

# Chemical Reactions: an example of non-equilibrium system

Ali Najafi

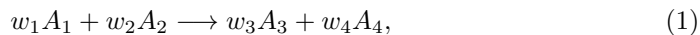
December 18, 2022

## Abstract

After a brief introduction to the thermodynamics of chemical reactions we provide a short discussion on chemical kinetics.

## 1 Chemical reaction

Consider a closed system composed of 4 chemical species  $A_i$  with molar masses  $M_i$  that react with the following reaction:



where stoichiometric coefficients  $w_i$  are assumed to be positive (negative) for products (reactants). Here  $w_1, w_2 < 0$  and  $w_3, w_4 > 0$ . Stoichiometric coefficients enforce the conservation of mass, meaning that  $-w_1 M_1 - w_2 M_2 = w_3 M_3 + w_4 M_4$ .

What fraction of the reacting mass corresponds to species  $i$ ? To answer this question, we define normalized stoichiometric (dimensionless) coefficients  $\nu_i$ . It is easy to show  $\nu_i = w_i M_i / (-w_1 M_1 - w_2 M_2)$ . Note that  $\sum_i \nu_i = 0$ ,  $\nu_1 + \nu_2 = -\nu_3 - \nu_4 = -1$ . A very elementary example is the following reaction:



where, we have:

$$w_1 = -2, \quad w_2 = -1, \quad w_3 = 2, \quad \nu_1 = -2 \frac{M_1}{2M_3}, \quad \nu_2 = -\frac{M_2}{2M_3}, \quad \nu_3 = 1.$$

## 2 Reaction rate

Each chemical reaction is characterized by a single reaction rate  $J$ . To define the reaction rate, assume that at time  $t$ , there is an amount of mass  $\mathcal{M}_i$  of each species present in a fixed volume  $V$ . The total mass of reactants and products are denoted by  $\mathcal{M}_r = \mathcal{M}_1 + \mathcal{M}_2$  and  $\mathcal{M}_p = \mathcal{M}_3 + \mathcal{M}_4$ , respectively. The reaction rate is defined as:

$$J = \frac{\dot{\mathcal{M}}_r}{V} = -\frac{\dot{\mathcal{M}}_p}{V}.$$

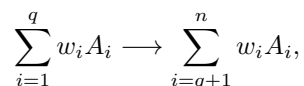
The dimension of reaction rate reads as  $[J] = \text{Kg m}^{-3}\text{s}^{-1}$ . We have provided the above definition for a unidirectional reaction but in general both forward and reverse reactions can contribute to the reaction rate. The time derivative of all masses can be expressed in terms of the reaction rate as:

$$\frac{\dot{\mathcal{M}}_i}{V} = \frac{w_i M_i}{-w_1 M_1 - w_2 M_2} J.$$

We now define the partial mass density of species  $i$  by  $\rho_i = \mathcal{M}_i/V$  then using the definition of  $\nu_i$ , we see that  $\dot{\rho}_i = \nu_i J$ . Alternatively, we can think of the molar density defined by  $n_i = \mathcal{M}_i/(M_i V)$ . Then its dynamics reads as:  $\dot{n}_i = w_i \bar{J}$ , where  $\bar{J} = J/(-w_1 M_1 - w_2 M_2)$  shows the molar reaction rate. Note that total density defined as  $\rho = \sum_i \rho_i$  is a conserved quantity ( $\sum \nu_i = 0$ ) but the total number of moles  $n = \sum_i n_i$  is not a conserved quantity ( $\sum w_i \neq 0$ ).

### 3 Thermodynamics

A closed system of chemically reacting components is an example of a non-equilibrium system. Consider that the system has  $n$  species with only one reaction:



that is determined with reaction rate  $J$ .

