

## CHAPTER 9 LECTURE NOTES

### 9.1, 9.2: Rate of a reaction

- For a general reaction of the type  $A + 3B \rightarrow 2Y$ , the rates of consumption of A and B, and the rate of formation of Y are defined as follows:

$$\text{Rate of consumption of A: } v_A = \frac{-d[A]}{dt},$$

$$\text{Rate of consumption of B: } v_B = \frac{-d[B]}{dt},$$

$$\text{Rate of formation of Y: } v_Y = \frac{d[Y]}{dt}.$$

Note the negative signs in front of the species whose concentrations decrease with time.

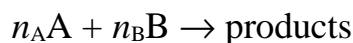
- These rates are related to each other and the rate of the reaction, denoted by  $v$ , as follows:

$$v = -v_A = \frac{-1}{3}v_B = \frac{1}{2}v_Y,$$

where we have defined  $v$  to be positive. Carefully note the relationship between the stoichiometric coefficients appearing in the balanced chemical reaction equation and the definition of the reaction rate. The rate of a reaction will have units of  $(\text{conc})(\text{time})^{-1}$ .

### 9.3 Empirical Rate Equations

- The “rate law” for a chemical reaction



is written as

$$v = k[A]^\alpha[B]^\beta,$$

where  $k$  is called the rate constant,  $\alpha$  is the order of the reaction with respect to A,  $\beta$  is the order with respect to B, and the sum  $\alpha + \beta$  is the total order of the reaction.

- In general,  $n_A \neq \alpha$ , and  $n_B \neq \beta$ , except in the case of **elementary reactions**, which are reactions that take place in a single step at the molecular level.
- Note that the rate law does not have anything to do with the products of the reaction.
- The rate constant is a proportionality constant independent of the concentrations but highly sensitive to temperature.

## Determination of Rate Law: A General Method

Determining the rate law of a reaction involves the determination of the order of the reaction with respect to each reactant and then the determination of the rate constant. The experimental method commonly used is the “method of constant concentrations.” For a reaction involving two reactants, this method requires a minimum of three trials. For a reaction involving three reactants, a minimum of four trials are required. During each trial, the reaction is initiated with known concentrations of each of the reactants and the initial rate (the rate of the reaction soon after it is started) is measured. During subsequent trials, the concentration of one of the reactants is held fixed and the other is changed. Let us assume that the data collected is as follows:

Trial #	[A] (M)	[B] (M)	Rate (M s <sup>-1</sup> )
1	$a_1$	$b_1$	$v_1$
2	$a_1$	$b_2$	$v_2$
3	$a_3$	$b_3$	$v_3$

Note that the concentration of A is held constant between trials 1 and 2. Now,

$$v = k[A]^\alpha[B]^\beta.$$

Taking the natural log of both sides for trials 1 and 2, we get

$$\ln v_1 = \ln k + \alpha \ln a_1 + \beta \ln b_1.$$

$$\ln v_2 = \ln k + \alpha \ln a_1 + \beta \ln b_2.$$

Subtracting the first equation from the second, we get

$$\ln \frac{v_2}{v_1} = \beta \ln \frac{b_2}{b_1},$$

from which  $\beta$  is easily found, once the rate measurements are made to determine  $v_1$  and  $v_2$ . Now, from trial 3 and one of the other trials, say trial 1, we get

$$\ln \frac{v_3}{v_1} = \alpha \ln \frac{a_3}{a_1} + \beta \ln \frac{b_3}{b_1}.$$

Once  $v_3$  has been determined by experiment, this equation can be rearranged to yield  $\alpha$  using the value of  $\beta$  found earlier.

### Problems: 9.1–9.3

## 9.4. Analysis of Kinetic Results

The rate law found above is called the “differential rate law” since the rate  $v$  is expressed as a differential with respect to time. For certain simple cases, it is possible to integrate the differential rate law to yield “integrated” rate laws that are far more useful in analyzing the results of kinetics experiments. We consider three special cases where the integration can be carried out without too much trouble.

### 1. First order reaction:

Consider the reaction  $A \rightarrow$  products. Let us assume that the reaction is initiated with a concentration  $a_0 \text{ mol dm}^{-3}$  of A. At time  $t$ ,  $x \text{ mol dm}^{-3}$  have reacted. This can be expressed in the form of the differential rate law as

$$\frac{-d[A]}{dt} = \frac{-d(a_0 - x)}{dt} = \frac{dx}{dt} = k(a_0 - x).$$

Rearranging and integrating, we get

$$k \int_0^{\tau} dt = \int_0^y \frac{dx}{(a_0 - x)}, \text{ which gives}$$
$$k\tau = -\ln \frac{a_0 - y}{a_0}.$$

