NAPOLEON BONAPARTE, FRENCH SCIENTISTS, CHEMICAL EQUILIBRIUM, AND MASS ACTION

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Introduction

This paper involves two intertwined themes. One is the relation of Napoleon Bonaparte (1769-1821) with leading French scientists of his time. The second is the beginning of two concepts important in chemistry: (a) reaction reversibility and chemical equilibrium, and (b) the role of relative masses of reactants and products in determining the position of equilibrium. These ideas are now taken as axiomatic, but they were introduced into chemistry only 200 years ago by the French chemist Claude Louis Berthollet (1748-1822), a friend and confidant of Napoleon.

The period from roughly 1750 to 1830 was a brilliant one for mathematics and chemistry in France. The mathematicians Joseph Louis Lagrange (1736-1813), Gaspard Monge (1746-1818), Pierre Simon Laplace (1749-1847), Adrien-Marie Legendre (1752-1833), and Joseph Fourier (1769-1830), and the chemists Antoine Lavoisier (1743-1794) and Claude Berthollet flourished during this period. A portion of this era, 1795-1815, describes the Napoleonic age, a time when Napoleon exercised power in France. What was the influence of Napoleon on the personal and scientific careers of these savants?

Some Historical Background

Berthollet: Modern chemistry developed rapidly during the latter half of the 18th century. Discovery of elements; development of a rational nomenclature for the naming of elements and compounds; determination of the constitution of air and water; and the explication of combustion occurred during this period. Lavoisier was the leading French chemist until he was beheaded in 1794. After Lavoisier, Berthollet was one of the most distinguished of the French chemists. Among other things, he had determined the composition of ammonia in 1785, prussic acid in 1787, and hydrogen sulfide in 1789. Berthollet pointed out that the absence of oxygen in HCN and H_2S disproved Lavoisier's hypothesis that all acids contain oxygen. As director of the Gobelin dye works, Berthollet studied the preparation of pigments and dyes. He discovered potassium chlorate and its explosive properties in 1788, and in 1785 he established the utility of chlorine and hypochlorites as bleaching agents (1,2). [As a matter of principle, Berthollet refused to file patents or make a profit from his work on bleach.] During the French Revolution Berthollet served as commissioner of the national mint and as commissioner of agriculture. Berthollet was the first French scientist to support Lavoisier's theory of combustion in 1785, and he helped to popularize Lavoisier's new system of chemical nomenclature.

Monge: Gaspard Monge, a good friend of Berthollet, was a mathematician and founder of descriptive geometry, engineer (author of *The Art of Making Cannon*), and public servant on the national stage (3). Monge also had connections with Lavoisier. In 1783 he proved the nonelementary nature of water by exploding

a mixture of hydrogen and oxygen with an electric spark and showing that water was the reaction product. Monge became the intermediary for the meeting of Berthollet with Napoleon and the subsequent friendship between chemist and general. The circumstances were unusual. As Minister for the Navy and the Colonies during 1792-93, Monge had occasion to welcome Napoleon in that capacity. Napoleon reminded Monge of this in his cordial letter to Monge in 1794. They met, liked each other, and became friends for life. Berthollet met Napoleon through Monge. Throughout the years, Monge and Berthollet were Napoleon's favorites among all the scientists.

Laplace: Laplace, mathematician and mathematical astronomer, also was associated with Lavoisier—surprisingly, as an experimentalist. Laplace was already at work on his *Celestial Mechanics* when he was recruited by Lavoisier in 1777 to help in planning and carrying out experiments on the effects of heat on various substances. They devised the first ice calorimeter, designed by Laplace, in order to measure heats of combustion, specific heats, and the "animal heat" generated by the respiration of a confined guinea pig. The Lavoisier-Laplace *Mémoire sur la Chaleur* was published by the Royal Printing Office in 1783 (4). The early work of Laplace on the stability of the solar system (1773) had earned him associate membership in the Academy of Sciences; he was promoted to full membership in 1785, the same year in which he, as professor of mathematics in the École Militaire, was an examiner of Napoleon when the 15-year old entered the school.

