CP303 — Set #1 (July-October 2013)

Reaction Kinetics: Rate Equations

(It is important to have this note set with you during all lecture classes.)

1.1 Rate of Reaction:

In a reaction of our interest, say, a moles of a component A reacts with b moles of a second component B to produce p moles of the component P. The above stoichiometric reaction is given by

$$a\,A + b\,B \longrightarrow p\,P \tag{1.1}$$

The rate of disappearance of A in the above reaction is in general modeled by the following rate equation:

$$r_A = -k\,C_A^n\,C_B^m \tag{1.2}$$

where k is the specific reaction rate (also known as the rate constant), and C_A and C_B are the concentration of A and B, respectively. The negative sign in (1.2) represents the fact A is disappearing during the reaction. When r_A is given by (1.2), the reaction is said to be n^{th} order in A and m^{th} order in B. The overall order of the reaction is $m+n$. Unit of r_A is mols per unit time per unit volume. And, unit of k depends on the overall reaction order.

In order to write (1.2), the given reaction should be a **homogeneous** reaction. That is, the reaction should take place either entirely in liquid phase or entirely in gas phase. We need not consider reaction taking place entirely in solid phase, since it is impossible for such reaction to happen in reality (why?).

Homogeneous reactions may be either **elementary** or **non-elementary**. Elementary reactions are those reactions that occur exactly as they are written, without any intermediate steps. These reactions almost always involve just one or two reactants. If the given reaction is an **elementary** reaction then $n = a$ and $m = b$, which are the stoichiometric values of A and B given in the reaction of (1.1), respectively. If the reaction is a non-elementary reaction then the numerical values of n and m must be found by carrying out experiments, as will be discussed latter in this lecture series.

Examples of elementary irreversible reactions:

Reaction 1:

$$C_2H_6(g) \longrightarrow C_2H_4(g) + H_2(g) \quad \text{which gives} \quad -r_{C_2H_6} = k\,C_{C_2H_6}$$

Reaction 2:

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \text{which gives} \quad -r_{NO} = k_{NO}\,(C_{NO})^2\,C_{O_2}$$

Reaction 3:

$$CH_2OCH_2(aq) + H_2O(aq) \longrightarrow (CH_2OH)_2(aq) \quad \text{which gives} \quad -r_{CH_2OCH_2} = k\,C_{CH_2OCH_2}$$

Explain why concentration of H_2O is not included in the rate equation above.

1.2 Specific Reaction Rate (or Rate Constant):

The specific reaction rate k is a function of temperature, and the temperature dependence of k in general is modeled by the Arrhenius equation as follows:

$$k = k_o \exp\left(\frac{-E}{RT}\right) \tag{1.3}$$

where k_o is the frequency factor, the unit of which depends on the overall reaction order as k does, E is the activation energy in J/mol, R is the gas constant in J/mol.K, and T is the absolute temperature in K.

Equation (1.3) can also be written as

$$\ln(k) = \ln(k_0) - \frac{E}{R}\left(\frac{1}{T}\right)$$

If we plot $\ln(k)$ versus $(1/T)$, we get a line with a slope of $-(E/R)$ and an intercept of $\ln(k_0)$. For large values of E, slope would be nearly vertical. It means small changes in T cause large changes in k. Therefore, we could conclude that the larger the activation energy, the more temperature sensitive k and thus the reaction rate.

If k is known as temperature T_1, then k at temperature T_2 could be expressed by the following expression:

$$k(T_2) = k(T_1)\exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

1.3 Relating the Rate of Reactions:

Since A and B are related by the stoichiometric relationship given in (1.1), the rate of reaction of B, denoted by r_B is related to r_A as follows:

$$\frac{r_A}{r_B} = \frac{a}{b} \tag{1.4}$$

Combining (1.2) and (1.4), we get

$$r_B = \frac{b}{a} r_A = -\frac{b}{a}\, k\, C_A^n\, C_B^m \tag{1.5}$$

Note that r_B should be a negative quantity, as in (1.5), since B is disappearing during the reaction.

Since the product P is related to A and B by the same stoichiometric relationship given in (1.1), the rate at which P is produced, denoted by r_P is related to r_A as follows:

$$\frac{r_P}{-r_A} = \frac{p}{a} \tag{1.6}$$

Combining (1.2) and (1.6), we get

$$r_P = \frac{p}{a}(-r_A) = \frac{p}{a}\, k\, C_A^n\, C_B^m \tag{1.7}$$

Note that r_P should be a positive quantity, as in (1.7), since P is generated during the reaction.