We denote by  $n_i$ , the molar concentrations (mole/ $V$ ) of species  $i$ , then the total molar density is given by  $n = \sum_i n_i$ . The total number of particles  $i$  is denoted by  $\mathcal{N}_i$ , and it is related to molar concentrations as  $\mathcal{N}_i = N_A V n_i$ . The chemical system with some given initial concentrations starts to evolve in time. We want to write the general dynamical equations that can describe the system. Obviously, temperature,  $T$ , pressure,  $p$ , and total density  $\rho$  are among the thermodynamic variables necessary to define the system's state. How about partial concentrations? Do we need to consider all concentrations as independent state variables? To find the answer, we proceed by considering the dynamics of  $n_i$ :

$$\partial_t n_i = w_i \bar{J}. \quad (3)$$

It should be noted that the above equation can be written as:  $\bar{J} = \partial_t(n_i/w_i)$ . As  $\bar{J}$  is independent of  $i$ , instead of  $n_i$  for  $i = 1 \dots n$ , we can work with a single quantity  $(n_i(t) - n_i(0))/(w_i)$  (that is independent of  $i$ ), so that:

$$\bar{J} = \frac{1}{N_A V} \partial_t \xi, \quad \xi(t) = N_A V \frac{n_i(t) - n_i(0)}{w_i} = \frac{\mathcal{N}_i(t) - \mathcal{N}_i(0)}{w_i}.$$

The variable  $\xi$  shows the progress of the reaction and it is called the progress variable. The extent or degree of reaction is another name for this progress variable. This observation suggests that all of the  $n$  variables can be replaced by a single new state variable,  $\xi$ . Our thermodynamic considerations will also validate this point. Careful analysis show that  $0 \leq \xi \leq \xi_m$ , where  $\xi = 0$  show the initial state and  $\xi = \xi_m$  corresponds to the case where all reactants have been transformed into products.

To study the thermodynamics of the reacting system, we denote by  $S$  and  $E$ , the entropy and internal energy of the system, respectively. At equilibrium, the entropy is a state function given by  $S = S(E, V, \mathcal{N}_i)$ . The first and second laws of thermodynamics for a differential process can be written as:

$$dE = dQ - pdV, \quad TdS = dE + pdV - \sum_{i=1}^n \mu_i d\mathcal{N}_i, \quad (4)$$

where  $dQ$  is the partial heat exchanged with the external reservoir and  $\mu_i$  shows the chemical potential of species  $i$ . Note that, as the system has no particle exchange with the external reservoir, then no term containing chemical potential appears in the first equation.

Following the general assumptions of non-equilibrium thermodynamics, we can proceed and calculate the rate by which the entropy produces in the system. These assumptions include the criteria of slow dynamics and local equilibrium. As a result of these assumptions, entropy preserves the same functional form of the state variables as it would have at the equilibrium conditions. Then combining the second law with the law of dynamics of densities ( $\partial_t \xi = \dot{\mathcal{N}}_i/w_i$ ), we will reach the following equation:

$$\partial_t S = \frac{1}{T} \partial_t E + \frac{p}{T} \partial_t V - \frac{A}{T} \partial_t \xi, \quad (5)$$

where affinity is defined as  $A = \sum_{i=1}^n w_i \mu_i$ . Affinity is the chemical force that drives the reaction. The form of the last term in this equation strongly validates our previous suggestion about the progress variable  $\xi$ . This means that temperature, pressure, and progress variable, form a complete set of state variables.

Chemical affinity and progress variables are conjugate variables:

$$A = \sum_{i=1}^n w_i \mu_i, \quad \xi = \frac{\mathcal{N}_i(t) - \mathcal{N}_i(0)}{w_i}.$$

In this case, the entropy has a functional form as  $S = S(E, V, \xi)$ . Equation 5 suggests that:  $A = -T(\partial S/\partial \xi)|_{E,V}$ . In terms of Helmholtz free energy  $F = E - TS$ , we see that  $A = (\partial F/\partial \xi)|_{V,T}$ .

For constant density, the rate of entropy production (associated with chemical reactions) can be written as:

$$\sigma = -N_A V \frac{\bar{J} A}{T} > 0, \quad A = \sum_{i=1}^n w_i \mu_i.$$

This form of entropy production suggests that  $A$  is a generalized force that initiates the reaction and the progress of the reaction corresponds to a generalized current  $J$  that is given by the speed of the progress variable. In the linear response regime, we can consider a linear relation like:

$$\bar{J} = -L \frac{A}{T} \quad \rightarrow \quad \sigma = N_A V L \left(\frac{A}{T}\right)^2 > 0,$$

where  $L$  is a phenomenological coefficient. To ensure the irreversibility (positive entropy production rate), this linear response coefficient should be positive,  $L > 0$ .

