

Chapter 2

Brief Introduction to Thermodynamics

Abstract This chapter is devoted to introducing the basic concepts of thermodynamics, specially as applied to chemistry. The reader must be aware that the material in this chapter is rather technical and succinct. Therefore, it is quite possible that some of the results are not clear, even after carefully reading the chapter material more than once. Of course, people interested in this field can go to the specialized literature. However, one of the mayor goals of the present book is to help make these things clear through some examples. So, if things seem a bit blurry after finishing this chapter, please do not despair and keep reading. It will soon get better, promise.

2.1 The First and Second Laws of Thermodynamics

Let us start by briefly reviewing some of the most important concepts in thermodynamics, beginning with the first law. The readers interested in reading about this subject with more detail are referred to the following books: (Planck 1945; Ben-Naim 2007; Beard and Qian 2008).

Denote by E the energy of the system under study. According to the first law of thermodynamics, E can change because energy in the form of heat enters the system, because mechanical work is performed on the system, or because the molecular counts of the various chemical species composing the system change (chemical work). In particular, if the system is a compressible fluid, the first law of thermodynamics can be written as (Planck 1945):

$$dE = \delta Q - PdV + \sum_i \mu_i dN_i. \quad (2.1)$$

In the above equation δQ denotes the amount of heat entering the system (the symbol δ represents an inexact differential), $-PdV$ is the amount of mechanical work performed on the system (P is the hydrostatic pressure and V is the system volume), and μdN is the so-called chemical work performed on the system (μ_i and N_i are respectively the chemical potential and the molecular count of the i th chemical species).

The second law of thermodynamics introduces a new variable called the entropy, usually denoted by S , which satisfies the following relation (Planck 1945):

$$TdS \geq \delta Q. \quad (2.2)$$

That is, the entropy increment of a system along a given process is always larger, or at least equal, than the influx of heat along such process, divided by the temperature T . The equality is satisfied when the system undergoes a reversible process.

In the particular case in which $\delta Q = 0$ (i.e. when the system suffers an adiabatic process) the second law takes the form:

$$dS \geq 0.$$

Meaning that the entropy of an isolated system never decreases. If we further consider that any isolated system evolves to a thermodynamic equilibrium state through an irreversible process, the above result implies that the equilibrium state is characterized by having the maximum possible entropy compatible with the constraints of constant internal energy, volume, and particle counts. This last result is known as the maximum entropy principle.

It is also possible to express the second law of thermodynamics as optimality principles in some other particular cases. For instance, by combining Eqs. (2.1) and (2.2) we obtain

$$dE \leq TdS - PdV + \sum_i \mu_i dN_i. \quad (2.3)$$

Hence, if S , V , and N_i are kept constant, then

$$dE \leq 0.$$

This means that the energy of a system kept at constant entropy, volume, and particle count can only decrease. Or equivalently, that the equilibrium state of a system subject to these constraints possesses the minimum possible energy compatible with them.

Yet another instance of second law of thermodynamics can be derived by introducing a new thermodynamic quantity, called the Gibbs free energy (Planck 1945):

$$G = E - TS - PV. \quad (2.4)$$

By differentiating Eq. (2.4) and substituting Eq. (2.3) we get

$$dG \leq -Sdt + VdP + \sum_i \mu_i dN_i. \quad (2.5)$$

Hence, the Gibbs free energy of a system that is kept at constant T , P , and N_i can only decrease, and so the corresponding equilibrium state is characterized by having the minimum possible G value.

Under the assumption that the system undergoes a reversible process Eq. (2.5) becomes

$$dG = SdT + VdP + \sum_i \mu_i dN_i.$$

Furthermore, since most biochemical processes take place at constant pressure and temperature, the last expression reduces under such conditions to

$$dG = \sum_i \mu_i dN_i. \quad (2.6)$$

Keep this last result in mind because we will extensively use it in the rest of the book.

