

## 1.6: The Concept of Equilibrium

We are familiar with the idea that a system undergoing change eventually reaches equilibrium. We say that a system is at equilibrium when no further change is possible. When we talk about change, we always have in mind some particular property. We measure the change in the system by the amount of change in this property. When the property stops changing, we infer that the system has stopped changing, and we say that the system has come to equilibrium. Of course, we may interest ourselves in a system in which many properties undergo change. In such cases, we recognize that the system as a whole cannot be at equilibrium until all of these properties stop changing.

On the other hand, we also recognize that the absence of observable change is not enough to establish that a system is at equilibrium with respect to all of the possible changes that it could undergo. We know that hydrogen burns readily in oxygen to form water, but a mixture of hydrogen and oxygen undergoes no change under ordinary conditions. This unchanging mixture is plainly not at equilibrium with respect to the combustion reaction. Only when a catalyst or an ignition source is introduced does reaction begin.

It is also possible, indeed probable, that a system can be at equilibrium with respect to one process and not be at equilibrium with respect to other processes, which, while possible, simply do not occur under the conditions at hand. For example, if an aqueous solution of the oxygen-carrying protein hemoglobin is added to the hydrogen—air system, the protein will add or lose coordinated oxygen molecules until the equilibrium composition is reached. If our investigation is focused on the protein—oxygenation reaction, we do not hesitate to say that the system is at equilibrium. The non-occurrence of the oxygen—hydrogen reaction is not relevant to the phenomenon we are studying.

It is even possible to reach a non-equilibrium state in which the concentrations of the reactants and products are constant. Such a system is said to have reached a **steady state**. In order for this to occur, the reaction must occur in an **open system**; that is, one in which materials are being added or removed; there must be continuous addition of reactants, and continuous removal of products. In Chapter 5, we discuss a simple system in which this can be achieved. A **closed system** is one that can neither gain nor lose material. An **isolated system** is a closed system that can neither gain nor lose energy; in consequence, its volume is fixed. In an isolated system, change ceases when equilibrium is reached, and conversely.

We will consider several commonly encountered kinds of change, including mechanical motions, heat transfers, phase changes, partitioning of a solute between two phases, and chemical reactions. Here we review briefly what occurs in each of these kinds of change. In Chapter 6, we review the characteristics that each of these kinds of change exhibits at equilibrium.

A system in **mechanical equilibrium** is stationary because the net force acting on any macroscopic portion of the system is zero. Another way of describing such a situation is to say that the system does not move because of the presence of constraints that prevent movement.

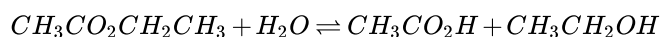
Two macroscopic objects are in **thermal equilibrium** if they are at the same temperature. We take this to be equivalent to saying that, if the two objects are in contact with one another, no heat flows between them. Moreover, if object A is in thermal equilibrium with each of two other objects, B and C, then we invariably find that objects B and C are in thermal equilibrium with one another. This observation is sometimes called the **zeroth law of thermodynamics**. It justifies the concept of temperature and the use of a standard system—a thermometer—to measure temperature.

For an isolated system to be in **phase equilibrium**, it must contain macroscopic quantities of two or more phases, and the amount of each phase present must be unchanging. For example, at 273.15 K and 1 bar, and in the presence of one atmosphere of air, liquid water and ice are in equilibrium; the amounts of water and ice remain unchanged so long as the system remains isolated. Similarly, a saturated aqueous solution of copper sulfate is in equilibrium with solid copper sulfate; if the system is isolated, the amounts of solid and dissolved copper sulfate remain constant.

If a system is in phase equilibrium, we can remove a portion of any phase without causing any change in the other phases. At equilibrium, the concentrations of species present in the various phases are independent of the absolute amount of each phase present. It is only necessary that some amount of each phase be present. To describe this property, we say that the **condition for equilibrium** for is the same irrespective of the amounts of the phases present in the particular system. For example, if one of the species is present in both a gas phase and a condensed phase, we can specify the equilibrium state by specifying the pressure and temperature of the system. However, we can change the relative amounts of the phases present in this equilibrium state by changing the volume of the system. (If its volume can change, the system is not isolated.)

Partitioning of a solute between two immiscible condensed phases is important in many chemical systems. If we add water and chloroform to the same vessel, two immiscible liquid phases are formed. Elemental iodine is very sparingly soluble in water and substantially more soluble in chloroform. If we add a small amount of iodine to the water–chloroform system, some of the iodine dissolves in the water and the remainder dissolves in the chloroform layer. We say that the iodine is distributed between the two phases. When the iodine concentrations become constant, we say that the system has reached **distribution equilibrium**.

