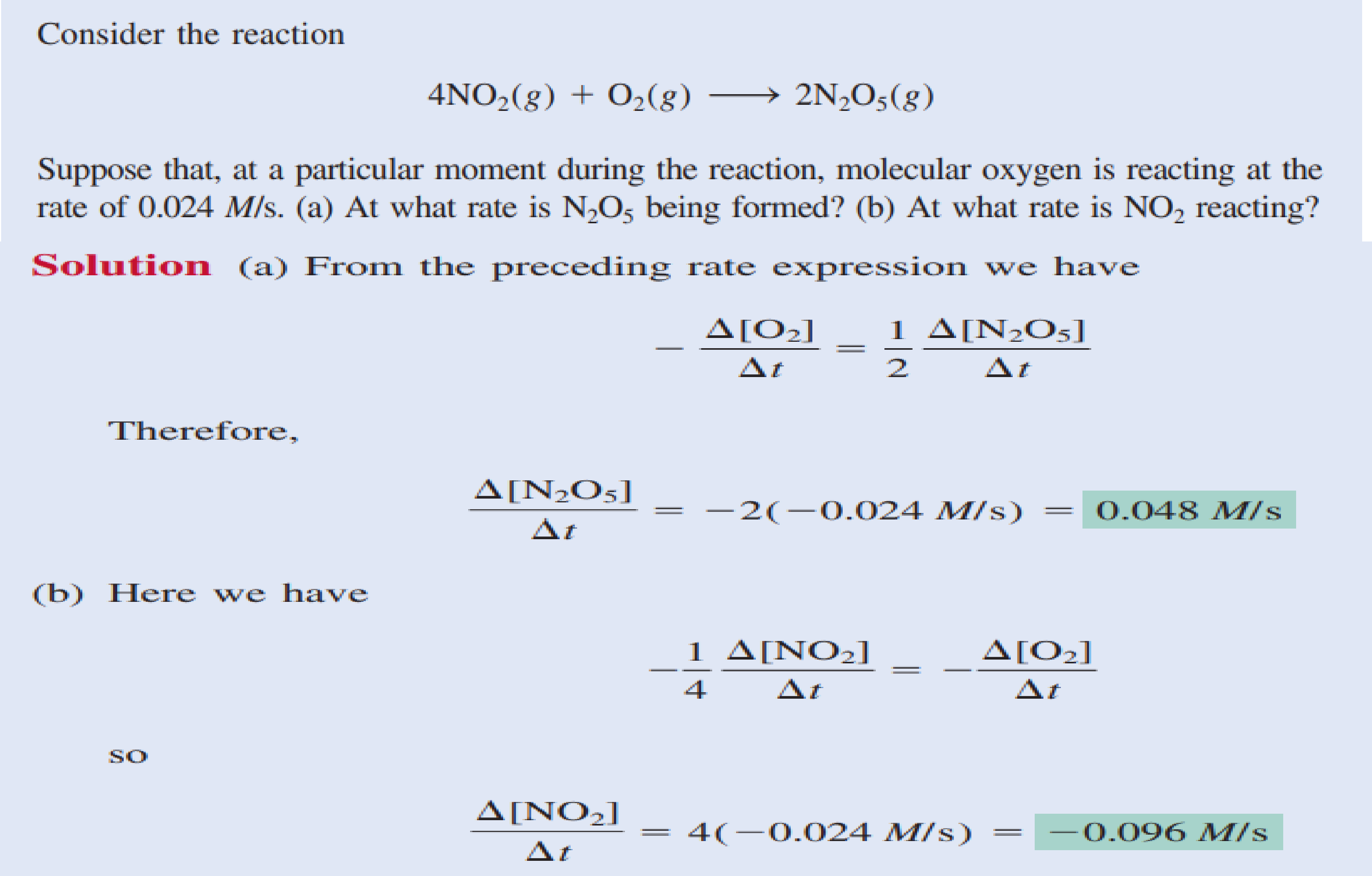
$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

$$\text{rate} = -\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$$

Reaction Rates and Stoichiometry



Consider the reaction

$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$$

Suppose that, at a particular moment during the reaction, molecular oxygen is reacting at the rate of 0.024 *M*/s. (a) At what rate is N_2O_5 being formed? (b) At what rate is NO_2 reacting?