2.2 Thermodynamics of Chemical Reactions

Assume that the molecular counts of all the chemical species change because of chemical reactions taking place within the system. Thus (de Groot and Mazur 2013):

$$dN_i = \sum_{\lambda} \delta_{i\lambda} d\zeta_{\lambda},$$

in which the sum is carried out over all the chemical reactions, $\delta_{i\lambda}$ is a stoichiometric coefficient that gives the change in the number of molecules of chemical species i when an individual event of the λ th reaction occurs, and ζ_{λ} is the degree of advance of the λ th reaction (it measures the number of individual events that have taken place since the beginning of the experiment). If the reactions are coupled, then all of them advance at the same rate ($\zeta_{\lambda} = \zeta$ for all λ), and

$$dN_i = \sum_{\lambda} \delta_{i\lambda} d\zeta, \quad (2.7)$$

Substitution of (2.7) into (2.6) leads to

$$\Delta G = \frac{dG}{d\xi} = \sum_{\lambda} \sum_i \delta_{i\lambda} \mu_i. \quad (2.8)$$

The newly defined quantity ΔG is the so-called total free energy change of the system due to the undergoing chemical reactions. A free energy change can be defined for each reaction:

$$\Delta G_{\lambda} = \sum_i \delta_{i\lambda} \mu_i.$$

And so

$$\Delta G = \sum_{\lambda} \Delta G_{\lambda}.$$

For simplicity, consider in what follows a chemical system in which only one chemical reaction is taking place. Stoichiometric coefficients can be positive (if the corresponding chemical species is a product of the reaction) or negative (if the chemical species is a reactant). Let us denote by $-\alpha_i$ all the negative stoichiometric coefficients, and by β_i all the positive ones. With this, Eq. (2.8) can be rewritten as

$$\Delta G = \sum_i \beta_i \mu_i - \sum_j \alpha_j \mu_j. \quad (2.9)$$

In the above equation we have omitted the sum over λ because of the assumption that only one chemical reaction occurs. Moreover, subindexes i and j respectively denote the reaction products and reactants.

In the following section we derive an expression for the chemical potential in terms of the system state variables. But for now let us just take the final result:

$$\mu = \mu^O + k_B T \ln \frac{c}{c^O}, \quad (2.10)$$

where $c = N/V$ is the molecule concentration of the corresponding chemical species (N is the molecule count and V is the volume), c^O and μ^O are respectively the molecule concentration and the chemical potential under reference conditions, and k_B is Boltzmann's constant. Thus, if we assume without loss of generality that the reference conditions are chosen in such a way that $c^O V = 1$, Eq. (2.10) transforms into

$$\mu = \mu^O + k_B T \ln N. \quad (2.11)$$

Substitution of Eq. (2.11) into (2.9) leads to

$$\Delta G = k_B T \sum_i \beta_i \ln \left(N_i e^{\mu_i^O / k_B T} \right) - k_B T \sum_j \alpha_j \ln \left(N_j e^{\mu_j^O / k_B T} \right).$$

We have seen that thermodynamic equilibrium implies that $dG = 0$. Then, it follows from (2.8) that a chemical reaction reaches equilibrium when $\Delta G = 0$, and so when

$$\frac{\prod_i \bar{N}_i^{\alpha_i}}{\prod_j \bar{N}_j^{\beta_j}} = \frac{e^{\sum_i \beta_i \mu_i^O / k_B T}}{e^{\sum_j \alpha_j \mu_j^O / k_B T}}, \quad (2.12)$$

where $\bar{N}_i$ denotes the equilibrium molecule count of the corresponding chemical species. Observe that this equation is strikingly similar to Eq. (1.20), suggesting that

$$K_D = \frac{e^{\sum_i \beta_i \mu_i^O / k_B T}}{e^{\sum_j \alpha_j \mu_j^O / k_B T}}. \quad (2.13)$$

In the following chapters we shall prove that Eqs. (2.12) and (1.20) are identical and indeed Eq. (2.13) is true.

2.3 Understanding the Chemical Potential Concept

Consider a system that has a countable number of available states and suppose that we know the probability (p_i) associated with each one of them. The system entropy can then be computed as (Ben-Naim 2007):

$$S = -k_B \sum_i p_i \ln p_i, \quad (2.14)$$

The problem with this approach is that one usually does not know the probability distribution p_i , but only the constraints the system is subject to. In order to solve this dilemma, one can make use of the second law of thermodynamics in one of its following versions (Planck 1945):

- Under conditions of constant energy (E), volume (V), and number of particles (N), the equilibrium state maximizes the system entropy (S).
- Under conditions of constant temperature (T), volume, and number of particles, the equilibrium state minimizes the Helmholtz free energy defined as: $F = E - TS$.
- Under conditions of constant temperature (T), pressure (P), and number of particles, the equilibrium state minimizes the Gibbs free energy defined as: $G = E - TS - PV$.

