2   Reaction Rate and Rate Law

2.1   Rate of reaction

(a)   (b)
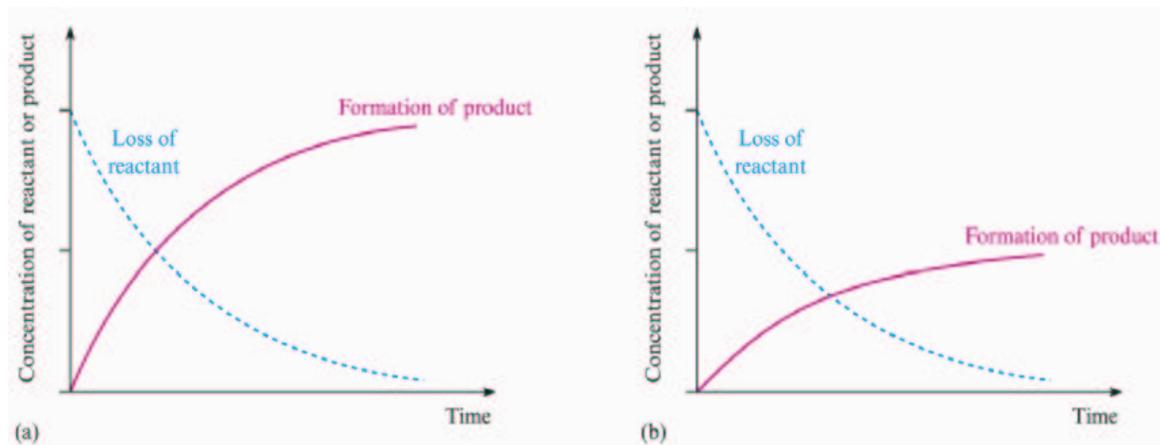
The graphs above show the change along time of the concentrations of the reactant and the product. The <u>rate</u> of the loss of the reactant at a particular moment is given by the slope of the tangent of the graph at that moment. (See also the diagram below.)

$$\text{Rate of loss of reactant (R)} = -\frac{d[\text{R}]}{dt} \qquad (9)$$

Similarly, the rate of the formation of the product at that moment is given by

$$\text{Rate of formation of product (P)} = +\frac{d[\text{P}]}{dt} \qquad (10)$$

Note the minus sign in (9): the reactant concentration [R] is decaying along time so that its derivative $d[\text{R}]/dt$ is negative, and therefore Eq (9) overall is positive.

In general, reaction rates change along time. As the graph below shows, the rate is usually the largest at the beginning ($t = 0$) and gradually decreases along time as the reaction proceeds and the concentrations approach to their asymptotic (equilibrium) values.
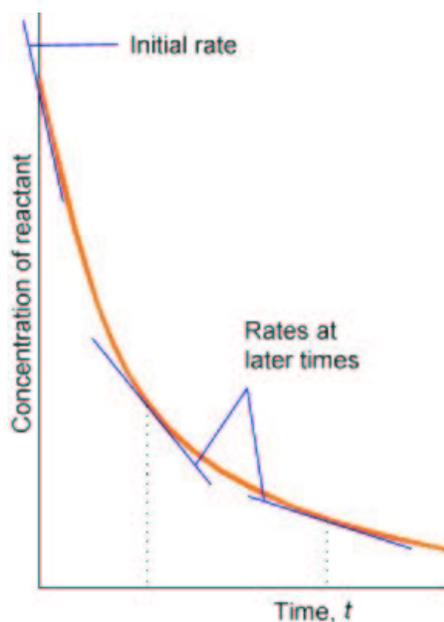
2.1.1 Stoichiometry

Let us consider a reaction A $\rightarrow$ B, where one mole of A produces one mole of B. The rates of the loss of A and the formation of B are related as

$$A \longrightarrow B \quad \Rightarrow \quad -\frac{d[A]}{dt} = \frac{d[B]}{dt} \tag{11}$$
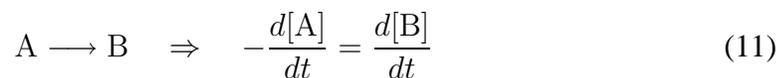
Now, how should (or should not) this be modified for a different reaction A $\rightarrow$ 2B ? In this case, because two moles of B is produced as one mole of A is lost, the rate of the former is twice as large as the latter. Therefore, we find

$$A \longrightarrow 2B \quad \Rightarrow \quad -\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt} \tag{12}$$
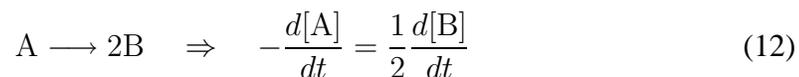
Similarly, for a reaction 2A $\rightarrow$ B,

$$2A \longrightarrow B \quad \Rightarrow \quad -\frac{d[A]}{dt} = (?)\frac{d[B]}{dt} \tag{13}$$

(Find the numerical coefficient.)