Solution (a) From the preceding rate expression we have

$$-\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$$

Therefore,

$$\frac{\Delta[N_2O_5]}{\Delta t} = -2(-0.024\ M/s) = 0.048\ M/s$$

(b) Here we have

$$-\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t}$$

so

$$\frac{\Delta[NO_2]}{\Delta t} = 4(-0.024\ M/s) = -0.096\ M/s$$

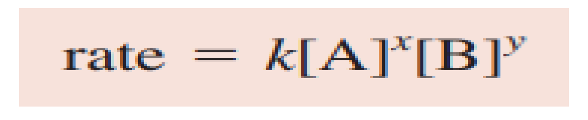
Rate Law

Rate law - expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

For the general reaction

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

the rate law takes the form



$$\text{rate} = k[A]^x[B]^y$$

x and y are numbers that must be determined experimentally.

In general, x and y are not equal to the stoichiometric coefficients a and b.

The exponents x and y specify the relationships between the concentrations of reactants A and B and the reaction rate.

Rate Law

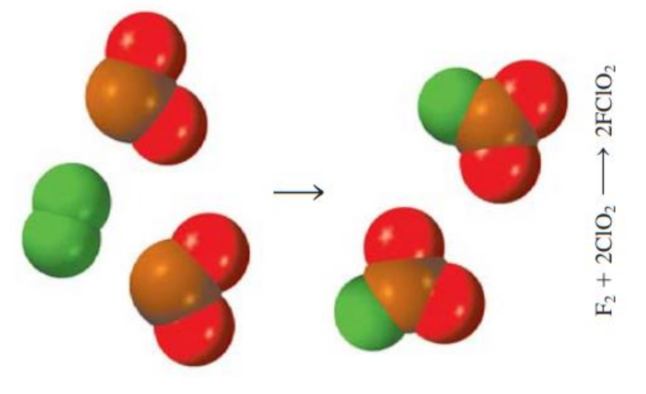
reaction order : defined as the sum of the powers to which all reactant concentrations appearing in the rate law are raised.

For Equation $\text{rate} = k[\mathrm{A}]^x[\mathrm{B}]^y$

the overall reaction order
is x + y. Alternatively, we can say that the reaction is xth order in A, yth order in B, and (x + y)th order overall.

let us consider the reaction between fluorine and chlorine dioxide:

$$F_2(g) + 2ClO_2\ (g) \rightarrow 2FClO_2\ (g)$$



One way to study the effect of reactant concentration on reaction rate is to determine how the initial rate depends on the starting concentrations.

