Physical Chemistry for Energy Engineering
(21st: 2018/11/28)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (as of Nov. 28)

Homework is uploaded on eTL. Please submit it to TA at the beginning of Dec. 12 class.

16	12-Nov	3. Chemical equilibrium-1
17	14-Nov	Answers of homework-2
18	19-Nov	Exam-02 (2 hour)
19	21-Nov	3. Chemical equilibrium-2
20	26-Nov	3. Chemical equilibrium-3
21	28-Nov	4. Chemical kinetics-1
22	3-Dec	4. Chemical kinetics-2
23	5-Dec	4. Chemical kinetics-3
24	10-Dec	4. Chemical kinetics-4
25	12-Dec	Answers of homework-3
26	17-Dec	Exam-03 (2 hour)

4.1. Chemical Kinetics I: rate laws

- Introduction: how long does it take to the minimum Gibbs energy state?-

(Example) Consider " H_2 (g) + ½ O_2 (g) $\rightleftharpoons$ H_2O (l) ",
for which $\Delta_r G° = -237\ \mathrm{kJ}\ mol^{-1}$ at 298.15 K.

In this case, $\Delta_r G°$ has a large negative value, thus basically H_2O (l) is much more stable than the reactants at 298.15 K. However, a mixture of H_2 (g) and O_2 (g) remains unchanged for a long time.

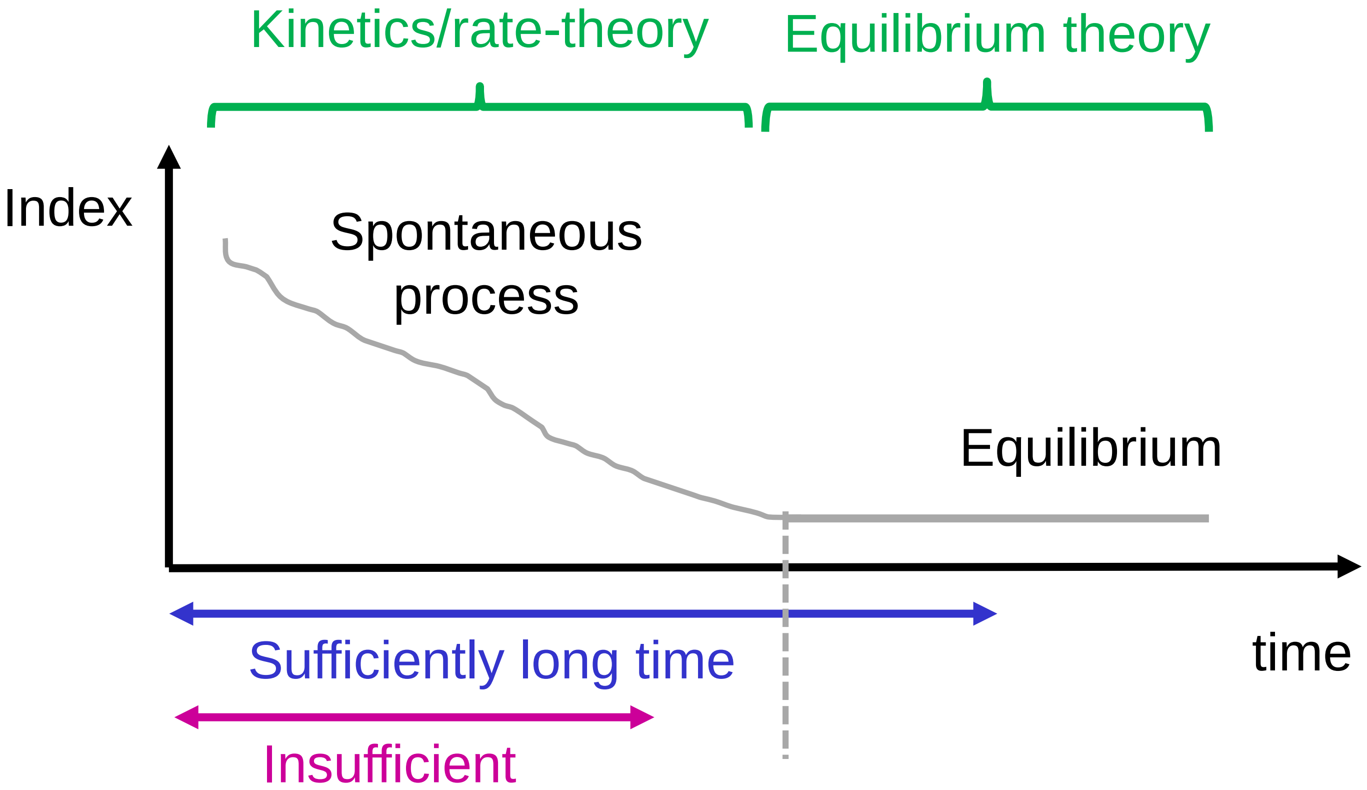
If a spark or a catalyst is introduced, then the reaction occurs explosively.

- ✓ The "no" is emphatic in thermodynamics: If thermodynamics insists that a certain process will not occur spontaneously, then it will not occur.
- ✓ On the other hand, the "yes" is actually "maybe". The fact that a process will occur spontaneously does not imply that it will occur at a detectable rate.
  - ➢ Diamond remains its form, although a graphite is more favorable energetically, is another example.

⇨ *The speed of reaction can be analyzed in the framework of* ***rate theory.***

4.1. Chemical Kinetics I: rate laws
- Introduction: scope of kinetics/rate theory-

- ✓ Theory of equilibrium is powerful, but it cannot indicate how long it takes to reach the equilibrium state.
- ✓ Kinetics and rate theory can analyze and give information on the speed of a reaction.



- ✓ We need to deal with non-equilibrium state in kinetics: however, we usually assume temperature and total pressure (or volume) are stable and fixed, like quasi-static. So, “non-equilibrium” character is often only for chemical composition.

4.1. Chemical Kinetics I: rate laws

- Introduction -

- ✓ We can establish classical thermodynamics (including equilibrium theory) just based on 3 laws. However, we cannot still build chemical kinetics with a small sets of postulates/laws.

- ✓ Presently, there are many different theoretical models for describing how chemical reactions occur: none is perfect but each has some merits.
  - ✓ So, for chemical kinetics, we need to become familiar with different ideas and sometimes concepts that seem unrelated.
- ✓ Indeed, this situation is common in scientific disciplines with which further research is needed in order to provide a more fundamental understanding of the subject.

- ✓ In this chapter, we will learn that the time-dependence of the reactant and product concentrations during a chemical reaction can be described by differential equations known as *rate laws*.
- ✓ We also learn mathematical formula for rate laws and temperature dependence of a reaction rate.

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

Consider a general chemical reaction: $\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$

✓ We employ *the extent of reaction, ξ*, which we utilized for chemical equilibrium ($26), in order to describe the amount of each compound:

$$n_A(t) = n_A(0) - \nu_A \xi(t), \qquad n_B(t) = n_B(0) - \nu_B \xi(t)$$

$$n_Y(t) = n_Y(0) + \nu_Y \xi(t), \qquad n_Z(t) = n_Z(0) + \nu_Z \xi(t)$$

where $n_j(0)$ denotes the initial amount of compound j.