## 4 Fluctuation around the equilibrium

Equilibrium in the chemical system corresponds to  $A = 0$  which will result in an equilibrium value for the progress variable denoted by  $\xi = \xi^{\text{eq}}(T, \rho)$ . To study the fluctuations around this equilibrium, we consider that  $\xi = \xi^{\text{eq}} + \delta\xi$  and  $A = \delta A = \left. \frac{\partial A}{\partial \xi} \right|_{\text{eq}} \delta\xi$ . In terms of the Helmholtz energy  $\delta A = \left. \frac{\partial^2 F}{\partial \xi^2} \right|_{\text{eq}} \delta\xi$ . Now using the linear response equation, we see that  $\partial_t \delta\xi = -\tau^{-1} \delta\xi$  where  $\tau^{-1} = (L/T\rho) \left. \frac{\partial^2 F}{\partial \xi^2} \right|_{\text{eq}}$ . At the equilibrium conditions, Helmholtz energy is minimum, meaning that  $\left. \frac{\partial^2 f}{\partial \xi^2} \right|_{\text{eq}} > 0$ . Furthermore, the positiveness of the linear response,  $L > 0$ , results in the stability of equilibrium where fluctuations relax to zero at time scale  $\tau$  as  $\delta\xi \sim \delta\xi(0)e^{-t/\tau}$ .

## 5 Chemical Kinetics

What quantities determine the rate of a chemical reaction? In general densities of all the species contributing to the reaction as reactants can enhance the reaction rate. This means that  $J = J(n_1, n_2, \dots)$ . Experimental pieces of evidence usually allow us to write phenomenological relations for reaction rate:

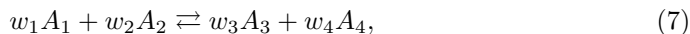
$$J = k_f n_1^\alpha n_2^\beta \dots$$

where  $k_f$  is called the rate constant and  $\alpha, \beta$  are numbers.  $\alpha = 0$  shows a zeroth order reaction,  $\alpha = 1$  is a first order reaction and so on. As an example consider the 4-species reaction that we started with and assume that the reaction is first order with respect to all species. Densities of all species evolve with the following equations:

$$\begin{aligned}\dot{n}_1 &= -k_f n_1 n_2 + k_r n_3 n_4, \\ \dot{n}_2 &= -k_f n_1 n_2 + k_r n_3 n_4, \\ \dot{n}_3 &= k_f n_1 n_2 - k_r n_3 n_4, \\ \dot{n}_4 &= k_f n_1 n_2 - k_r n_3 n_4.\end{aligned}\tag{6}$$

## 6 Ideal gas limit

A very dilute solution of chemical species behaves like ideal gas. This will allow us to present simple relations for the reaction rate which is called the law of mass action. Consider the following reactions:



note that two reactions of forward and reverse directions are considered in a single notation. A successful collision of  $w_1$  particles of type  $A_1$  with  $w_2$  particles of type  $A_2$  is necessary to start the forward reaction. At a very dilute regime, we can proceed by assuming that the collision probability is proportional to the density of the particles. In this case, the following simple relation can be written for the reaction rate:

$$\bar{J} = (k_f n_1^{-w_1} n_2^{-w_2} - k_r n_3^{w_3} n_4^{w_4}),$$

where two rate constants for forward and reverse reactions, are defined by  $k_f$ , and  $k_r$ , respectively. The form of the above reaction rate is called the rule of mass action. For an ideal gas, the chemical potential can be written as  $\mu_i = k_B T \ln(c_i/c_0) + \mu_i^0$  where,  $\mu_i^0(T)$  is the part of the chemical potential that is independent of density. Now we can rewrite the above equation as:

$$\bar{J} = k_r n_3^{w_3} n_4^{w_4} \left( \frac{k_f}{k_r} \times n_0^{-\sum w_i} \times e^{\sum w_i \mu_i^0 / k_B T} e^{-\frac{A}{k_B T}} - 1 \right).$$