We now substitute back the more familiar variables of  $t$  and  $x$  and rearrange to get

$$kt = \ln \left( \frac{a_0}{a_0 - x} \right). \quad (9.28)$$

This is one of the forms of the integrated first order rate law. The equation may be rearranged in the following ways:

- $\ln(a_0 - x) = \ln a_0 - kt$ , which implies that a plot of  $\ln(a_0 - x)$  vs.  $t$  will yield a straight line with a slope of  $-k$  and an intercept of  $\ln a_0$ .
- Rearranging and taking inverse log of both sides of equation (1) yields

$$(a_0 - x) = a_0 e^{-kt}. \quad (9.30)$$

- Equations (9.28) and (9.30) are very useful for kinetic data analysis.
- Half-life of a reaction is defined as the time it takes for the initial concentration to be reduced to half its original value. In other words, the time required for  $[A] = a_0$  to become  $[A] = a_0/2$ . Substituting in Eq. (1), this gives

$$kt_{1/2} = \ln \left( \frac{a_0}{a_0/2} \right) = \ln 2. \quad (9.38)$$

The half-life of a first order reaction is, therefore, a constant. We have

$$k = \ln 2/t_{1/2} \text{ or } t_{1/2} = \ln 2/k. \quad (9.39)$$

**Problems: 9.4, 9.5, 9.7, 9.8, 9.12**

## 2. Second order reaction (case 1):

Consider the second order reaction  $2A \rightarrow \text{products}$ . As before, the differential rate law can be written as

$$\frac{dx}{dt} = k(a_0 - x)^2,$$

which, after the usual rearrangement and integration, yields

$$\begin{aligned} kt &= \frac{1}{(a_0 - x)} - \frac{1}{a_0}, \text{ or} \\ kt &= \frac{x}{a_0(a_0 - x)}. \end{aligned} \tag{9.35}$$

The half-life of the reaction can be found as before:

$$\begin{aligned} kt_{1/2} &= \frac{1}{(a_0/2)} - \frac{1}{a_0} = \frac{1}{a_0}, \text{ or} \\ t_{1/2} &= \frac{1}{ka_0}. \end{aligned} \tag{9.40}$$

For the second order reaction, the half-life explicitly depends on the initial concentration.

## 2. Second order reaction (case 2):

Consider the second order reaction  $A + B \rightarrow \text{products}$ . The differential rate law can be written as

$$\frac{dx}{dt} = k(a_0 - x)(b_0 - x).$$

Rearranging and integrating with respect to  $x$  yields

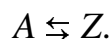
$$kt = \frac{1}{(a_0 - b_0)} \ln \frac{b_0(a_0 - x)}{a_0(b_0 - x)}; \quad a_0 > b_0. \tag{9.37}$$

In this case, it is meaningless to speak of a half-life unless the initial concentrations of the two species happen to be identical.

**Problem: 9.6, 9.9, 9.10, 9.11, 9.15, 9.17, 9.20**

## Reversible Reactions:

A reversible reaction that is first order in both directions is a very simple but useful case:



Denoting the forward rate constant as  $k_1$  and the reverse rate constant as  $k_{-1}$ , we get

$$\frac{dx}{dt} = k_1(a_0 - x) - k_{-1}x, \quad (9.45)$$

where we have assumed that initially no  $Z$  is present.

At equilibrium, the forward and reverse rates become equal and therefore the net change in concentrations becomes zero:

$$0 = k_1(a_0 - x_e) - k_{-1}x_e. \quad (9.46)$$

From this equation, we get the definition of the equilibrium constant

$$K_C = x_e/(a_0 - x_e) = k_1/k_{-1}.$$

Now, subtracting (9.46) from (9.45), we get

$$\frac{dx}{dt} = (k_1 + k_{-1})(x_e - x),$$

which, when re-arranged and integrated between appropriate limits, yields

$$(k_1 + k_{-1})t = \ln \left[ \frac{(x_e - x)_0}{(x_e - x)} \right].$$

Now, since  $x = 0$  at  $t = 0$ , this equation reduces to

$$(k_1 + k_{-1})t = \ln \left[ \frac{x_e}{(x_e - x)} \right].$$

This equation is, in every way, equivalent to Eq. (9.48). Another form of this equation is obtained by taking the inverse log of both sides and re-arranging to get

$$(x_e - x) = x_e e^{-(k_1 + k_{-1})t},$$

which is comparable to Eq. (9.30). This equation describes the approach to equilibrium from a non-equilibrium state and finds applications in various “pulse” methods used to study very fast reactions. The time scale given by  $t^* = 1/(k_1 + k_{-1})$  is called “relaxation time.”