Let us focus in the second case. The system average energy can be computed in terms of the probability distribution as:

$$E = \sum_i \epsilon_i p_i, \quad (2.15)$$

in which ϵ_i is the energy associated with the i th state. Then, by combining Eqs. (2.14) and (2.15) we obtain the following expression for the Helmholtz free energy in terms of the probability distribution:

$$F = \sum_i p_i (\epsilon_i + k_B T \ln p_i). \quad (2.16)$$

With this, we can figure out what the equilibrium probability distribution is when the system temperature, volume, and number of particles are constrained. All we need to do is to find the probability distribution that minimizes Eq. (2.16), subject to the normalization condition:

$$\sum_i p_i = 1.$$

This is a classical problem of calculus that can be solved using the technique of Lagrange multipliers. We leave for the reader to prove that the solution is the renowned Boltzmann distribution:

$$P_i^{eq} = \frac{e^{-\epsilon_i/k_B T}}{Z}, \quad (2.17)$$

where

$$Z = \sum_i e^{-\epsilon_i/k_B T} \quad (2.18)$$

is known as the partition function. Substitution of Eq. (2.17) into Eq. (2.16) finally leads to the following expression for F :

$$F = -k_B T \ln Z. \quad (2.19)$$

A molecule in solution can be seen as a system complying with constant T , V , and N . Let $Z^{(1)}$ denote its partition function. Having the partition function a probabilistic interpretation, the partition function of a composite system equals the product of the components' partition functions, unless they are identical and indistinguishable. Consider for instance a system composed of N identical, indistinguishable molecules in solution. In this case, the system partition function is:

$$Z = \frac{Z^{(1)N}}{N!}. \quad (2.20)$$

$N!$ is the number of ways in which the N molecules can be permuted. By introducing the factor $N!$ we have taken into account the fact that, due to the indistinguishability of molecules, all of the permutations account for the same state. In other words, by dividing by $N!$ one avoids to count the same state multiple times while computing the system free energy—see Eq. (2.19).

By substituting Eq. (2.20) into Eq. (2.19) we obtain for Helmholtz free energy the following expression:

$$F = k_B T (N \ln N - N - N \ln Z^{(1)}). \quad (2.21)$$

In the derivation of Eq. (2.21) we have made use of Stirling's approximation: $\ln N! \approx N \ln N - N$.

If we differentiate $F = E - TS$ and take into consideration Gibbs fundamental relation ($dE = TdS - PdV + \sum_i \mu_i dN_i$) we get

$$dF = SdT - PdV + \mu dN.$$

Hence

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V}. \quad (2.22)$$

Finally, substitution of (2.21) into (2.22) leads to

$$\mu = k_B T \ln N - k_B T \ln Z^{(1)}.$$

By introducing a few extra factors, without altering the equality, this equation can be rewritten as

$$\mu = \mu^O + k_B T \ln \frac{c}{c^O}, \quad (2.23)$$

in which $c = N/V$ is the molecule concentration, c^O is the concentration at some standard conditions, and

$$\mu^O = -k_B T \ln \frac{Z^{(1)}}{V c^O}$$

is the system chemical potential when $c = c^O$, which depends only on the molecules' chemical nature. Equation (2.23) is the standard formula for the chemical potential found in textbooks (Beard and Qian 2008).

2.4 Summary

This chapter was devoted to introducing the thermodynamic concepts and formalism essential to understand chemical reactions. Thus, we reviewed the first and second laws of thermodynamics, introduced the concept of thermodynamic equilibrium, defined the free energy change, and used it to prove that thermodynamic and chemical equilibrium are equivalent concepts. Interestingly, we were able to obtain the law of mass action from purely thermodynamic considerations, suggesting that the thermodynamic and the chemical kinetics approaches are closely related. This connection is explored in detail in the next chapter. Finally, the last section of the chapter was dedicated to understanding the concept of chemical potential from the perspective of statistical mechanics. In later chapters we tackle this same question from different angles.

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