If we consider a very general equation given by

$$a\,A + b\,B + c\,C + \cdots \longrightarrow p\,P + q\,Q + s\,S + \cdots \tag{1.8}$$

the reaction rates of the different components in (1.8) are related to each other by

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{-r_C}{c} = \cdots = \frac{r_P}{p} = \frac{r_Q}{q} = \frac{r_S}{s} = \cdots \tag{1.9}$$

1.4 Rate of Reaction for a Reversible Reaction:

The reaction of our interest, say, is a reversible reaction given by

$$A + B \quad \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \quad P + Q \tag{1.10}$$

with the specific reaction rate for the forward reaction as k_f and that for the backward reaction as k_b.

Let us say that both the forward and the backward reactions are elementary reactions in the given reversible reaction, and we have to determine the rate of reaction of A.

In the reversible reaction, A is disappearing during the forward reaction but its is generated during the backward reaction. Therefore, rate equation for A must have two components, which could be obtained if we look at the reaction given by (1.10) as two separate reactions as follows:

Consider the forward reaction,

$$A + B \quad \overset{k_f}{\longrightarrow} \quad P + Q$$

Since it is said to be an elementary reaction, we could write

$$(r_A)_{forward\,reaction} = -k_f\,C_A\,C_B \tag{1.11}$$

Consider the backward reaction,

$$P + Q \quad \overset{k_b}{\longrightarrow} \quad A + B$$

Since it is said to be an elementary reaction, we could write

$$-r_P = (r_A)_{backward\,reaction} = k_b\,C_P\,C_Q \tag{1.12}$$

Combining (1.11) and (1.12), we get

$$\begin{aligned}(r_A)_{net} &= (r_A)_{forward\,reaction} + (r_A)_{backward\,reaction}\\ &= -k_f\,C_A\,C_B + k_b\,C_P\,C_Q\end{aligned}$$

1.5 Rate of Reaction for Series Reactions:

An example of a series reaction is given by

$$A \xrightarrow{k_1} P \xrightarrow{k_2} Q$$

which could be considered as two separate reactions given as follows:

$$A \xrightarrow{k_1} P \tag{1.13}$$

$$P \xrightarrow{k_2} Q \tag{1.14}$$

If (1.13) and (1.14) are taken to be elementary reactions, for the reaction given by (1.13) we could write

$$-r_A = (r_P)_{A \to P} = k_1\, C_A \tag{1.15}$$

and for the reaction given by (1.14) we could write

$$(-r_P)_{P \to A} = r_Q = k_2\, C_P \tag{1.16}$$

From (1.15) and (1.16), we get the following:

$$\begin{aligned} r_A &= -k_1\, C_A \\ (r_P)_{net} &= -k_2\, C_P + k_1\, C_A \\ r_Q &= k_2\, C_P \end{aligned}$$

1.6 Rate of Reaction for Parallel Reactions:

An example of a parallel reaction is given by

$$A \xrightarrow{k_1} P \quad \text{and} \quad A \xrightarrow{k_2} Q$$

which could be considered as two separate reactions given as follows:

$$A \xrightarrow{k_1} P \tag{1.17}$$

$$A \xrightarrow{k_2} Q \tag{1.18}$$

If (1.17) and (1.18) are taken to be elementary reactions, for the reaction given by (1.17) we could write

$$(-r_A)_{A \to P} = (r_P) = k_1\, C_A \tag{1.19}$$

and for the reaction given by (1.18) we could write

$$(-r_A)_{A \to Q} = (r_Q) = k_2\, C_A \tag{1.20}$$

From (1.19) and (1.20), we get the following:

$$\begin{aligned}(r_A)_{net} &= -k_1\,C_A - k_2\,C_A\\ r_P &= k_1\,C_A\\ r_Q &= k_2\,C_A\end{aligned}$$

1.7 Rate of Reaction for Combined Reactions:

Determine the net rate of reaction of A, P, Q and S in the following set of elementary reactions:

$$A \xrightarrow{k_1} P \underset{k_3}{\overset{k_2}{\rightleftharpoons}} Q \quad \text{and} \quad A \xrightarrow{k_4} 2\,S$$

which could be seen as the following separate elementary reactions:

$$A \xrightarrow{k_1} P \tag{1.21}$$

$$P \xrightarrow{k_2} Q \tag{1.22}$$

$$Q \xrightarrow{k_3} P \tag{1.23}$$

$$A \xrightarrow{k_4} 2\,S \tag{1.24}$$

We get from (1.21) to (1.24) the following respective rate equations:

$$(-r_A)_{A\to P} = r_P = k_1\,C_A \tag{1.25}$$

$$(-r_P)_{P\to Q} = r_Q = k_2\,C_P \tag{1.26}$$

$$(-r_Q)_{Q\to P} = r_P = k_3\,C_Q \tag{1.27}$$

$$(-r_A)_{A\to S} = \frac{r_S}{2} = k_4\,C_A \tag{1.28}$$

From (1.25) and (1.28), we get the following:

$$\begin{aligned}(r_A)_{net} &= -k_1\,C_A - k_4\,C_A = -(k_1+k_4)\,C_A\\ (r_P)_{net} &= -k_2\,C_P + k_1\,C_A + k_3\,C_Q\\ (r_Q)_{net} &= k_2\,C_P - k_3\,C_Q\\ (r_S)_{net} &= 2\,k_4\,C_A\end{aligned}$$