✓ The extent of reaction, ξ, has units of moles and connects the amount of reaction that has occurred to the stoichiometry dictated by the balanced chemical equation. The change in $n_j(t)$ with time is then given by:

$$\frac{dn_A(t)}{dt} = -\nu_A \frac{d\xi(t)}{dt}, \qquad \ldots., \qquad \frac{dn_Y(t)}{dt} = \nu_Y \frac{d\xi(t)}{dt}, \qquad \ldots.$$

✓ Most experimental techniques measure the concentration as a function of time. If the volume (V) of the system is constant, then dividing these equations by V gives the corresponding expressions for the time-dependent concentrations,

$$\frac{1}{V}\frac{dn_A(t)}{dt} = \frac{d[A]}{dt} = -\frac{\nu_A}{V}\frac{d\xi(t)}{dt}, \qquad \ldots., \qquad \frac{1}{V}\frac{dn_Y(t)}{dt} = \frac{d[Y]}{dt} = \frac{\nu_Z}{V}\frac{d\xi(t)}{dt}, \ldots.$$

where $[A]$, for example, is equal on $n_A(t)/V$.

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

Consider a general chemical reaction: $\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$

- ✓ We derived expressions for the time-dependent concentrations,

$$\frac{1}{V}\frac{dn_A(t)}{dt} = \frac{d[A]}{dt} = -\frac{\nu_A}{V}\frac{d\xi(t)}{dt}, \qquad \ldots, \qquad \frac{1}{V}\frac{dn_Y(t)}{dt} = \frac{d[Y]}{dt} = \frac{\nu_Y}{V}\frac{d\xi(t)}{dt}, \ldots$$

  where $[A]$, for example, is equal to $n_A(t)/V$.

- ✓ Then, we define *the rate of reaction, $v(t)$,*

$$v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

(Example-1) 2 $NO(g)$ + $O_2(g)$ → 2 $NO_2(g)$

$$v(t) = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

- ✓ For most chemical reactions, $v(t)$ is related to the concentration of the various chemical species present at time t. The relationship between $v(t)$ and the concentrations is called the *rate law*. Rate laws must be determined from experimental measurements.
- ✓ In the example-1 case, for example, experimental data show

$$v(t) = k[NO]^2[O_2]$$

  where k is a constant, called "rate constant".

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

(Example-1) 2 NO(g) + O_2(g) → 2 NO_2(g)

$$v(t) = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$$

$v(t) = k[NO]^2[O_2]$, where k is a constant.

- ✓ This equation shows that the rate is proportional to $[NO]^2[O_2]$. The proportionality constant, k, is called the *rate constant* for the reaction.
- ✓ For this particular rate law, the rate depends differently on the concentrations of the two reactants.
  - ✓ A doubling of the oxygen concentration results in a doubling of the reaction rate.
  - ✓ A doubling of the nitrogen monoxide causes a quadrupling of the reaction rate.

- ✓ The rate laws often have the form

$$v(t) = k[A]^{m_A}[B]^{m_B}\cdots$$

where *[A], [B],* … are the concentrations of the various reactants; the exponents or *orders*, m_A, m_B, … are constants. But note that the orders are generally not equal/proportional to the stoichiometric coefficients.

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

- ✓ As given in the previous slide, the rate laws often have the form

$$v(t) = k[A]^{m_A}[B]^{m_B}\cdots$$

where *[A], [B],* … are the concentrations of the various reactants and the exponents or *orders*, *m_A, m_B,* … are constants. But note that the orders are generally not equal/proportional to the stoichiometric coefficients.

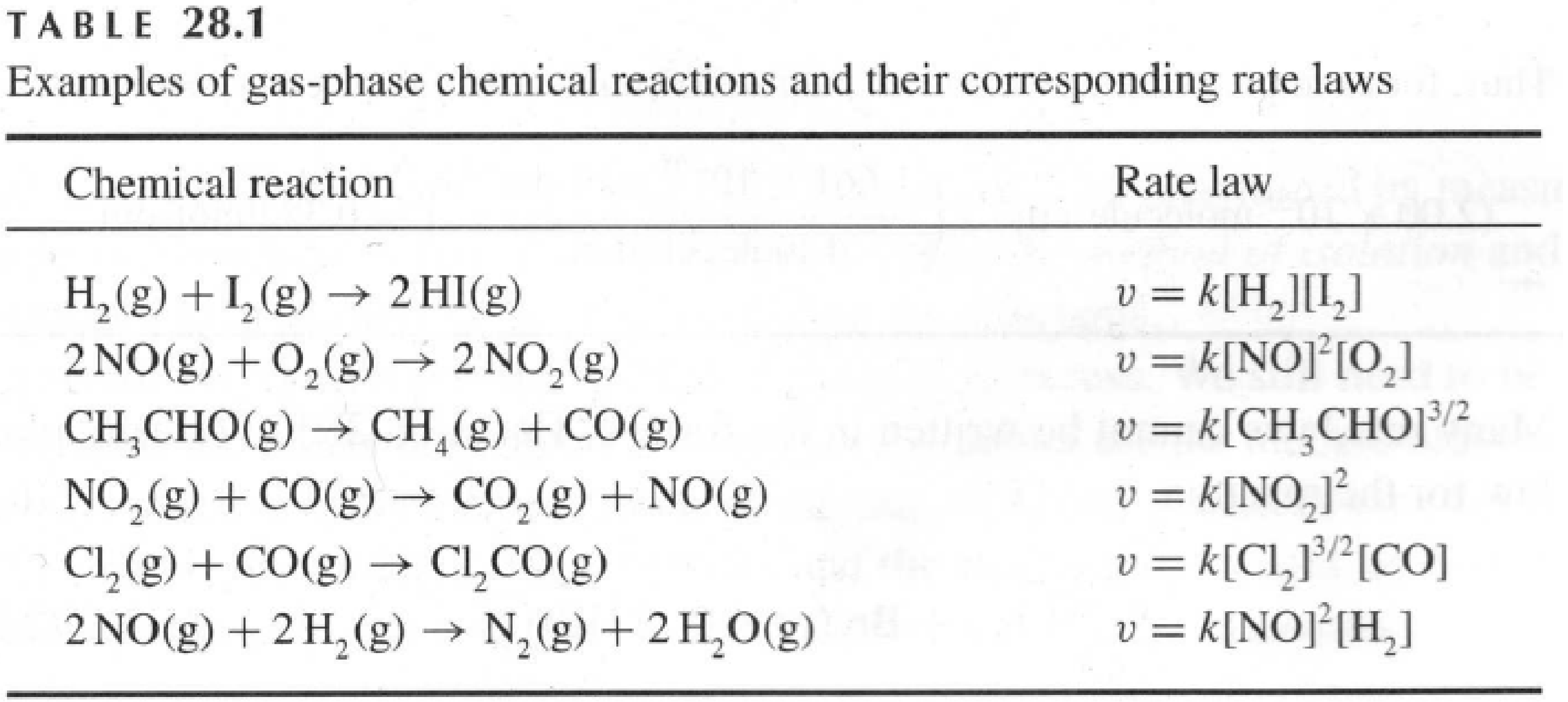


TABLE 28.1

Examples of gas-phase chemical reactions and their corresponding rate laws

Chemical reaction	Rate law
$H_2(g) + I_2(g) \rightarrow 2HI(g)$	$v = k[H_2][I_2]$
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	$v = k[NO]^2[O_2]$
$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$	$v = k[CH_3CHO]^{3/2}$
$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$	$v = k[NO_2]^2$
$Cl_2(g) + CO(g) \rightarrow Cl_2CO(g)$	$v = k[Cl_2]^{3/2}[CO]$
$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$	$v = k[NO]^2[H_2]$

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

Consider a general chemical reaction: $\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$

- ✓ The rate law concept applies to all reactions regardless of the phases of the reactants, products, and surrounding medium, because it derives from an equation that does not assume a specific phase:

$$v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

  - ➢ However, many chemical reactions cannot be described with such a simple equation “$v(t) = k[A]^{m_A}[B]^{m_B}$”, to be shown later.