Fourier: Fourier, orphaned at age 8, chose mathematics over priesthood as a profession. When the short-lived École Normale was created in 1794, Fourier became chair of mathematics, and he became a professor in the successor institution École Polytechnique. Fourier was recruited by Berthollet to participate in

Napoleon's 1798 expedition to Egypt. He was made secretary of the Institut d'Egypte when it was established by Napoleon in 1798.

Napoleon: Napoleon's meteoric rise to power is well known. He was commissioned as a 2nd lieutenant in the artillery at age 16, appointed captain at age 23, brigadier general at 25, commander of the Army of Italy at 26, and First Consul at 30. He crowned himself emperor at age 35. Less well known are Napoleon's special interest and ability in mathematics, already evident during his teenage years (5,6). His continuing interest in mathematics and applied science may partially explain the closeness that developed between Napoleon, Monge, and Berthollet in later years. Other factors were their mutual respect and the fact that as trusted advisors, Monge and Berthollet were nonthreatening to Napoleon as competitors for power.

Napoleon

Napoleon's Italian Campaign

An early sign of the special regard in which Napoleon held Monge and Berthollet is their selection, by the Directoire, at Napoleon's recommendation, to visit Italy in 1796 as members of a six-person "Governmental Commission for the Research of Artistic and Scientific Objects in Conquered Countries." Their assignment was to choose and send back to Paris valuable objects of art and church treasures. Monge informed his wife that 300 crates were needed to convey to France the objects taken from Italy; the Mona Lisa was included. Berthollet, born in Savoy, spoke Italian as well as French. He was also an early writer on techniques for restoring fine art; in one of his reports from Italy he discussed means of restoring several paintings of Raphael.

Napoleon's Campaign in Egypt

After a proposed invasion of England was canceled, in 1798 Napoleon undertook a campaign in Egypt (7). Napoleon asked Berthollet to organize a "Committee on the Arts and Sciences" to accompany the army. Among the recruits were Monge, Fourier, the zoologist

Étienne St. Hilaire (1772-1844), Nicolas-Jacques Conté (1755-1805, inventor of the graphite pencil and the Conté crayon), the mineralogist Déodat de Dolomieu (1750-1801, whose name is given to the Dolomites in the Alps and to the mineral dolomite), and the physicist Étienne Malus (1775-1812), discoverer of the polarization of light by reflection.

In Egypt Napoleon established the Institut d'Egypte, modeled after the French institution. He named Monge as its first president and himself as vice-president. Berthollet succeeded Monge as the second president. After initial military successes, things went poorly for Napoleon in Egypt, and he decided to make a sudden and secret return to France in 1799. Of the scientists, Napoleon chose only Monge and Berthollet to accompany him on the dangerous voyage back. Both Monge and Berthollet were later cited, by Napoleon and by his chief-of-staff, General Berthier, for bravery in Egypt.

Honors, Appointments

After the Egyptian campaign, Napoleon showered titles and well-paying positions on many of the scientists who had been participants in Egypt — and on many who had not. The list is long. In 1802 Napoleon created the Order of the Legion of Honor; Lagrange and Laplace were made Grand Officers of the Legion of Honor. Berthollet, Laplace, Lagrange, and Monge were made Counts and were named to the French Senate. Senators were appointed for life, at an annual salary of 25,000 francs. In 1803 Napoleon established a system of "Senatoriates" (or "superprefect" positions) in which France was divided into 15 districts for legal appeals. Monge and Berthollet were two of only three scientists selected for these positions. Appointment to a Senatoriate entailed an additional annual revenue of 20,000-25,000 francs, along with a residential palace in an urban seat.

When Fourier returned to France from Egypt in 1801, he was appointed by Napoleon as prefect of the Department of Isère, headquartered in Grenoble. His administration there was outstanding during a 12-year tenure, and Napoleon made him a Baron in 1808. Although Fourier had difficulty in surviving Napoleon's downfall, he was finally appointed Director of the Statistical Bureau of the Seine and elected to the Académie des Sciences, the Académie de Medicine, and the Académie Française.

Laplace was named Minister of the Interior by Napoleon, but he was a poor administrator and was replaced by Napoleon after only six weeks in office. Laplace successfully shifted loyalty under numerous changes in regime. After the Bourbon restoration, Louis XVIII raised him to the peerage as the Marquis de Laplace.

What Did the Scientists Gain from Their Interaction with Napoleon?

Why did Napoleon bestow honors and high positions on the scientists? Were Napoleon's thoughts and actions influenced by the scientists? In a long-term sense, the answer is probably not. However, the work of the scientists on short-term, utilitarian problems was probably useful to the general. Napoleon always emphasized the utility of science and technology to improve the quality of life and to increase the economic status of the French people. The physical circumstances of the scientists were influenced, of course, by Napoleon's predilection to favor scholarly scientific prominence. The personal lives of the scientists were greatly affected by the rewards of titles and well-paying positions bestowed by Napoleon. When Berthollet managed to fall into debt in 1807, Napoleon sent him 150,000 francs to clear his record.

A more difficult question is: To what extent were the professional activities of the scientists changed by their association with Napoleon? In most cases the answer is, not very much. Laplace, for instance, proceeded with his investigations of celestial mechanics and produced a five-volume treatise plus a summary volume, along with a two-volume work on the mathematics of probability.

In a few cases the circumstances of Napoleonic interaction led to new features of intellectual life for the scientists. Fourier is one example. While in Egypt as a participant in Napoleon's venture there, Fourier had suggested that a record of French discoveries in Egypt be prepared. As a result, Fourier had a major role in writing the 21 volumes of the *Description de l'Egypte*, which appeared between 1809 and 1828. Fourier can be remembered as an early Egyptologist as well as a major figure in mathematical analysis. The influence of Napoleon on the professional career of Berthollet is considered in the following section.

Elective Affinity, Chemical Equilibrium, Mass Action

Elective Affinity: The question, "Why do chemicals react?" has been an enduring one. One prominent an-

swer during the nineteenth century was, "Because they have an affinity for each other." Elaborated theories of chemical affinity were proposed. The Swedish chemist Torbern Bergman (1735-1784), among others, published tables in which substances were ranked according to the intensity of their affinity. Substances of greater affinity were considered capable of displacing others with lesser affinity. If two substances combined, they were thought to have a selective or "elective" affinity for each other. Moreover, if a reaction proceeded, it went to completion (8,9). The ideas of equilibrium in a chemical reaction and the role of reactant mass became of general interest only after Berthollet's visit to the Egyptian "Natron Lakes" in 1798.

The Natron Lakes: In Egypt Napoleon gave Berthollet various practical assignments. These included finding fuels for bread ovens, substitutes for hops in the brewing of beer, and raw materials for the manufacture of gunpowder. A special assignment in 1798 was to visit and evaluate the Natron Lakes, a series of small lakes located in a depression, below sea level, in the desert about 45 miles northwest of Cairo. The Natron Lakes were of interest because they were bordered by a thick crust of natron (hydrated sodium carbonate). Berthollet's observations at the lakes led to a problem in interpretation. Berthollet knew that the reaction

$$Na_2CO_3 + CaCl_2 \rightarrow 2NaCl + CaCO_3$$
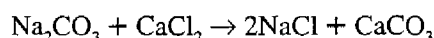
goes essentially to completion in the laboratory. In the Natron Lakes, where salt water and underlying limestone were in contact, this reaction seemed to be partially reversed. Such a reversal is contrary to the doctrine of elective affinity, which postulates all-or-none reactions. The unexpected phenomenon at the Natron Lakes led to an "Aha!" insight for Berthollet. He correctly inferred that chemical reactivity depends not only on the "elective affinities" of the reactants, but also on the relative masses of reactants and products. His conclusions, publicized in a lecture in Egypt (10) and in greater detail in an 1801 volume (11), constituted the first qualitative presentations of the concepts of reaction reversibility, equilibrium in chemical reactions, and the role of the masses of reactants and products in establishing the position of equilibrium in a given reaction. By the time of the 1801 volume, Berthollet was able to give other instances where a reversal of an expected reaction could be observed. These typically involved solubilizing a relatively insoluble product: barium sulfate, calcium oxalate, or calcium phosphate, for example.