Self-study 1:

Give real life examples of one irreversible reaction, one reversible reaction, one series reaction, one parallel reaction and one combined reaction along with the respective stoichiometry and the rate equations.

1.8 Rate of Reaction for Non-elementary Reactions:

Elementary reactions are single step reactions that occur exactly as they are written, without any intermediate steps. Non-elementary reactions are multistep reactions, which means they occur through series of reaction steps. Elementary reactions are simple in nature whereas non-elementary reactions are complex in nature. For elementary reaction, the order of reaction agrees with the stoichiometry which is not the case for non-elementary reactions.

Examples of non-elementary irreversible reactions:

Reaction 1:

$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$$

which has the following rate equation:

$$r_{HBr} = \frac{k_1\,(C_{H_2})\,(C_{Br_2})^{(0.5)}}{k_2\,+\,(C_{HBr})/(C_{Br_2})}$$

Reaction 2: Dissolved oxygen readily oxidizes ferrous iron to ferric hydroxide according to

$$O_2 + 4\,Fe^{++} + 8\,OH^{-} + 2\,H_2O \longrightarrow 4\,Fe(OH)^3$$

which has the following rate equation:

$$-r_{O_2} = k\;(C_{O_2})\;(C_{Fe^{++}})\;(C_{OH^-})^2$$

Exercise:

It is hypothesized that the dissociation of acetaldehyde, given by $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$, can be broken down to the following scheme of elementary reactions:

Initiation: $CH_3CHO \overset{k_1}{\longrightarrow} CH_3\bullet + \bullet CHO$

Propagation(1): $CH_3\bullet + CH_3CHO \overset{k_2}{\longrightarrow} CH_3\bullet CO + CH_4$

Propagation(2): $CH_3\bullet CO \overset{k_3}{\longrightarrow} CH_3\bullet + CO$

Termination: $2\,CH_3\bullet \overset{k_4}{\longrightarrow} C_2H_6$

The above proposed mechanism is considered reliable since small amounts of C_2H_6 and H_2 are observed when the dissociation of acetaldehyde is carried out experimentally. Starting from these elementary reactions, derive the equation for the rate of formation of CH_4.

Solution to the Exercise

From the above hypothesized mechanism, we can write

$$r_{CH_4} = k_2\,[CH_3\bullet][CH_3CHO]$$

where the notation [.] denotes concentration.

Since the free radical $CH_3\bullet$ does not appear in the final product, we need to remove $[CH_3\bullet]$ from the above equation. It can be done by taking the net rate of production of intermediates (such as the free radicals $CH_3\bullet$ and $CH_3\bullet CO$) which do not appear in the final product to be zero.

Therefore, we get

$$r_{CH_3\bullet} = k_1\,[CH_3CHO] - k_2\,[CH_3\bullet][CH_3CHO] + k_3\,[CH_3\bullet CO] - k_4\,[CH_3\bullet]^2 = 0$$

and

$$r_{CH_3\bullet CO} = k_2\,[CH_3\bullet][CH_3CHO] - k_3\,[CH_3\bullet CO] = 0$$

Adding the above two equations, we get

$$k_1\,[CH_3CHO] = k_4\,[CH_3\bullet]^2$$

which gives

$$[CH_3\bullet] = \sqrt{(k_1/k_4)\,[CH_3CHO]}$$

Therefore, we get

$$\begin{aligned} r_{CH_4} &= k_2\,\sqrt{(k_1/k_4)\,[CH_3CHO]}\,[CH_3CHO] \\ &= k_2\,\sqrt{(k_1/k_4)}\,[CH_3CHO]^{1.5} \\ &= k_5\,[CH_3CHO]^{1.5} \end{aligned}$$

where $k_5 = k_2\,\sqrt{(k_1/k_4)}$.

Self-study 2:

Carry out a literature search for the proposed mechanism of the reaction $H_2(g)+Br_2(g) \longrightarrow 2\,HBr(g)$ and derive the following rate equation:

$$r_{HBr} = \frac{k_1\,[H_2]\,[Br_2]^{0.5}}{k_2 + [HBr]/[Br_2]}$$