- ✓ When the rate law can be written as in “$v(t) = k[A]^{m_A}[B]^{m_B} \cdots$” form, the sum of the exponents is commonly referred to as the overall order of the chemical reaction.

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

- ✓ The unit of a rate constant depend on the form of the rate law.

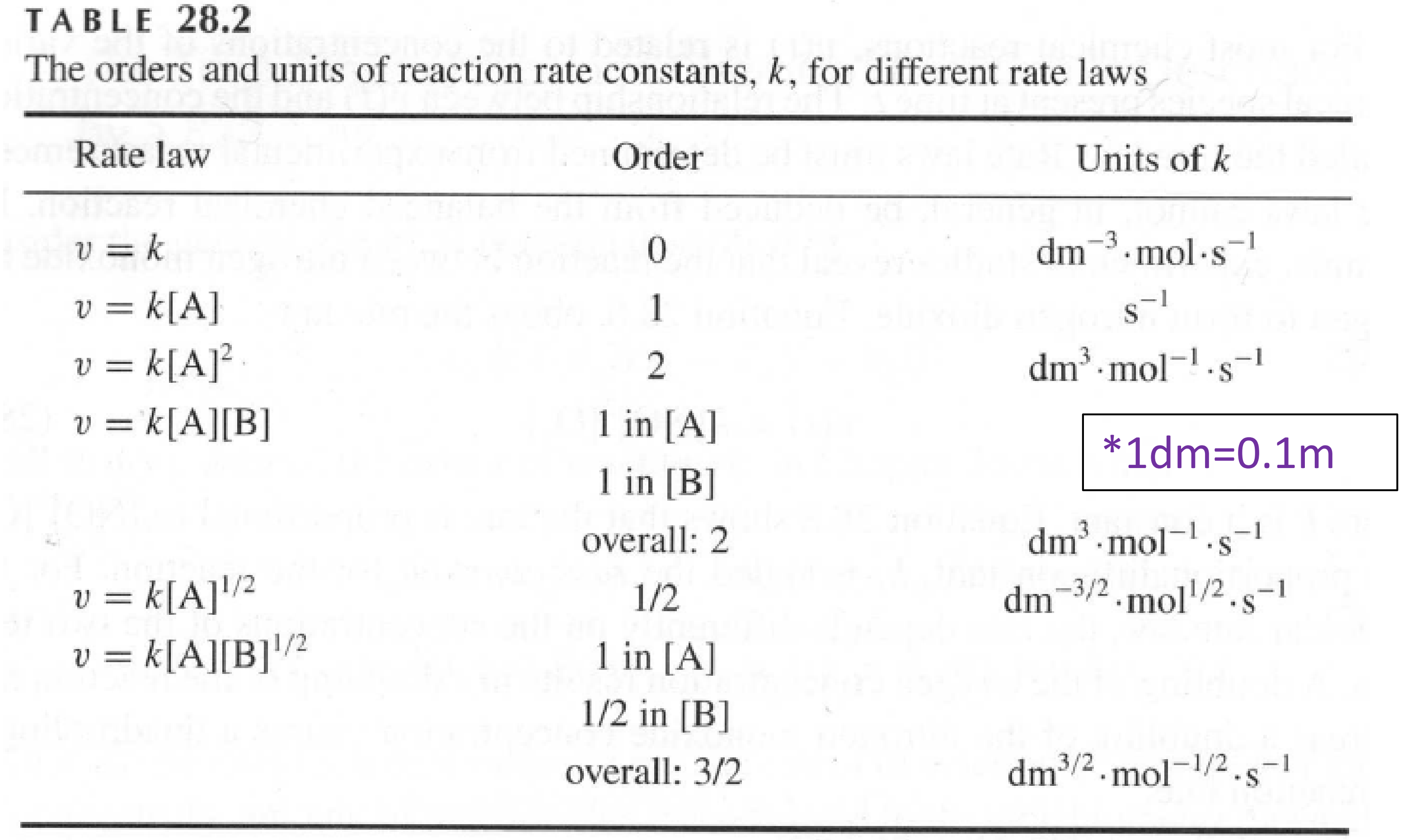


TABLE 28.2

The orders and units of reaction rate constants, k, for different rate laws

Rate law	Order	Units of k
$v = k$	0	$dm^{-3} \cdot mol \cdot s^{-1}$
$v = k[A]$	1	s^{-1}
$v = k[A]^2$	2	$dm^3 \cdot mol^{-1} \cdot s^{-1}$
$v = k[A][B]$	1 in [A] 1 in [B] overall: 2	$dm^3 \cdot mol^{-1} \cdot s^{-1}$
$v = k[A]^{1/2}$	1/2	$dm^{-3/2} \cdot mol^{1/2} \cdot s^{-1}$
$v = k[A][B]^{1/2}$	1 in [A] 1/2 in [B] overall: 3/2	$dm^{3/2} \cdot mol^{-1/2} \cdot s^{-1}$

*1dm=0.1m

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

4.1. Chemical Kinetics I: rate laws

- $28-1: The time dependence of a chemical reaction is described by a rate law-

Indeed, many rate laws cannot be written in "$v(t) = k[A]^{m_A}[B]^{m_B}\cdots$" form.

We seen an example: $H_2(g) + Br_2(g) \rightarrow 2HBr\ (g)$

- ✓ The rate law of this reaction is given by

$$v(t) = \frac{k'[H_2]\,[Br_2]^{1/2}}{1 + k"[HBr]\,[Br_2]^{-1}}$$

where k' and k" are rate constants.

  - ➢ In this case, the concept of reaction order is not applicable. (we cannot define the reaction order)
  - ➢ In the next chapter ($29), we will learn such a complicated rate law tells us that the chemical reaction is composed by multiple processes.

4.1. Chemical Kinetics I: rate laws
- $28-2: Rate laws must be determined experimentally -

In this section ($28-2), we will examine two experimental techniques that chemists use to determine rate laws. For this purpose, we work with the general chemical equation.

$$\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$$

And assume that the rate law has the form:

$$v(t) = k[A]^{m_A}[B]^{m_B}$$

$$v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt} = \frac{1}{V}\frac{d\xi}{dt}$$

- ✓ Here if we know the reaction orders m_A and m_B, we pursue the concentration change in experiments and then can determine rate constant k.
- ✓ So, the first problem is how to determine the values of m_A and m_B.
    - ✓ If m_A and m_B are determined, we have got a system of ODEs. Then, it can be solved analytically or numerically.

4.1. Chemical Kinetics I: rate laws
- $28-2: Rate laws must be determined experimentally -

<Method-1: the method of isolation>

- ✓ Suppose the initial reaction mixture has a large excess concentration of A, where the concentration A remains essentially constant as the reaction takes place:

  $v(t) = k[A]^{m_A}[B]^{m_B} \sim k'[B]^{m_B}$, where $k' = k[A]^{m_A}$ is re-assigned as a constant.