At equilibrium  $\bar{J} = A = 0$  then we can arrive at a relation for the equilibrium constant of the reaction that is defined as  $K_{\text{eq}} = k_f/k_r$ :

$$K_{\text{eq}} = k_f/k_r = n_0^{\sum w_i} e^{-\frac{\sum w_i \mu_i^0}{k_B T}}.$$

As  $k_f$  and  $k_r$  are constant numbers, we can use this last equation and rewrite the reaction rate as below:

$$\bar{J} = k_r n_3^{w_3} n_4^{w_4} \left( e^{-\frac{A}{k_B T}} - 1 \right).$$

very near to equilibrium, we can approximate the above equation as:

$$\bar{J} \sim -k_r n_{3,\text{eq}}^{w_3} n_{4,\text{eq}}^{w_4} \times \frac{A}{k_B T}, \quad A \ll k_B T.$$

This last equation resembles the linear response relation. As it is seen, the linear response relation can be recovered for cases where  $A \ll k_B T$ .

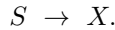
## 7 Catalytic reactions

The enzymes are biological catalysts that help the biophysical processes to take place. These are usually proteins that help to transform a certain type of substrate molecules denoted by  $S$  to product molecule  $X$ . We denote by  $E$ , the enzyme molecules. The transformation process from  $S$  to  $X$  can be considered a two-step process involving the appearance of an intermediate complex denoted by  $ES$ . The reactions are:



We assume that all reactions are first order and the first reaction is in equilibrium. Reaction constants for each reaction are denoted in the above equation. The equilibrium assumption can be justified for systems where  $n_S \gg n_E$ .

The question that we want to address is the effective reaction rate of the following reaction:



We call the effective reaction rate of this process  $J_{\text{eff}}$ . It should be noted that  $J_{\text{eff}} = \dot{n}_X = -\dot{n}_S$  in such a way that  $J_{\text{eff}}$  is a function of  $n_X$  and  $n_S$ . To obtain this effective

reaction rate, we begin by writing the kinetic equations for the first set of reactions which are assumed to be first order:

$$\begin{aligned}
\dot{n}_S &= -k_f n_S n_E + k_r n_{ES}, \\
\dot{n}_E &= -k_f n_S n_E + k_r n_{ES} + q_f n_{ES}, \\
\dot{n}_{ES} &= k_f n_S n_E - k_r n_{ES} - q_f n_{ES}, \\
\dot{n}_X &= q_f n_{ES}.
\end{aligned} \tag{8}$$

Regarding our initial assumption, the first reaction (formation of ES complex) is an equilibrium reaction, the number density of E and ES should be conserved  $\dot{n}_E = \dot{n}_{ES} = 0$ , then  $n_E + n_{ES} = n_E^0$  is a constant that effectively measures the total number of enzymes in the system. Furthermore, the equilibrium condition gives that  $k_f n_S n_E - k_r n_{ES} - q_f n_{ES} = 0$ . These conditions will allow us to write the number of ES complexes as a function of  $n_S$ :

$$n_{ES} = \frac{\alpha n_S}{n^\infty + n_S}, \quad \alpha = n_E^0, \quad n^\infty = \frac{k_r + q_f}{k_f},$$

then the effective reaction rate reads as:

$$J_{\text{eff}} = \dot{n}_X = q_f n_{ES} = \frac{\alpha q_f n_S}{n^\infty + n_S}.$$

It is seen that for high concentration of substrates  $\dot{n}_X \sim \alpha q_f$  while for low concentration  $\dot{n}_X \sim (\alpha q_f / n^\infty) n_S$ .

The law of consumption of substrate in a catalytic reaction is called the Michaelis-Menton law:

$$\dot{n}_S = -\alpha q_f \frac{n_S}{n^\infty + n_S}.$$