8
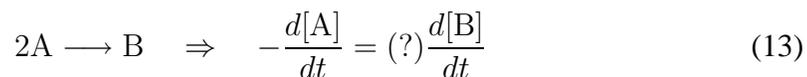
Question:

Consider the reaction

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

Find the numerical coefficients in

$$-\frac{d[N_2O_5]}{dt} = (?)\frac{d[NO_2]}{dt} = (?)\frac{d[O_2]}{dt}$$
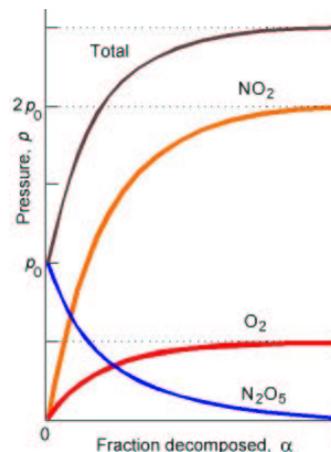
Here is a useful formula for general reactions

$$n_1\,R_1 + n_2\,R_2 + \cdots \longrightarrow m_1\,P_1 + m_2\,P_2 + \cdots \tag{14}$$
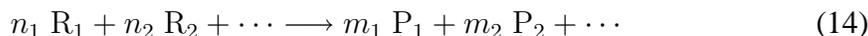
We simply put the inverse of the molar coefficients in front of the derivatives $d[R]/dt$ etc., remembering the minus signs for the reactants;

$$-\frac{1}{n_1}\frac{d[R_1]}{dt} = -\frac{1}{n_2}\frac{d[R_2]}{dt} = \cdots = +\frac{1}{m_1}\frac{d[P_1]}{dt} = +\frac{1}{m_2}\frac{d[P_2]}{dt} = \cdots \tag{15}$$

2.2 Rate Law

As we have seen, the reaction rates changes along time, normally decreases along with the progress of the reaction. This implies that the rate decreases as the number of reactant molecules decreases. Normally, as the concentrations [†] of the reactants decreases, the chance of their reactive encounter will also decrease. (On the other hand, the increase of the product concentrations may inhibit the reaction.)

We **often** observe that the reaction rates are proportional to the concentrations or the square of the concentrations of the reactants. We **sometimes** observe the reaction rates proportional to the cube or the square-root of the concentrations. These may be described in a form,

$$\text{Rate} = k[A]^n[B]^m \cdots \tag{16}$$

where the coefficient k is called the **rate constant** of the reaction. n and m are the **orders** with respect to the reactants A and B, respectively. They are most often 1 or 2, and sometimes 3 or 1/2. We also define the **overall order** by $n + m$.

[†]For gas phase reactions, we usually consider partial pressures of the species instead of concentrations. The partial pressure is proportional to the concentration for ideal gases at a given temperature and volume, $pV = nRT \Rightarrow p = RT(n/V)$.

It is very important to note that the orders cannot be predicted simply from the stoichiometry of the reaction. Let us see the following two examples:

Example 1.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \tag{17}$$
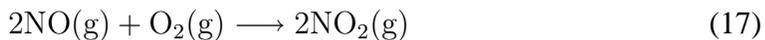
$$\text{Observed rate law: Rate} = k[NO]^2[O_2]$$

Example 2.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \tag{18}$$
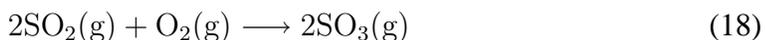
$$\text{Observed rate law: Rate} = k[SO_2][SO_3]^{-\frac{1}{2}} = k\frac{[SO_2]}{\sqrt{[SO_3]}}$$

Note that these two reactions have the same stoichiometry of

$$2A + O_2 \longrightarrow 2AO \tag{19}$$

but the observed rate laws (the orders) are totally different. This means that we cannot predict the rate law just by looking at the equation of the reaction. Generally, the rate laws must be determined from experiments. The experimental methods and their theoretical background will be discussed in the next section.

As we will see in the subsequent discussions, different rate laws come from different **mechanisms** of the reaction. Namely, different involvements of the **elementary steps** and the associated **intermediate species**. In other words, by carefully examining the rate law, we expect to be able to clarify the mechanism of the reaction. This is indeed the major motivation to study Chemical Kinetics. From the analysis of the rate laws derived from experiments, we can discuss and infer the mechanism of the reactions.

Question: State the orders with respect to each specie and the overall order for Examples 1 and 2. Does the rate increase or decrease as the concentration of SO_3 increases in Example 2? What could be the chemical reason for this?

2.3 Temperature Dependence

2.3.1 Arrhenius law

Normally, the reaction rates increase by raising the temperature. This sounds natural since the reactant molecules will move more actively in higher temperature, and hence the chance of their reactive encounter will be larger. It was found from a number of