- ✓ Likewise, if B is initially present in a large excess:

  $v(t) = k[A]^{m_A}[B]^{m_B} \sim k"[A]^{m_A}$, where $k" = k[B]^{m_B}$ is a constant.

This technique is called *the method of isolation*.

- ➢ To use this method, we have to always hold excess amount of A (or B) enough to consider $[A]^{m_A}$ (or $[B]^{m_B}$) is constant.
- ➢ However, sometimes it is not possible to have a reactant in excess. In this case, the method of isolation is not applicable

4.1. Chemical Kinetics I: rate laws
- $28-2: Rate laws must be determined experimentally -

<Method-2: the method of initial rates>

- ✓ Ideally, if we have many measurement data of the rate $d[A]/dt$ at various concentrations of $[A]$ and $[B]$, the orders of the reactants and the rate constant could be determined directly by fitting the data to

$$v(t) = k[A]^{m_A}[B]^{m_B}$$

- ✓ In reality, it is not possible to measure the differential, $d[A]/dt$. However, we can measure the concentration change for a finite time period, Δt; in other words, we can measure $\Delta[A]/\Delta t$. If we equate such a measurement to the reaction rate, then

$$v = -\frac{d[A]}{\nu_A dt} \sim -\frac{\Delta[A]}{\nu_A \Delta t} = k[A]^{m_A}[B]^{m_B}$$

- ✓ The approximate equality between $d[A]/dt$ and $\Delta[A]/\Delta t$ is more accurate the shorter the time period of the measurement and is exact as $\Delta t \rightarrow 0$.

4.1. Chemical Kinetics I: rate laws
- $28-2: Rate laws must be determined experimentally -

<Method-2: the method of initial rates (cont'd)>

- ✓ Consider what happens if two different measurements of the initial rate (from $t = 0$ to $t = t$) are made in which the initial concentration of A, $[A]_0$, is the same, while the initial concentration of B is varied.
- ✓ The rates of reaction for these two sets of initial conditions are given by:

$$v_1 = -\left(\frac{d[A]}{\nu_A dt}\right)_1 = k[A]_0^{m_A}[B]_1^{m_B} \sim -\frac{1}{\nu_A}\left(\frac{\Delta[A]}{\Delta t}\right)_1$$

$$v_2 = -\left(\frac{d[A]}{\nu_A dt}\right)_2 = k[A]_0^{m_A}[B]_2^{m_B} \sim -\frac{1}{\nu_A}\left(\frac{\Delta[A]}{\Delta t}\right)_2$$

where the subscripts 1 and 2 are used to distinguish between the two different experiments with different initial concentrations of [B].

- ✓ Here, we divide the first equation with the second, then taking the logarithm of both sides gives us:

$$m_B = ?$$

- ✓ Likewise, we can also determine m_A. This procedure for determining the reaction orders is called the *method of initial rates.*

4.1. Chemical Kinetics I: rate laws
- $28-2: Rate laws must be determined experimentally -

<Method-2: the method of initial rates (cont'd)>

- ✓ Consider what happens if two different measurements of the initial rate (from $t = 0$ to $t = t$) are made in which the initial concentration of A, $[A]_0$, is the same, while the initial concentration of B is varied.
- ✓ The rates of reaction for these two sets of initial conditions are given by:

$$v_1 = -\left(\frac{d[A]}{\nu_A dt}\right)_1 = k[A]_0^{m_A}[B]_1^{m_B} \sim -\frac{1}{\nu_A}\left(\frac{\Delta[A]}{\Delta t}\right)_1$$

$$v_2 = -\left(\frac{d[A]}{\nu_A dt}\right)_2 = k[A]_0^{m_A}[B]_2^{m_B} \sim -\frac{1}{\nu_A}\left(\frac{\Delta[A]}{\Delta t}\right)_2$$

where the subscripts 1 and 2 are used to distinguish between the two different experiments with different initial concentrations of [B].

- ✓ Here, we divide the first equation with the second, then taking the logarithm of both sides gives us:

$$m_B = \frac{\ln(v_1/v_2)}{\ln([B]_1/[B]_2)}$$

- ✓ Likewise, we can also determine m_A. This procedure for determining the reaction orders is called the *method of initial rates.*

4.1. Chemical Kinetics I: rate laws
- $28-2: Rate laws must be determined experimentally -

- ✓ In using either *the method of isolation* or *the method of initial rates*, we have assumed that the reactants can be mixed in any desired proportions and the reaction rate can then be measured.
- ✓ In the laboratory, two solutions can be thoroughly mixed in approximately a millisecond.
- ✓ For many reactions, the time required to mix the reactants is long compared with the reaction process itself, and thus the rate law and rate constant cannot be determined using either of the techniques discussed in this section.
- ✓ To study fast reactions, different experimental approaches must be used.
  - ✓ We will discuss some techniques that are used to study faster reactions, called *relaxation method,* to be explained later.

4.1. Chemical Kinetics I: rate laws

- $28-3: First-order reactions show an exponential decay of reactant concentration with time -

Consider a reaction: $A + B \rightarrow products$

- ✓ This chemical equation does not tell us anything about its rate law. Suppose the rate law is first order in $[A]$. Then,

$$v(t) = -\frac{d[A]}{dt} = k[A]$$

- ✓ If the concentration of A is $[A]_0$ at $t = 0$, and $[A]$ at $t = t$, this equation can be integrated to give

(Example-2) $N_2O_5(g) \rightarrow 2\,NO_2(g) + \frac{1}{2}\,O_2(g)$

$$v(t) = -\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{2d[O_2]}{dt} = k[N_2O_5]$$

4.1. Chemical Kinetics I: rate laws

- $28-3: First-order reactions show an exponential decay of reactant concentration with time -

Consider a reaction: $A + B \rightarrow products$

- ✓ This chemical equation does not tell us anything about its rate law. Suppose the rate law is first order in $[A]$. Then,

$$v(t) = -\frac{d[A]}{dt} = k[A]$$

- ✓ If the concentration of A is $[A]_0$ at $t = 0$, and $[A]$ at $t = t$, this equation can be integrated to give

$$\ln([A]/[A]_0) = -kt, \qquad \text{then} \qquad \ln[A] = \ln[A]_0 - kt\text{, or}$$