### Read Section 9.5.

**Problems:** 9.24, 9.35–9.37

## 9.6. Influence of Temperature on Rate Constants.

The influence of temperature on rate constants were first studied by van't Hoff and Svante Arrhenius. The Arrhenius expression is

$$k(T) = Ae^{-E_a/RT}, \quad (9.59)$$

where  $k$  is explicitly shown as a function of temperature  $T$ ,  $A$  is called the pre-exponential factor,  $E_a$  is called the activation energy and  $R$  is the gas constant.

Taking natural log of both sides, we get

$$\ln k = \ln A - E_a/RT,$$

which indicates that a plot of  $\ln k$  vs.  $1/T$  will yield a line with a slope equal to  $-E_a/R$ . Measuring the rate constant over a range of temperatures, therefore, allows the activation energy to be calculated. The equation can also be written for two temperatures  $T_1$  and  $T_2$  as

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where  $k_1$  is the value of the rate constant at  $T_1$  and  $k_2$  is the value at  $T_2$ .

Modern experiments over wide temperature ranges have shown that the Arrhenius expression, which assumes that the pre-exponential factor is a constant independent of temperature, is an oversimplification. The modern expression for the temperature dependence of rate constants is often written as

$$k(T) = BT^n e^{-E/RT},$$

where both  $B$  and  $n$  are empirical constants ( $n$  is not usually an integer) to be found by experiment or calculation. The  $E$  in this expression obviously does not have the same physical interpretation or numerical value as the  $E_a$  in the Arrhenius expression.

**Problems:** 9.25–9.33

## 9.9. The Preexponential Factor

There is much interest in accounting for the magnitude of the pre-exponential factor from a theoretical point of view. Two theories have been used to do this: (a) Hard-Sphere Collision Theory, and (b) Transition State Theory. We will now briefly examine each of these theories. The former explicitly applies to gas phase reactions only while the latter can be applied to solution reactions with some modifications.

## Hard Sphere Collision Theory

The main assumptions are the following:

- Collision density, i.e., total number of collisions per unit time per unit volume, in a sample of gas is given by

$$Z_{AA} = \frac{1}{2} \sqrt{2} \pi d_{AA}^2 \left( \frac{8k_B T}{\pi m_A} \right)^{1/2} \left( \frac{N_A}{V} \right)^2, \quad (9.71)$$

where  $d_{AA}$  is the diameter of the atoms/molecules A, the quantity within the square-root is the mean molecular velocity [see Eq. (9.72)], and  $N_A/V$  is the number of molecules per unit volume in units of molecules  $\text{m}^{-3}$ .

- The corresponding expression for collisions between two different species A and B is given by

$$Z_{AB} = \left[ \pi d_{AB}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \right] \left( \frac{N_A}{V} \right) \left( \frac{N_B}{V} \right),$$

where  $\mu = m_A m_B / (m_A + m_B)$  is called the “reduced mass.” The use of  $\mu$  instead of  $m_A + m_B$  in the expression for the mean velocity automatically yields the mean *relative* velocity of the colliding masses [the  $\sqrt{2}$  appearing in Eq. (9.71) serves the same purpose]. The collision diameter  $d_{AB} = r_A + r_B$ .

- In these equations, the quantity  $\pi d^2$  is called the collision cross section. If every collision resulted in reaction, the quantity within the square brackets above will be equal to the rate constant  $k$ . However, only collisions having energy above a certain threshold,  $\epsilon^*$ , yields a reaction. This suggests that a “reaction cross section,” which depends on the collision energy but approaches the value of the collision cross section at very high energies, be defined. One physically intuitive model for the reaction cross-section is

$$\text{Reaction cross section} = \begin{cases} 0 & \text{for } \epsilon \leq \epsilon^* \\ \pi d_{AB}^2 \left( 1 - \frac{\epsilon^*}{\epsilon} \right) & \text{for } \epsilon > \epsilon^* \end{cases}$$

- This threshold energy  $\epsilon^*$  is not the same as the Arrhenius activation energy  $E_a$ . The actual nature of the threshold energy  $\epsilon^*$  will be discussed later, in connection with Transition State Theory.
- Taking the Maxwell-Boltzmann distribution of energies and the reaction cross section into account, we obtain the final expression for the rate constant as

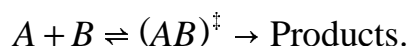
$$k = \pi d_{AB}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-\epsilon^*/k_B T}.$$

