

## CHAPTER 9. CHEMICAL KINETICS

In the following chapters we will present various chemical reaction mechanisms controlling the abundance of stratospheric ozone, the oxidizing power of the atmosphere, smog, and acid rain. We first review here some basic notions of chemical kinetics.

### 9.1 RATE EXPRESSIONS FOR GAS-PHASE REACTIONS

#### 9.1.1 Bimolecular reactions

A *bimolecular* reaction involves the collision of two reactants A and B to yield two products C and D. The collision produces an *activated complex*  $AB^*$  which decomposes rapidly either to the original reactants A and B or to the products C and D. The reaction is written



and its rate is calculated as

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d}{dt}[C] = \frac{d}{dt}[D] = k[A][B] \quad (9.1)$$

where  $k$  is the *rate constant* for the reaction. In this expression the concentrations [ ] are number densities so that the product  $[A][B]$  is proportional to the frequency of collisions. The rate of the reaction depends on the frequency of collisions and on the fate of the activated complex. Typically  $k$  is given in units of  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ , in which case  $[A]$  and  $[B]$  must be in units of  $\text{molecules cm}^{-3}$ .

A special case of bimolecular reaction is the *self-reaction*:



for which the rate expression is

$$-\frac{1}{2}\frac{d}{dt}[A] = \frac{d}{dt}[B] = \frac{d}{dt}[C] = k[A]^2 \quad (9.2)$$

#### 9.1.2 Three-body reactions

A *three-body* reaction involves reaction of two species A and B to yield one single product species AB. This reaction requires a *third body* M to stabilize the excited product AB\* by collision:



The third body M is any inert molecule (in the atmosphere, generally N<sub>2</sub> and O<sub>2</sub>) that can remove the excess energy from AB\* and eventually dissipate it as heat. Common practice is to write the overall reaction as



to emphasize the need for a third body.

The rate of a three-body reaction is defined as the formation rate of AB by reaction (R5):

$$\frac{d[AB]}{dt} = k_5[AB^*][M] \quad (9.3)$$

The excited complex AB\* has a very short lifetime and reacts as soon as it is produced. We may therefore assume that it is in steady state at all times (see section 3.1.2 for a discussion of this *quasi steady state*):

$$k_3[A][B] = k_4[AB^*] + k_5[AB^*][M] \quad (9.4)$$

Rearranging and replacing into (9.3):

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d[AB]}{dt} = \frac{k_3k_5[A][B][M]}{k_4 + k_5[M]} \quad (9.5)$$

where the equality between production of AB on the one hand, and losses of A and B on the other hand, follows from the steady state assumption for AB\*. In the atmosphere, [M] is simply the number density of air  $n_a$ .

Equation (9.5) is the general rate expression for a three-body reaction (a more detailed analysis would include a small correction

factor). There are two interesting limits. In the low-density limit  $[M] \ll k_4/k_5$  (called the *low-pressure limit*), (9.5) simplifies to

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d[AB]}{dt} = \frac{k_3 k_5}{k_4} [A][B][M] \quad (9.6)$$

so that the rate of the overall reaction depends linearly on  $[M]$ . One refers to  $k_o = k_3 k_5/k_4$  as the low-pressure limit rate constant. In the high-density limit  $[M] \gg k_4/k_5$  (called the *high-pressure limit*), (9.5) simplifies to

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d[AB]}{dt} = k_3 [A][B] \quad (9.7)$$

which means that the rate of AB production is limited by production of  $AB^*$  and is independent of  $[M]$ ; M is sufficiently abundant to ensure that all  $AB^*$  complexes produced stabilize to AB. Since the rate of the overall reaction is then determined by the rate of (R3), one refers to (R3) in the high-pressure limit as the *rate-limiting step* for production of AB, and  $k_\infty = k_3$  as the high-pressure limit rate constant. Rewriting (9.5) in terms of  $k_o$  and  $k_\infty$  makes the two limits apparent:

$$-\frac{d}{dt}[A] = -\frac{d}{dt}[B] = \frac{d[AB]}{dt} = \frac{k_o [A][B][M]}{1 + \frac{k_o}{k_\infty} [M]} \quad (9.8)$$

The rate constant of a three-body reaction is sometimes given as one of the two limits; you can tell from the units of  $k$  ( $\text{cm}^6 \text{molecule}^{-2} \text{s}^{-1}$  for the low-pressure limit,  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$  for the high-pressure limit) and you should then assume that the appropriate limit holds.

## 9.2 REVERSE REACTIONS AND CHEMICAL EQUILIBRIA

Reactions are reversible. If we can write



then simply from mass conservation we can also write



The reverse reaction may however be extremely slow. If we wish to emphasize the reversible nature of a reaction then we need to write it as a two-way reaction,



Eventually, steady state is reached between the forward and reverse reactions:

$$k_8[A][B] = k_9[C][D] \quad (\text{9.9})$$

from which we define an *equilibrium constant*  $K_{10}$  for the two-way reaction (R10):

$$K_{10} = \frac{k_8}{k_9} = \frac{[C][D]}{[A][B]} \quad (\text{9.10})$$

The equilibrium constant is a thermodynamic quantity and depends only on the free energies of molecules A, B, C, and D.