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

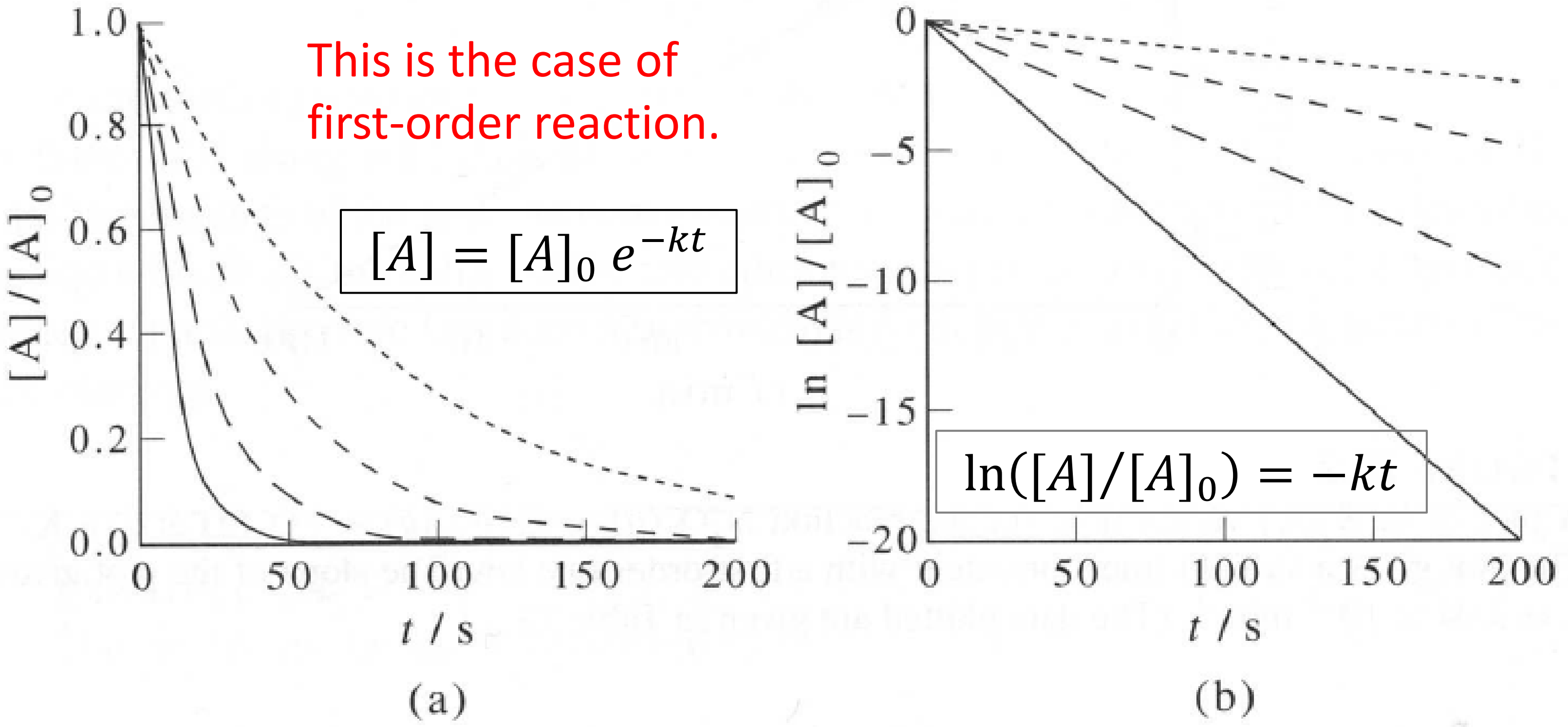
- ✓ This equation shows that $[A]$ decays exponentially with time.

(Example-2) $N_2O_5(g) \rightarrow 2\,NO_2(g) + ½\,O_2(g)$

$$v(t) = -\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = \frac{2d[O_2]}{dt} = k[N_2O_5]$$

4.1. Chemical Kinetics I: rate laws

- $28-3: First-order reactions show an exponential decay of reactant concentration with time -



This is the case of first-order reaction.

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

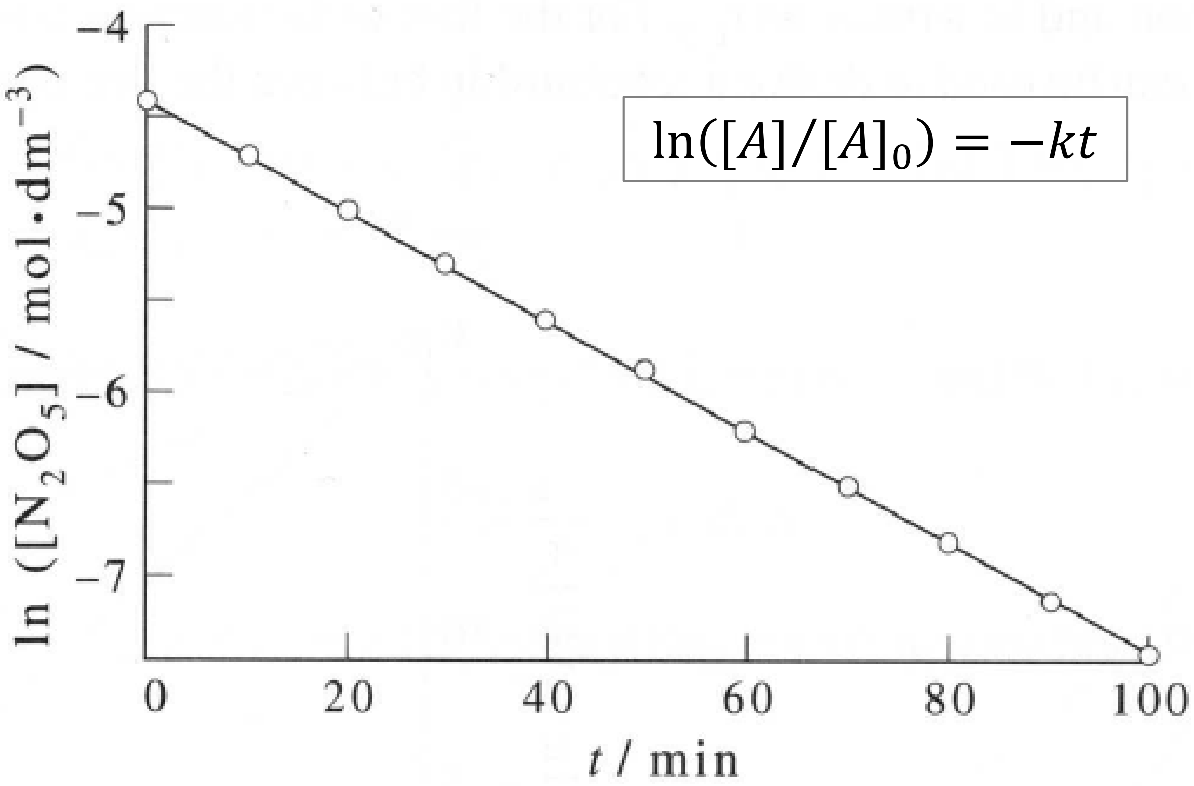
$$\boxed{\ln([A]/[A]_0) = -kt}$$

FIGURE 28.1
Kinetic plots for a first-order chemical reaction. (a) [A] is plotted as a function of t for values of the rate constant k of 0.0125 s^{-1} (dotted line), 0.0250 s^{-1} (dashed line), 0.0500 s^{-1} (long dashed line), and 0.100 s^{-1} (solid line). (b) The curves in part (a) are plotted as ln [A] versus t. The slope of the line is equal to $-k$ (see Equation 28.24).

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

4.1. Chemical Kinetics I: rate laws

- $28-3: First-order reactions show an exponential decay of reactant concentration with time -



$$\ln([A]/[A]_0) = -kt$$

FIGURE 28.2
A plot of $\ln[N_2O_5]$ versus time for the reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ at 318 K. The plot gives a straight line, consistent with a first-order rate law. The slope of the plot gives $k = 3.04 \times 10^{-2}\ \text{min}^{-1}$. (The data plotted are given in Table 28.3.)