Rate Law

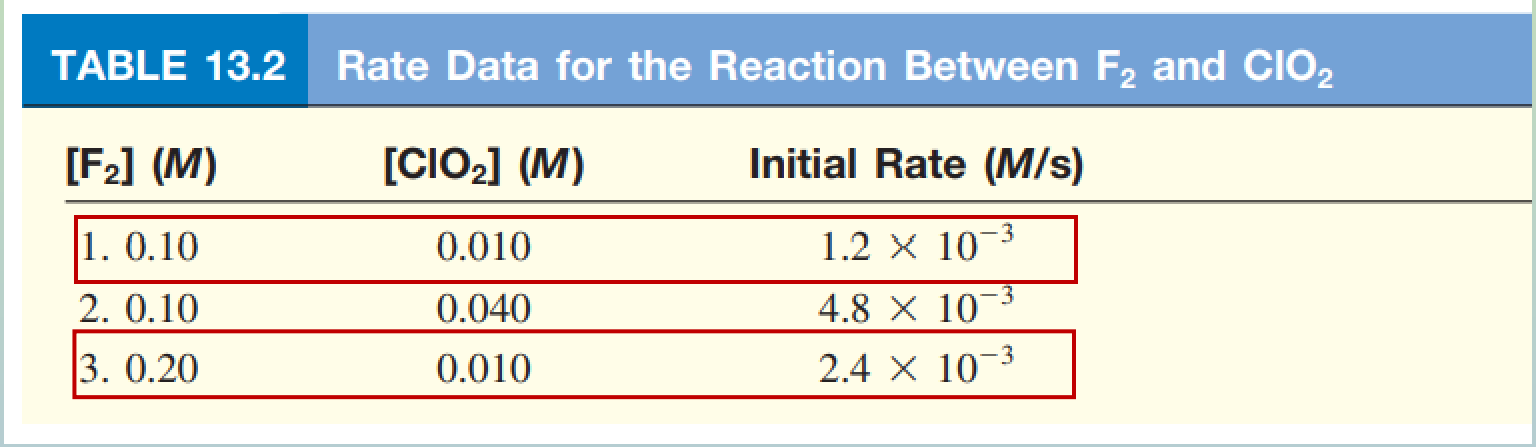
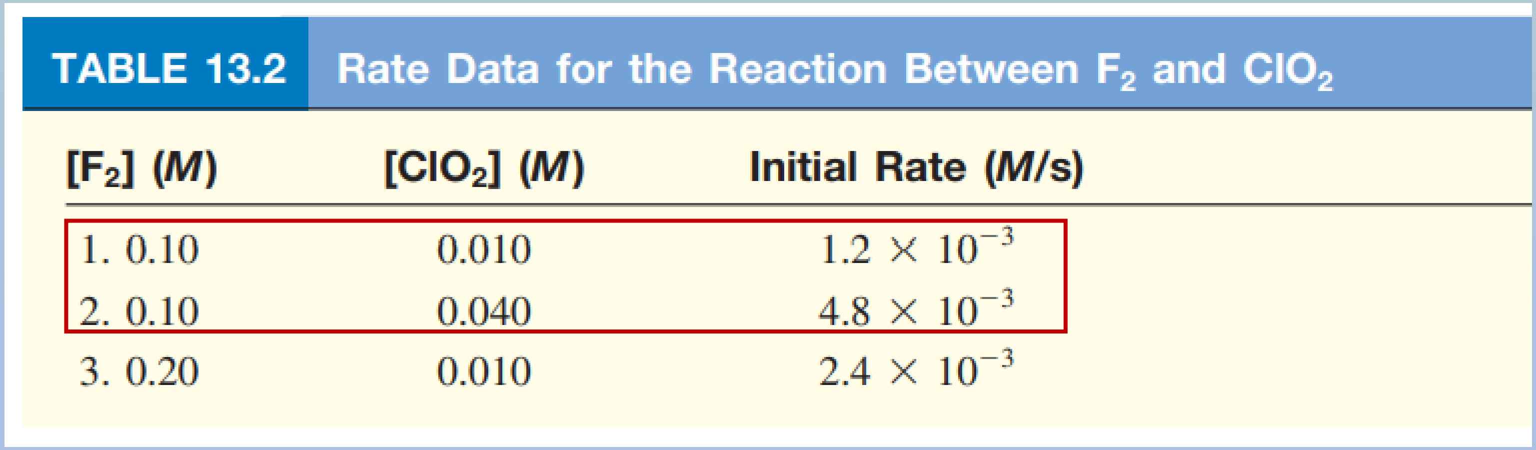


TABLE 13.2 Rate Data for the Reaction Between F_2 and ClO_2

$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1. 0.10	0.010	1.2×10^{-3}
2. 0.10	0.040	4.8×10^{-3}
3. 0.20	0.010	2.4×10^{-3}

the rate is directly proportional to $[F_2]$.



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3. 0.20	0.010	2.4×10^{-3}

the rate is also directly proportional to $[\mathrm{Cl}O_2]$.

