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$_2$CO$_3$, 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. 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.

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

From his experience in the laboratory, Berthollet knew that adding solid Na$_2$CO$_3$ 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$_2$CO$_3$ 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$_2$CO$_3$.

Natron is another name for the mineral sodium carbonate, Na$_2$CO$_3$$•$10H$_2$O. In nature, it usually contains impurities of NaHCO$_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$_2$CO$_3$ 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$_2$CO$_3$, 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.
Berthollet's reasoning that reactions are reversible was an important step in understanding chemical reactivity. When we mix together solutions of Na₂CO₃ and CaCl₂ they react to produce NaCl and CaCO₃. If during the reaction we monitor the mass of Ca²⁺ remaining in solution and the mass of CaCO₃ that precipitates, the result looks something like Figure 6.1. At the start of the reaction the mass of Ca²⁺ decreases and the mass of CaCO₃ 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](http://chemwiki.ucdavis.edu/Analytical_Chemistry/Analytical_Chemistry_2.0/06_Equilibrium_Chemistry/6A_Reversible_Reactions_and_Chemical_Equilibria)

**Figure 6.1** Graph showing how the masses of Ca²⁺ and CaCO₃ change as a function of time during the precipitation of CaCO₃. The dashed line indicates when the reaction reaches equilibrium. Prior to equilibrium the masses of Ca²⁺ and CaCO₃ 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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