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

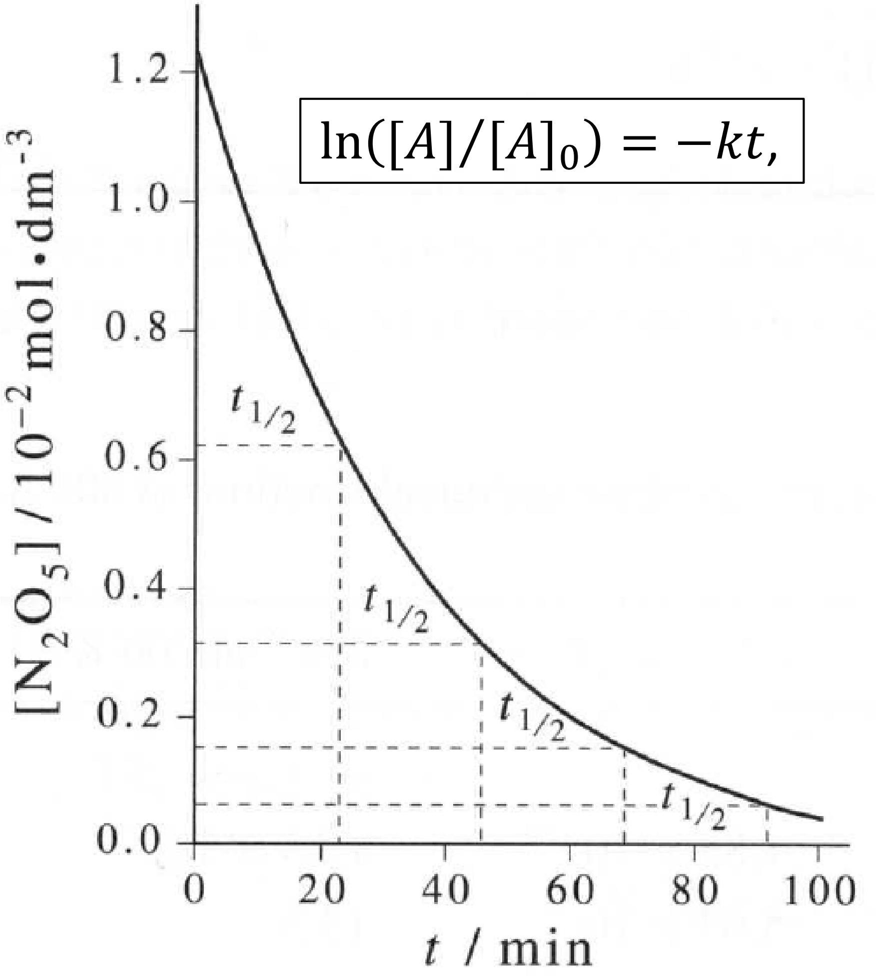
4.1. Chemical Kinetics I: rate laws

- $28-3: First-order reactions show an exponential decay of reactant concentration with time -

- ✓ The length of time required for half of the reactant to disappear is called the *half-life* of the reaction and is written as $t_{1/2}$.
- ✓ For the first-order reaction previously considered, $\ln([A]/[A]_0) = -kt$ can be used to correlate between k and $t_{1/2}$. Specifically, at time $t = t_{1/2}$, the concentration of A equals $[A] = ([A]_0/2)$ is applied to the equation, then:

$$\ln\frac{1}{2} = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$



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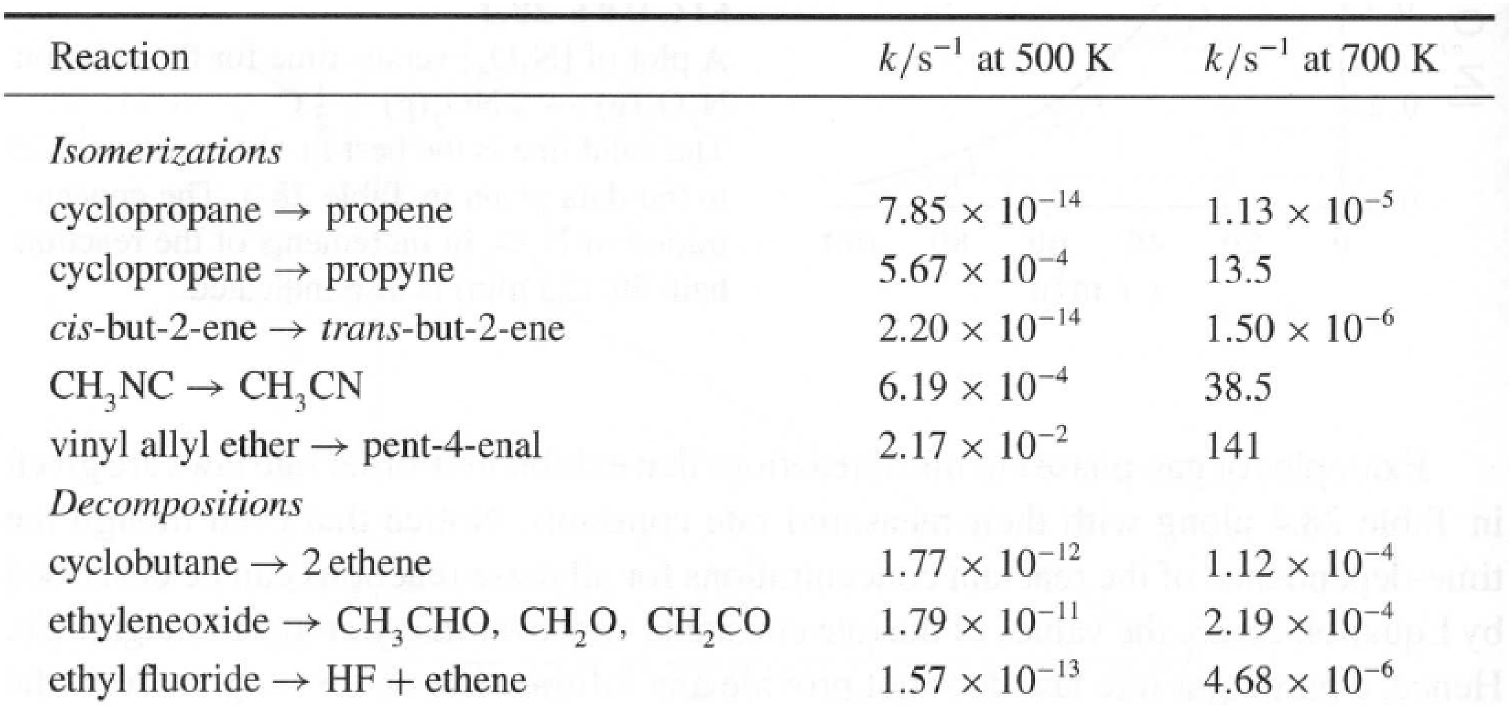
4.1. Chemical Kinetics I: rate laws

- $28-3: First-order reactions show an exponential decay of reactant concentration with time -

- ✓ In table below, the time-dependence of the reactant concentrations for all these reactions can be described by $[A] = [A]_0\, e^{-kt}$.
- ✓ However, the values of the rate constants vary over many orders of magnitude. Hence, a particular rate law does not provide any information on the magnitude of the rate constant.