Rate Law

We can summarize our observations by writing the rate law as

$$\text{rate} = \text{k}[F_2][\text{Cl}O_2]$$

Because both $[F_2]$ and $[\text{Cl}O_2]$ are raised to the first power, the reaction is first order in F_2 , first order in $\text{Cl}O_2$, and (1 + 1) or second order overall.

[ClO2] is raised to the power of 1 whereas its stoichiometric coefficient in the overall equation is 2.

$$\text{k} = \frac{\text{rate}}{[\text{F2}][\text{ClO2}]}$$

$$= \frac{1.2 \times 10^{-3}\ \text{M/s}}{(0.10\ \text{M})(0.010\ \text{M})}$$

$$= 1.2/\text{M.s}$$

Rate Law

$$\text{rate} = k[A][B]^2$$

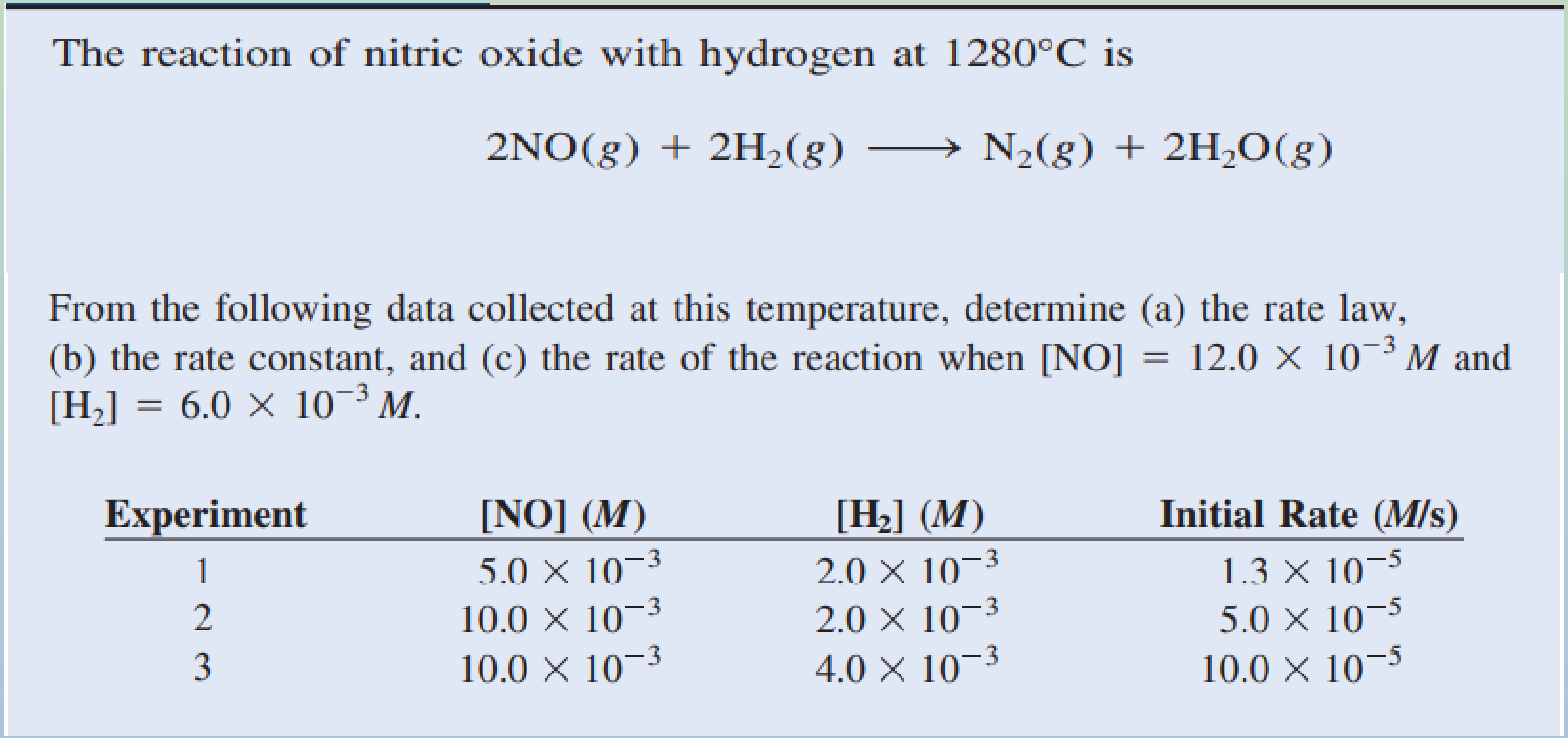
$$\begin{aligned}\text{rate} &= k[A]^0[B] \\ &= k[B]\end{aligned}$$

