Reversible Reactions and Chemical Equilibria

In 1798, the chemist Claude Berthollet accompanied Napoleon's military expedition to Egypt. While visiting the Natron Lakes, a series of salt water lakes carved from limestone, Berthollet made an observation that led him to an important discovery. When exploring the lake's shore Berthollet found deposits of Na_2CO_3, a result he found surprising. Why did Berthollet find this result surprising and how did it contribute to an important discovery? Answering these questions provides an example of chemical reasoning and introduces us to the topic of this chapter.

Napoleon's expedition to Egypt was the first to include a significant scientific presence. The Commission of Sciences and Arts, which
included Claude Berthollet, began with 151 members, and operated in Egypt for three years. In addition to Berthollet's work, other results included a publication on mirages, and detailed catalogs of plant and animal life, mineralogy, and archeology. For a review of the Commission's contributions, see Gillispie, C. G. "Scientific Aspects of the French Egyptian Expedition, 1798-1801," *Proc. Am. Phil. Soc.* **1989**, *133*, 447–474.

At the end of the 18th century, chemical reactivity was explained in terms of elective affinities.[1] If, for example, substance A reacts with substance BC to form AB

$$A+BC \rightarrow AB+C$$

then A and B were said to have an elective affinity for each other. With elective affinity as the driving force for chemical reactivity, reactions were understood to proceed to completion and to proceed in one direction. Once formed, the compound AB could not revert to A and BC.

AB + C --X-> A+ BC

From his experience in the laboratory, Berthollet knew that adding solid Na_2CO_3 to a solution of $CaCl_2$ produces a precipitate of $CaCO_3$.

$$Na_2CO_3(s)+CaCl_2(aq) \rightarrow 2NaCl(aq)+CaCO_3(s)$$

Understanding this, Berthollet was surprised to find solid Na_2CO_3 forming on the edges of the lake, particularly since the deposits formed only when the lake's salt water was in contact with limestone, $CaCO_3$. Where the lake was in contact with clay soils, there was little or no Na_2CO_3.

Natron is another name for the mineral sodium carbonate, $Na_2CO_3 \bullet 10H_2O$. In nature, it usually contains impurities of $NaHCO_3$,
and NaCl. In ancient Egypt, natron was mined and used for a variety of purposes, including as a cleaning agent and in mummification.

Berthollet's important insight was recognizing that the chemistry leading to the formation of Na_2CO_3 is the reverse of that seen in the laboratory.

$$2NaCl(aq)+CaCO_3(s) \rightarrow Na_2CO_3(s)+CaCl_2(aq)$$

Using this insight Berthollet reasoned that the reaction is reversible, and that the relative amounts of NaCl, $CaCO_3$, Na_2CO_3, and $CaCl_2$determine the direction in which the reaction occurs and the final composition of the reaction mixture. We recognize a reaction's ability to move in both directions by using a double arrow when writing the reaction.

$$Na_2CO_3(s) + CaCl_2(aq) \rightleftharpoons 2NaCl(aq) + CaCO_3(s)$$

Berthollet's reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of Na_2CO_3 and $CaCl_2$ they react to produce NaCl and $CaCO_3$. If during the reaction we monitor the mass of Ca^{2+} remaining in solution and the mass of $CaCO_3$ that precipitates, the result looks something like Figure 6.1. At the start of the reaction the mass of Ca^{2+}decreases and the mass of $CaCO_3$ increases. Eventually the reaction reaches a point after which there is no further change in the amounts of these species. Such a condition is called a state of **equilibrium**.

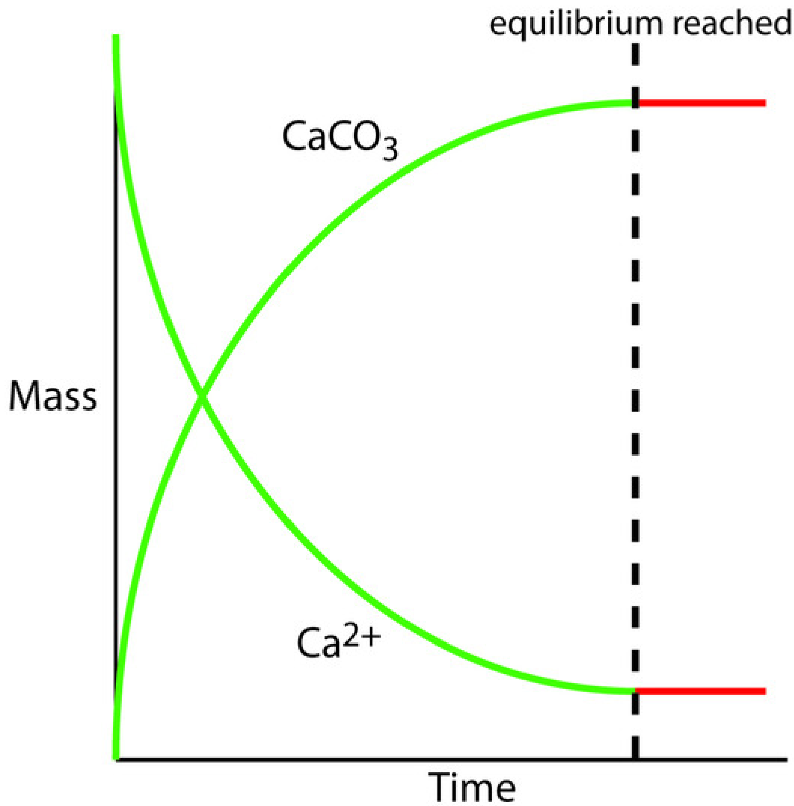

Figure 6.1 Graph showing how the masses of Ca^{2+} and $CaCO_3$ change as a function of time during the precipitation of $CaCO_3$. The dashed line indicates when the reaction reaches equilibrium. Prior to equilibrium the masses of Ca^{2+} and $CaCO_3$ are changing; after reaching equilibrium, their masses remain constant.

Although a system at equilibrium appears static on a macroscopic level, it is important to remember that the forward and reverse reactions continue to occur. A reaction at equilibrium exists in a **steady-state**, in which the rate at which a species forms equals the rate at which it is consumed.

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