### 9.3 PHOTOLYSIS

A *photolysis* reaction involves the breaking of a chemical bond in a molecule by an incident photon. The reaction is written



and the rate of reaction is calculated as

$$-\frac{d}{dt}[X] = \frac{d}{dt}[Y] = \frac{d}{dt}[Z] = k[X] \quad (\text{9.11})$$

where  $k$  (units of  $s^{-1}$ ) is a *photolysis rate constant* or *photolysis frequency*.

Consider an elemental slab of air of vertical thickness  $dz$  and unit horizontal area. The slab contains  $[X]dz$  molecules of X (where  $[X]$  is a number density). A photon incident on a molecule of X has a probability  $\sigma_X/A$  of being absorbed, where  $A$  is the cross-sectional area of the molecule and  $\sigma_X$  is the absorption cross-section (units of  $\text{cm}^2 \text{ molecule}^{-1}$ ) which defines the absorption characteristics of X. The molecules of X in the elemental slab absorb a fraction  $\sigma_X[X]dz$

of the incoming photons. We define the *actinic flux*  $I$  as the number of photons crossing the unit horizontal area per unit time from any direction (photons  $\text{cm}^{-2} \text{s}^{-1}$ ) and the *quantum yield*  $q_X$  (units of molecules  $\text{photon}^{-1}$ ) as the probability that absorption of a photon will cause photolysis of the molecule X. The number of molecules of X photolyzed per unit time in the slab is  $q_X \sigma_X [X] I dz$ . To obtain the photolysis rate constant  $k$ , we divide by the number  $[X] dz$  of molecules of X in the slab:

$$k = q_X \sigma_X I \quad (9.12)$$

Absorption cross-sections and quantum yields vary with wavelength. For polychromatic radiation, as in the atmosphere, equation (9.12) must be integrated over the wavelength spectrum:

$$k = \int_{\lambda} q_X(\lambda) \sigma_X(\lambda) I_{\lambda} d\lambda \quad (9.13)$$

where  $I_{\lambda}$  is the actinic flux distribution function defined in the same way as the flux distribution function  $\phi_{\lambda}$  in chapter 7. The difference between the actinic flux  $I_{\lambda}$  and the radiation flux  $\phi_{\lambda}$  is that the former measures the number of photons crossing the unit horizontal surface surface from any direction, while the latter measures the photon energy flow perpendicular to the surface. Solar photons in the atmosphere originate from a multiplicity of directions due to scattering by air molecules, aerosols, and clouds; the relationship between  $\phi_{\lambda}$  and  $I_{\lambda}$  varies depending on the angular distribution of the photons.

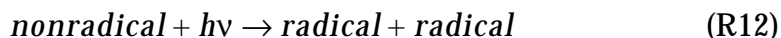
## 9.4 RADICAL-ASSISTED REACTION CHAINS

Gases in the atmosphere are present at low concentrations - considerably lower than the concentrations generally used in laboratory experiments or in industrial processes. As a result, collisions between molecules are relatively infrequent. With few exceptions, the only reactions between molecules that proceed at appreciable rates in the atmosphere are those involving at least one *radical species*.

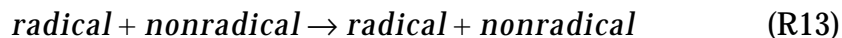
Radicals are defined as chemical species with an unpaired electron in the outer (*valence*) shell. Because of this unpaired electron, radicals have high free energies and are much more reactive than nonradical species whose electrons are all paired up. You can

figure out whether or not a species is a radical by counting its electrons; an odd number identifies a radical and an even number a nonradical. For example NO is a radical ( $7+8 = 15$  electrons), while  $\text{HNO}_3$  is a nonradical ( $1+7+(3 \times 8) = 32$  electrons). An important exception to this rule is atomic oxygen, which has 8 electrons but *two* unpaired valence shell electrons in its “triplet”  $\text{O}(^3P)$  ground state ( $2s^2 2p_x^2 2p_y^1 2p_z^1$ ) and is therefore a radical (or more exactly a *biradical*). Atomic oxygen with all electrons paired ( $2s^2 2p_x^2 2p_y^2$ ) is in a higher-energy “singlet”  $\text{O}(^1D)$  state and is actually even more reactive than  $\text{O}(^3P)$ .

Because radicals have high free energies, their formation from nonradical species is in general endothermic; an external source of energy is required. In the atmosphere, this source of energy is supplied by solar radiation:



Generation of radicals by reaction (R12) provides the *initiation step* for radical reaction chains which are *propagated* by subsequent reactions of radicals with nonradical species:



Note that reaction of a radical with a nonradical must always produce a radical in order to conserve the total odd number of electrons. The radical produced in (R13) goes on to react with another nonradical, propagating the chain, and in this manner a large number of nonradicals can be processed through the chain. During the propagation cycle, a nonradical species produced by a reaction of type (R13) may photolyze following (R12) to produce additional radicals; the photolysis is called a *branching reaction* as it accelerates (or “branches”) the chain by augmenting the pool of radicals.

*Termination* of the chain requires reactions taking place between radicals:



or



Termination reactions are generally slower than propagation reactions because radicals are present at low concentrations and

collisions between radicals are therefore relatively infrequent. In subsequent chapters we will encounter many types of radical-assisted chains following the general schematic (R12)-(R15). Due to the critical importance of solar radiation in initiating radical-assisted chain mechanisms in the atmosphere, these mechanisms are often referred to as *photochemical*.

*Further reading:*

**Levine, I.N., *Physical Chemistry*, 4th ed., McGraw-Hill, New York, 1995.**