The rate of this reaction is independent of the concentration of A

Reaction order can also be a fraction.

1. Rate laws are always determined experimentally. From the concentrations of reactants and the initial reaction rates we can determine the reaction order and then the rate constant of the reaction.
2. Reaction order is always defined in terms of reactant (not product) concentrations.
3. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

Rate Law



The reaction of nitric oxide with hydrogen at 1280°C is

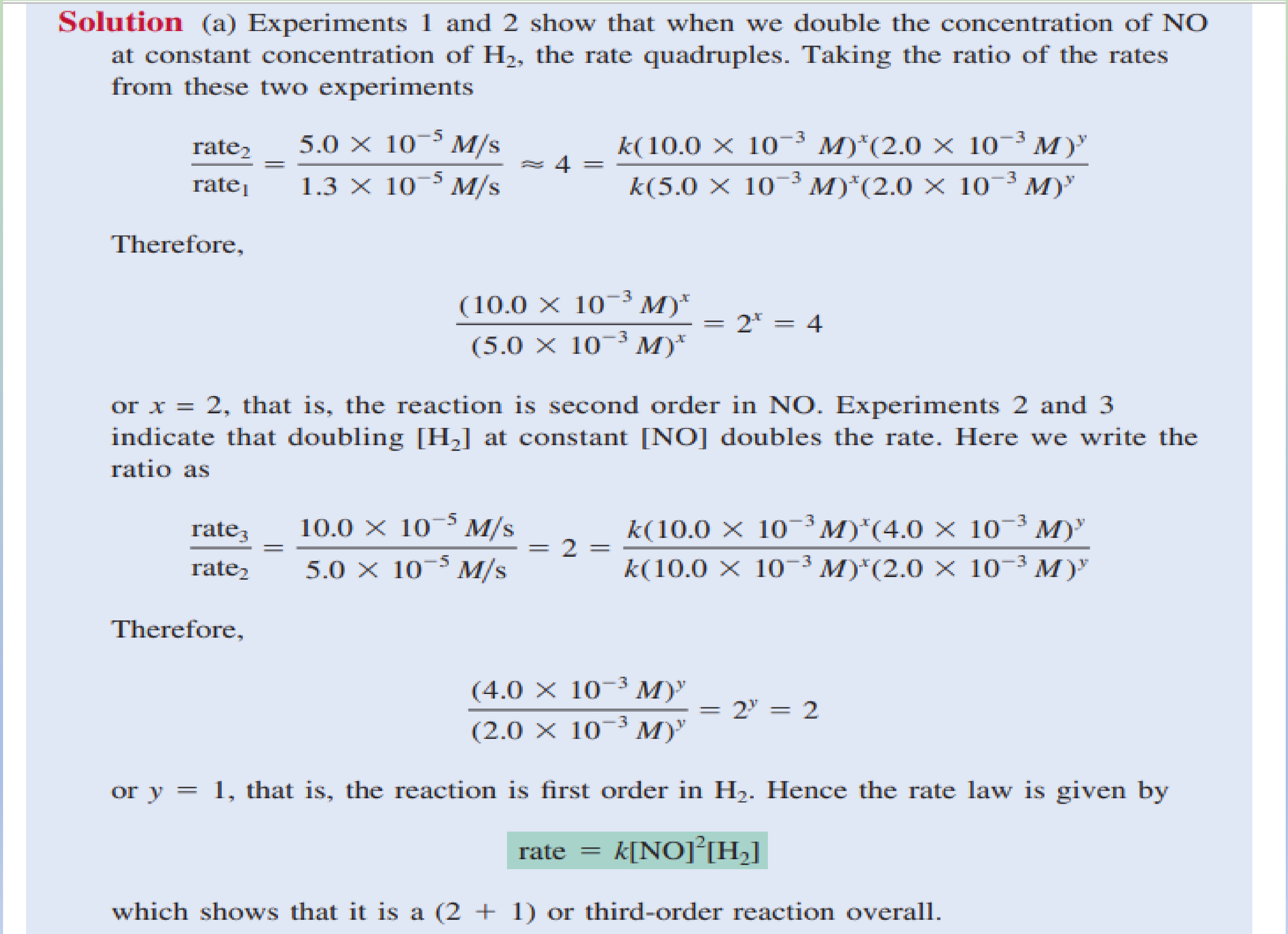
$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