Consider as an illustration the reaction:

$$Ba(OH)_2 + K_2SO_4 \rightarrow 2KOH + BaSO_4$$
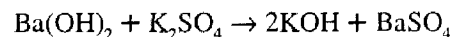
Berthollet showed that treatment of barium sulfate with potassium hydroxide in boiling water gave a solution containing potassium sulfate. Furthermore, with a large excess of potassium hydroxide, the barium sulfate could be almost completely dissolved. In his 1801 book Berthollet summarized his conclusions (11):

> The doctrine of Bergman is founded entirely on the supposition that elective affinity is an invariable force, and of such a nature, that a body which expels another from its combination, cannot possibly be separated from the same by the body which is eliminated. It is my purpose to prove that elective affinity, in general, does not act as a determinative force, by which one body separates completely another from a combination; but that, in all the compositions and decompositions produced by elective affinity, there takes place a partition of the base, or subject of the combination, between the two bodies whose actions are opposed; and that the proportion of the partition are determined, not merely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies; so that an excess of quantity of the body whose affinity is the weaker, compensates for the weakness of affinity.
> If I can prove that a weaker degree of affinity can be compensated by an increase of quantity, it will follow, that the action of any body is proportionate to the quantity of it which is necessary to produce a certain degree of saturation. This quantity, which is the measure of the capacity of saturation of different bodies, I shall call *mass* [Emphasis by Berthollet].

Berthollet's concepts were qualitative in nature, and there was no quantitative development for many decades. Why was this so?

Quantitative Developments: Reaction Kinetics and Equilibrium

Berthollet's mass action ideas were well ahead of his time. Only in 1850 did the German chemist Ludwig Wilhelmy publish the first quantitative measurements of the rate of a chemical reaction, the acid-catalyzed inversion of sucrose. Wilhelmy showed that his data could be fitted by a rate equation corresponding to a pseudo first-order irreversible reaction.

Extensions of Wilhelmy's work to the kinetics of a reversible reaction did not occur for more than another decade—by Marcelin Berthelot and Péan de St. Gilles in France (1862-1863) and by Cato Maximilian Guldberg

and Peter Waage in Norway (1864, 1867, 1879). Meanwhile, Augustus G.V. Harcourt and William Esson at Oxford (1865-1867) published rate laws for complex irreversible reaction schemes, e.g., a series reaction in which the first step is first-order and the following one is second-order.

We return to the question of why there was a fifty-year delay in creating a quantitative framework for Berthollet's ideas and can only speculate about its answer. Of several possible contributing factors, one may be the slow realization that quantitative physical laws had important applications in chemistry. Physical chemistry was explicitly recognized as a new subdiscipline only in the latter half of the nineteenth century. Another contributing factor was the common failure of authors to reference earlier work by others; and the multiplicity of European languages was a further deterrent. Berthollet and Berthelot published only in French; Wilhelmy only in German; Harcourt and Esson in English; and the first paper of Guldberg and Waage appeared in Norwegian. Wilhelmy's 1850 papers included no mention of Berthollet's publications fifty years earlier. In turn, Wilhelmy's studies of sugar inversion went unnoticed and were not mentioned by either Berthelot and St. Gilles, Guldberg and Waage, or Harcourt and Esson. The first citation of Wilhelmy was by Ostwald in 1884 in the context of his own research on the same reaction, the inversion of sucrose (12). Of historical interest is the seminal 1889 paper of Svante Arrhenius (13), in which the exponential dependence of rate constant on temperature in the inversion of cane sugar by acids was proposed.

The papers of Harcourt and Esson, published several years after the 1862 publications of Berthelot and St. Gilles, show no awareness of Berthelot's work on kinetics or of Guldberg and Waage's 1864 publications. Finally, although Guldberg and Waage in 1864 referenced the 1862 experimental results of Berthelot and St. Gilles, they ignored Berthelot's own theoretical treatment of the kinetics for a reversible reaction—even as a subject for criticism.

On the other hand, Berthollet's work on equilibrium was explicitly cited with admiration by his eminent countryman, Berthelot, some sixty years later. The astonishing story of Berthelot, a founder of thermochemistry, pioneer of organic chemistry, discoverer of the explosion wave, and foreign minister of France, among other things, warrants a separate communication.

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