- As written, this second order rate constant has units of  $(\text{m}^{-3})^{-1} \text{s}^{-1}$  (verify this!). The proper units of the rate constant should be  $(\text{molecules m}^{-3})^{-1} \text{s}^{-1}$ , but the “molecules” part is implied (as is the case for the units of the Avogadro number).
- The more common units are, of course,  $(\text{moles dm}^{-3})^{-1} \text{s}^{-1}$ , which we can get as follows:

$$\begin{aligned} k(\text{moles dm}^{-3})^{-1} \text{s}^{-1} &= k(\text{molecules m}^{-3})^{-1} \text{s}^{-1} \times L \text{ molecules mol}^{-1} \times 10^3 \text{ dm}^3 \text{ m}^{-3} \\ &= 10^3 L \times \pi d_{AB}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-\varepsilon^*/k_B T}. \end{aligned}$$

## Transition State Theory

Transition State Theory (TST) begins with the following assumption:



The entity represented as  $(AB)^\ddagger$  is called the transition state or the “activated complex.” This is a “super-molecule” in which one or more atoms have either supersaturated or unsaturated valencies which means that the transition state is usually a high energy, unstable species than the reactants or the products. The transition state is assumed to be in equilibrium with the reactants [equilibrium constant  $K_C^\ddagger = \exp(-\Delta G^\ddagger/RT)$ , where  $\Delta G^\ddagger$  is called the *free energy of activation*] and it also undergoes a first order decomposition reaction (rate constant  $k^\ddagger$ ) to yield products. So, the rate of formation of products can be written as

$$\frac{dx}{dt} = k^\ddagger [(AB)^\ddagger] = k^\ddagger K_C^\ddagger [A][B].$$

The experimentally observed second-order rate constant,  $k$ , for the overall reaction is, of course, the composite quantity  $k^\ddagger K_C^\ddagger$ . Therefore, we write

$$k = k^\ddagger e^{-\Delta G^\ddagger/RT} = k^\ddagger \exp\left[-\frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right],$$

whereby we have introduced the quantities *enthalpy of activation* and *entropy of activation*. The first order rate constant  $k^\ddagger$  can almost always be associated with the frequency of one of the vibrational modes of the transition state. Furthermore, using the definition of the equilibrium constant from statistical mechanics (Chapter 15), it is possible to replace it with the quantity  $(k_B T/h)$ , where  $h$  is the Planck’s constant. The expression for the second order rate constant then, is

$$k = \left[ \left( \frac{k_B T}{h} \right) e^{\Delta S^\ddagger/R} \right] e^{-\Delta H^\ddagger/RT}.$$

It is very tempting at this point to associate the quantity in the square brackets with the Arrhenius pre-exponential factor and the enthalpy of activation with the

activation energy. However, these associations are not quite correct. Let us now try to arrive at the correct associations.

From one form of the Arrhenius equation, we get  $\ln k = \ln A - E_a/RT$ . Therefore,

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}, \text{ or } E_a = RT^2 \frac{d \ln k}{dT}.$$

The second equation can be considered to be the definition of activation energy. Now, turning to the TST expression for the rate constant, we get

$$\ln k = \ln\left(\frac{k_B T}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}.$$

We now recall that  $\Delta H^\ddagger = \Delta U^\ddagger + \Delta n^\ddagger(RT)$  for gas phase reactions and  $\Delta H^\ddagger = \Delta U^\ddagger$  for solution reactions, where  $\Delta n^\ddagger$  is the change in the number of moles of gases in going from reactants to the transition state. Since the transition state is always a single super-molecule,  $\Delta n^\ddagger = 1 - n$ , where  $n$  is the molecularity of the reaction. Substituting for  $\Delta H^\ddagger = \Delta U^\ddagger + (1 - n)RT$ , we get

$$\ln k = \ln\left(\frac{k_B T}{h}\right) + \frac{\Delta S^\ddagger}{R} + (n - 1) - \frac{\Delta U^\ddagger}{RT}.$$

Now, differentiating with respect to  $T$  and multiplying throughout by  $RT^2$ , we get

$$E = RT^2 \frac{d \ln k}{dT} = \Delta U^\ddagger + RT,$$

which provides the connection between the activation energy  $E$  and the internal energy of activation  $\Delta U^\ddagger$ . Therefore, we have

$$\begin{aligned} k &= \left[ \left( \frac{k_B T}{h} \right) e^{\Delta S^\ddagger / R + (n-1)} \right] e^{-E_a / RT} e^1 \\ &= \left[ \left( \frac{k_B T}{h} \right) e^{\Delta S^\ddagger / R + n} \right] e^{-E_a / RT}. \end{aligned}$$

The last equation clearly provides an expression for the Arrhenius pre-exponential factor for a gas phase reaction, typically with  $n = 2$ . Setting  $n = 0$ , we also get the expression for a solution reaction. Therefore, we can calculate all of the thermodynamic state properties of the transition state from an expression for the temperature dependence of the rate coefficient in the Arrhenius form.

**Problems: 9.38–9.45**