From the following data collected at this temperature, determine (a) the rate law, (b) the rate constant, and (c) the rate of the reaction when [NO] = 12.0×10^{-3} *M* and $[H_2] = 6.0 \times 10^{-3}$ *M*.

Experiment	**[NO] (*M*)**	**[H_2] (*M*)**	**Initial Rate (*M*/s)**
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

$$\text{Rate} = k[\text{NO}]^x[H_2]^y$$

Rate Law



Solution (a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H_2, the rate quadruples. Taking the ratio of the rates from these two experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{5.0 \times 10^{-5}\ M/\text{s}}{1.3 \times 10^{-5}\ M/\text{s}} \approx 4 = \frac{k(10.0 \times 10^{-3}\ M)^x(2.0 \times 10^{-3}\ M)^y}{k(5.0 \times 10^{-3}\ M)^x(2.0 \times 10^{-3}\ M)^y}$$

Therefore,

$$\frac{(10.0 \times 10^{-3}\ M)^x}{(5.0 \times 10^{-3}\ M)^x} = 2^x = 4$$

or $x = 2$, that is, the reaction is second order in NO. Experiments 2 and 3 indicate that doubling $[H_2]$ at constant [NO] doubles the rate. Here we write the ratio as

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{10.0 \times 10^{-5}\ M/\text{s}}{5.0 \times 10^{-5}\ M/\text{s}} = 2 = \frac{k(10.0 \times 10^{-3}\ M)^x(4.0 \times 10^{-3}\ M)^y}{k(10.0 \times 10^{-3}\ M)^x(2.0 \times 10^{-3}\ M)^y}$$