In a **chemical reaction**, one or more chemical substances (reactants) undergo a change to produce one or more new chemical substances (products). We are accustomed to representing chemical substances by symbols and representing their reactions by chemical equations. Thus, for the hydrolysis of ethyl acetate, we write



A chemical equation like this expresses a stoichiometric relationship between reactants and products. Often we invoke it as a symbol for various distinctly different physical situations. For example:

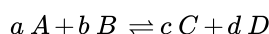
1. We may view the equation as a symbolic representation of a *single solution* that contains the four compounds ethyl acetate, water, acetic acid, and ethanol—and possibly other substances.
2. We may view the equation as a symbolic representation of a *relationship between two systems* whose proportions are arbitrary. The first system comprises ethyl acetate and water. The second system comprises acetic acid and ethanol. The equation represents the idea that the first system can be converted into the second.
3. We may view the symbols on each side of the equation as representing mixtures of the indicated chemical substances in the specified stoichiometric proportions.
4. We may view the equation as representing the specified stoichiometric proportions of pure, unmixed chemical substances. When we are discussing changes in “standard” thermodynamic properties that accompany a chemical reaction, this is the interpretation that we have in mind.

When we discuss a chemical equation, the intended interpretation is normally evident from the context. Indeed, we often skip back and forth among these interpretations in the course of a single discussion. Nevertheless, it is important to avoid confusing them.

By doing experiments, we can discover that there is an equation that uniquely defines the position of a chemical reaction at equilibrium, an equation that we usually think of as the definition of the **equilibrium constant**. If our measurements are not too accurate, or we confine our study to a limited range of concentrations, or the system is particularly well behaved, we can express the equilibrium constant as a function of concentrations<sup>2</sup>. For the hydrolysis of ethyl acetate, we find

$$K = \frac{[CH_3CO_2H][HOCH_2CH_3]}{[CH_3CO_2CH_2CH_3][H_2O]}$$

In general, for the reaction



we find

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

That is, at equilibrium the indicated function of reactant concentrations always computes to approximately the same numerical value.

When our concentration measurements are more accurate, we find that we must introduce new quantities that we call **chemical activities**. We can think of an activity as a corrected concentration. The correction compensates for the effects of intermolecular attraction and repulsion. Denoting the activity of substance  $X$  as  $\tilde{a}_x$ , we find that

$$K_a = \frac{\tilde{a}_C^c \tilde{a}_D^d}{\tilde{a}_A^a \tilde{a}_B^b}$$

gives a fully satisfactory characterization of the equilibrium states that are possible for systems in which this reaction occurs.  $K_a$ , the equilibrium constant computed as a function of reactant activities, always has exactly the same numerical value.

We can develop the equilibrium constant expression from three distinctly different theoretical treatments. We develop it first from some basic ideas about the rates of chemical reactions. Then we obtain same result from both the macroscopic-behavior considerations of classical thermodynamics and the molecular-property considerations of statistical thermodynamics.

Our most basic concept of equilibrium is based on the observation that change in an isolated system eventually ceases; once change ceases, it never resumes. In this book, we call the idea of a static state of an isolated system the **primitive equilibrium**. We also observe that change eventually ceases in a closed system that is not isolated but whose temperature, pressure, and volume are kept constant. Conversely, if a system is at equilibrium, its temperature, pressure, and volume are necessarily constant; all interactions between such a system and its surroundings can be severed without changing any of the properties of the system. We can view any particular equilibrium state as a primitive equilibrium state.

A system whose temperature, pressure, or volume is established by interactions between the system and its surroundings is inherently more variable than an isolated system. For a given isolated system, only one equilibrium state exists; for a system that interacts with its surroundings, many different equilibrium states may be possible. In chemical thermodynamics, our goal is to develop mathematical models that specify the equilibrium states available to a system; we seek models in which the independent variables include pressure, temperature, volume, and other conditions that can be imposed on the system by its surroundings. In this conception, an equilibrium system is characterized by a set of points in a variable space. We can think of this set of points as a surface or a manifold in the variable space; every point in the set is a different primitive-equilibrium state of the system. By imposing particular changes on some variables, a particular equilibrium system can be made to pass continuously through a series of primitive-equilibrium states.

For reasons that become apparent as we proceed, we use the name **Gibbsian equilibrium** to denote this more general conception. When we talk about equilibrium in thermodynamics, we usually mean Gibbsian equilibrium. In Chapter 6, we see that the idea of (Gibbsian) equilibrium is closely related to the idea of a **reversible process**. We also introduce Gibbs' phase rule, which amounts to a more precise definition, from the perspective of classical thermodynamics, of what we mean by (Gibbsian) equilibrium in chemical systems.

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