Reaction	k/s^{-1} at 500 K	k/s^{-1} at 700 K
Isomerizations		
cyclopropane → propene	7.85×10^{-14}	1.13×10^{-5}
cyclopropene → propyne	5.67×10^{-4}	13.5
cis-but-2-ene → *trans*-but-2-ene	2.20×10^{-14}	1.50×10^{-6}
$CH_3NC \rightarrow CH_3CN$	6.19×10^{-4}	38.5
vinyl allyl ether → pent-4-enal	2.17×10^{-2}	141
Decompositions		
cyclobutane → 2 ethene	1.77×10^{-12}	1.12×10^{-4}
ethyleneoxide → CH_3CHO, CH_2O, CH_2CO	1.79×10^{-11}	2.19×10^{-4}
ethyl fluoride → HF + ethene	1.57×10^{-13}	4.68×10^{-6}

$$\boxed{t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}}$$

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4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

- ✓ For a first-order reaction, we learned that the concentrations of the reactants decay exponentially with time.
- ✓ However, different reaction orders exhibit different functional forms for the time dependence of reactant concentrations, which gives us information on the mechanism of the reaction though.

<Second-order reaction>

Consider the equation: "*A + B → products*" assuming that experimental data indicate the following rate law, which is of a *second-order reaction*:

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

4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

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- ✓ However, different reaction orders exhibit different functional forms for the time dependence of reactant concentrations, which gives us information on the mechanism of the reaction though.

<Second-order reaction>

Consider the equation: "*A + B → products*" assuming that experimental data indicate the following rate law, which is of a *second-order reaction*:

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

- ✓ Given that the initial concentration at $t = 0$ is $[A]_0$ and the concentration at $t = t$ is $[A]$, then the differential equation is solved as:

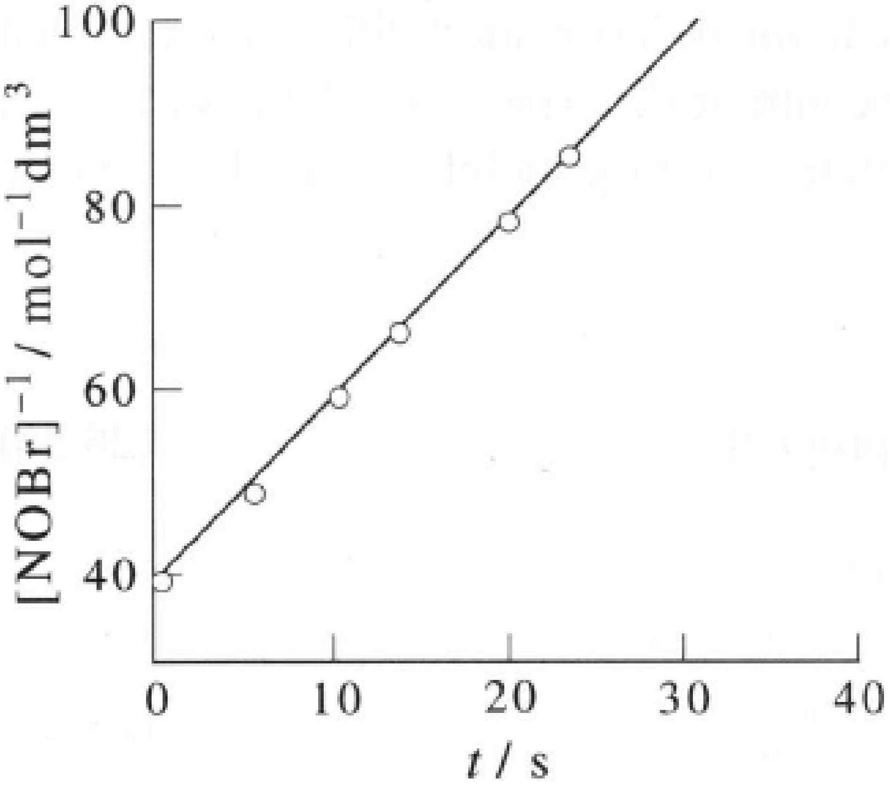
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

- ✓ For example, the reaction "*NOBr(g) → NO(g) + ½ Br*$_2$*(g)*" is a second-order reaction and thus the rate law is:

$$v = k[NOBr]^2$$

4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -



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

FIGURE 28.4
A plot of 1/[NOBr] versus time for the reaction $NOBr(g) \rightarrow NO(g) + \frac{1}{2} Br_2(g)$. The experimental data are given in Table 28.5. The linear dependence of 1/[NOBr] on time is consistent with a second-order rate law, Equation 28.28. The value of the rate constant, given by the slope of the line, is equal to $2.01\ dm^3 \cdot mol^{-1} \cdot s^{-1}$.

*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

<Second-order reaction>

Consider the equation: *“A + B → products”* assuming that experimental data indicate the following rate law, which is of a *second-order reaction*:

$$-\frac{d[A]}{dt} = k[A]^2 \quad , \qquad \frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

✓ The half-life of a second-order reaction can be written as

4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

<Second-order reaction>

Consider the equation: *"A + B → products"* assuming that experimental data indicate the following rate law, which is of a *second-order reaction*:

$$-\frac{d[A]}{dt} = k[A]^2 \quad , \qquad \frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

✓ The half-life of a second-order reaction can be written as

$$t_{1/2} = \frac{1}{k[A]_0}$$

➢ Note that, differently from a first-order reaction ($t_{1/2} = \frac{\ln 2}{k}$), the half-life depends on the initial concentration of the reactant.

We consider another type of second-order reaction: *"A + B → products"* assuming that experimental data indicate the following rate law:

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

✓ The overall order is 2nd also in this case.

4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

<Second-order reaction>

We consider another type of second-order reaction: "*A + B → products*" assuming that experimental data indicate the following rate law:

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

- ✓ Taking integral, we obtain: $kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[A][B]_0}{[B][A]_0}$
- ✓ If $[A]_0 = [B]_0$, then: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ or $\frac{1}{[B]} = \frac{1}{[B]_0} + kt$

*This equations are consistent with the one in the previous case.

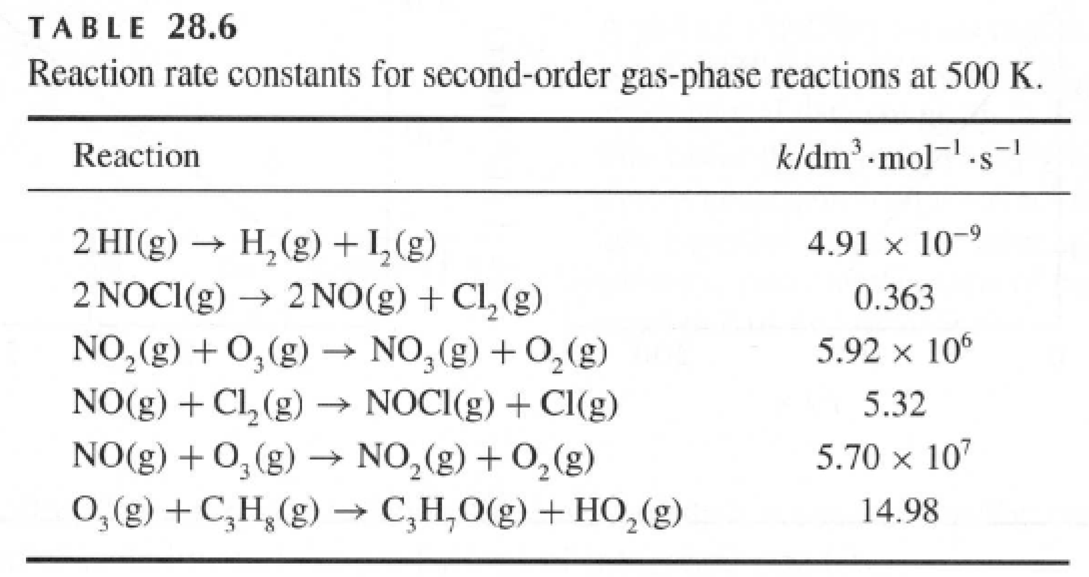


TABLE 28.6

Reaction rate constants for second-order gas-phase reactions at 500 K.

Reaction	$k/\mathrm{dm^3 \cdot mol^{-1} \cdot s^{-1}}$
$2\,HI(g) \rightarrow H_2(g) + I_2(g)$	4.91×10^{-9}
$2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g)$	0.363
$NO_2(g) + O_3(g) \rightarrow NO_3(g) + O_2(g)$	5.92×10^{6}
$NO(g) + Cl_2(g) \rightarrow NOCl(g) + Cl(g)$	5.32
$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$	5.70×10^{7}
$O_3(g) + C_3H_8(g) \rightarrow C_3H_7O(g) + HO_2(g)$	14.98

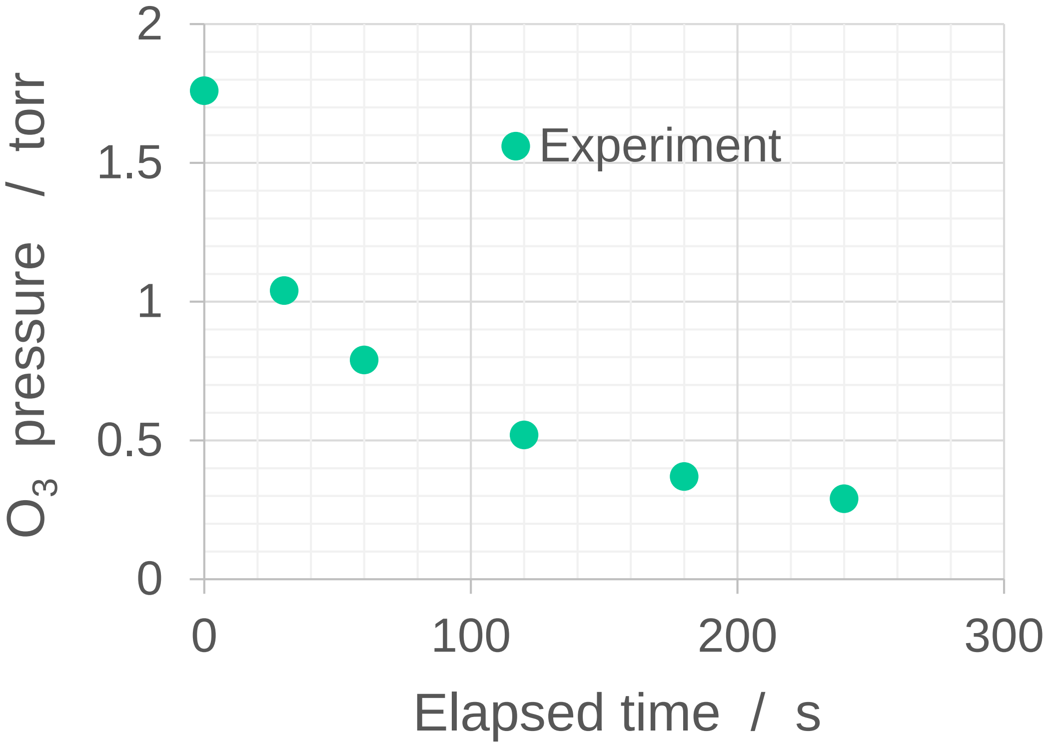
*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

4.1. Chemical Kinetics I: rate laws

- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

(Example-3) *"$CS_2(g) + 2\ O_3(g) \rightarrow CO_2(g) + 2\ SO_2(g)$"*
Assuming that an experiment has done with a large excess of CS_2 and the following data were achieved:

Time / s	0	30	60	120	180	240
Ozone pressure / torr	1.76	1.04	0.79	0.52	0.37	0.29



4.1. Chemical Kinetics I: rate laws

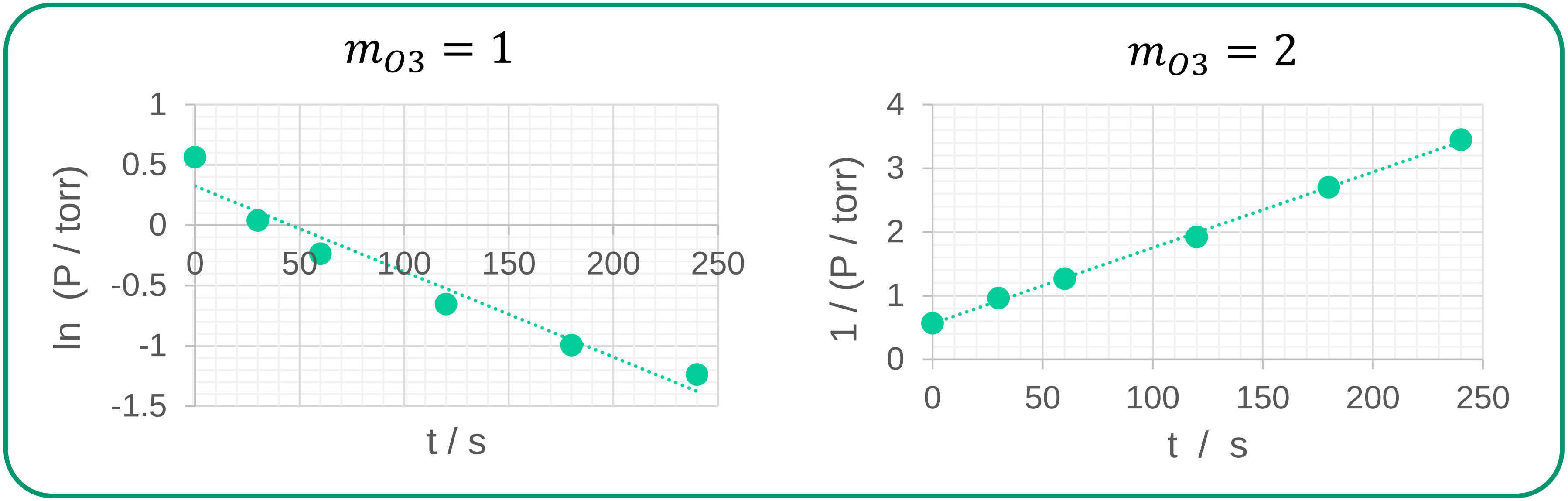
- $28-4: The rate laws for different reaction orders predict different behaviors for time-dependent reactant concentrations -

(Example-3) “$CS_2(g) + 2\,O_3(g) \rightarrow CO_2(g) + 2\,SO_2(g)$”

Time / s	0	30	60	120	180	240
Ozone pressure / torr	1.76	1.04	0.79	0.52	0.37	0.29

Because CS_2 is present in excess, $[CS_2]$ is essentially constant ad then:

$$v = k[CS_2]^{m_{CS2}}[O_3]^{m_{O3}} \sim k'[O_3]^{m_{O3}} \propto {P_{O_3}}^{m_{O3}}$$



$m_{O3} = 1$

$m_{O3} = 2$

The comparison of plots indicate that the reaction is second order in ozone concentration.