Therefore,

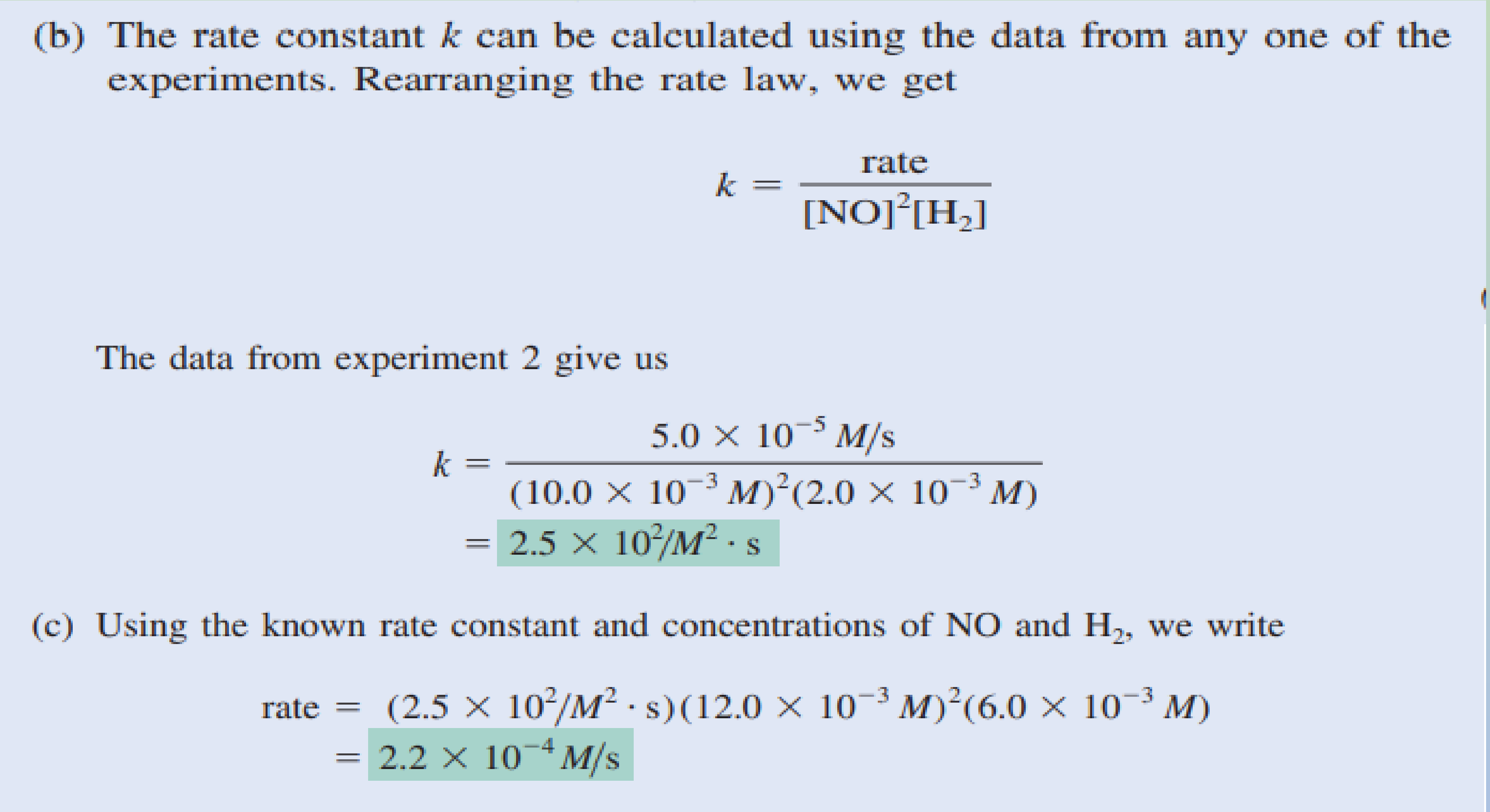
$$\frac{(4.0 \times 10^{-3}\ M)^y}{(2.0 \times 10^{-3}\ M)^y} = 2^y = 2$$

or $y = 1$, that is, the reaction is first order in H_2. Hence the rate law is given by

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

which shows that it is a (2 + 1) or third-order reaction overall.

Rate Law



(b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{H}_2]}$$

The data from experiment 2 give us

$$k = \frac{5.0 \times 10^{-5}\ M/\text{s}}{(10.0 \times 10^{-3}\ M)^2(2.0 \times 10^{-3}\ M)}$$

$$= 2.5 \times 10^2/M^2 \cdot \text{s}$$

(c) Using the known rate constant and concentrations of NO and H_2, we write

$$\text{rate} = (2.5 \times 10^2/M^2 \cdot \text{s})(12.0 \times 10^{-3}\ M)^2(6.0 \times 10^{-3}\ M)$$

$$= 2.2 \times 10^{-4}\ M/\text{s}$$

Note that the reaction is first order in H2, whereas the stoichiometric coefficient for H2 in the balanced equation is 2. The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation