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LECTURE TEXT

How the concept of chemical affinity evolved and how it contributed to chemical science

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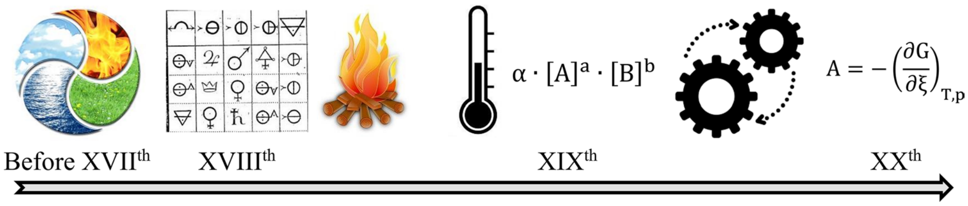
Abstract

This historiographic paper traces the evolution of the concept of chemical affinity from its antique origins until the end of the twentieth century. It shows how this concept changed over time, which important problems in the chemical science it revealed, and how it contributed to the development of chemical thermodynamics and kinetics, solution theory, electrochemistry, and nonequilibrium thermodynamics.

Graphical abstract



Keywords Chemical affinity · Chemical equilibrium · Chemical kinetics · Solution theory · Electrochemistry · Non-equilibrium thermodynamics

Introduction

Several hundreds or even thousands of various terms, concepts, and ideas exist in the chemical science, and even more have been proposed and vanished throughout the development of chemistry. Some of them relate only to very narrow branches of the chemical science and are not known outside it, others are known in several branches, and only a few of them are recognizable by any chemist. One of these well-known concepts is the concept of *chemical affinity*, which was born in the ancient times and survived until now. The scientific and philosophical importance of this concept significantly changed over time and also changed the world around. Many scientists dealing with the problem of chemical affinity contributed to the rise and development of new scientific fields and branches. This paper presents a short historiographic overview of the key developments related to chemical affinity.

The rise of chemical affinity in the ancient and medieval times

Even at the dawn of all civilizations, in the epoch of domination of the natural philosophical world view and the doctrine of the magical properties of the four prime elements (earth, water, fire, and air) the philosophers asked the question about the reasons and mechanisms of the interaction of these elements with

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each other and the processes caused by them. The first theories trying to explain these interactions were anthropomorphic by their nature [SM1].[1] One of the brightest examples of such kind of theories is the doctrine of the Ancient Greek philosopher Empedocles (Ἐμπεδοκλῆς) (c. 494 –c. 434 BCE) on the principles of “love” (φιλότης) and “strife” (νεῖκος) that cause the various forms of matter born by four prime elements combine with each other or separate one from the others [SM2]. In that time the first notions on *affinity* (in Latin, *affinitas*) rise, as on the measuring quantity of the tendency of elements and compounds for interaction.

The idea of *elective affinities* of the elements to each other is one of the central paradigms of ancient alchemy. The following savants of Medieval and Renaissance periods have discussed affinity: the German philosopher Albertus Magnus (c. 1200–1280) [SM3], Pseudo-Geber (presumed author or group of authors of alchemical writings dating to the late thirteenth and early fourteenth century) [SM4], the Swiss physician and alchemist Paracelsus (Philippus Aureolus Theophrastus Bombastus von Hohenheim) (c. 1493 –1541) [SM5], the Anglo-Irish natural philosopher Robert Boyle (1627–1691) [SM6], the English chemist John Mayow (1641–1679) [SM7], the German–Dutch alchemist Johann Rudolf Glauber (1604–1670) [SM8], the English scientist Sir Isaac Newton (1642, Julian calendar/1643, Gregorian calendar –1726) [SM9, SM10], and the developer of phlogiston theory, the German chemist and philosopher Georg Ernst Stahl (1659–1734) [SM11, SM12]. It is worth to mention that Boyle argued that the chemical interaction is not a result of “love” of two substances, but, vice versa, the representation of their “battle” against each other [SM13]. Such chemists as the German Andreas Libavius (c. 1550–1616) [SM14] and the Italian Angelo Sala (1576–1637) [SM15] wrote about the ability of one element to displace another from its solution (without linking it to the affinities of these elements). In the middle of the seventeenth century, the French iatrochemist Jean Béguin (1550–1620) for the first time presented an equation of the chemical reaction symbolically [SM16, see also SM17]. In his famous treatise “*Opticks*” [SM9, SM10], Isaac Newton proposed a mechanistic theory of chemical interactions. He thought that the chemical forces that cause the elements to interact with each other are similar to the gravitational ones. Later many generations of chemists until the end of the nineteenth century relied on this theory.

At the end of the seventeenth and the beginning of the eighteenth century, the German natural philosopher Wilhelm Homberg (known also as Guillaume Homberg) (1652–1715) for the first time focused the attention on the importance of such a factor as *time* when considering chemical reactions [see SM18, SM19]. He ranged the strength of acids according to how fast they react with the solid bases and assumed that time could be a measure of affinity of these acids to bases [SM20–SM22]. His ideas, however, were not noticed and accepted.

The eighteenth century and the affinity diagrams

At the beginning of the eighteenth century, sufficient material has accumulated concerning the properties of the various chemical compounds and the idea came up that some substances react with each other more likely than with others [SM23, SM24]. The idea of clear and informative visualization of this knowledge was realized for the first time in 1718 by the French chemist Étienne François Geoffroy (1672–1731) [SM25, SM26, see also SM27, SM28]. He labeled his tables as “tables of the chemical relations of the various substances” (Fig. 1). These tables were later republished in a collection “Recueil de planches, sur les sciences, les arts libéraux, et les arts méchaniques” [SM29]. The subsequent authors employed the term “tables of elective affinities.” During the eighteenth century, more than two dozen variants of such tables were proposed [SM30–SM49], which differ by the number of rows and the level of “detalization” of interactions [see SM50–SM53]. Figures 2 and 3 reproduce the affinity tables proposed by Gergens and Höchheimer [SM44] and by the German physicist and chemist Friedrich Albrecht Carl Gren (1760–1798) [SM45]; more tables can be found in other papers [SM27, SM52, SM53]. The most substantial development for the elective affinity theory was made by the Swedish mineralogist Torbern Olof Bergmann (1735–1784) [SM40, SM54–SM56]. He assumed that the chemical affinity is an unique quantity for each pair of interacting substances that depends on their aggregate state, size of the reacting particles, and the temperature of environment [SM54]. He proposed a method of semi-quantitative determination of the affinity coefficients based on the analysis of the series of substitution reactions [SM56]. Bergmann also developed Béguin’s idea on the symbolical representation of chemical reactions [SM55].

Bergmann’s ideas were developed further by the French chemist Louis Bernard Guyton de Morveau (1737–1816) [SM36, SM57, SM58]. He formulated a series of rules concerning affinities, introduced the numerical values of the affinities, collected them into tables and proposed methods of predicting the possibility or impossibility of common exchange reactions. Moreover, while Bergmann and his predecessors usually interpreted their tables in terms of phlogiston theory, Guyton de Morveau actively employed the oxidation theory proposed by the French chemist Antoine-Laurent Lavoisier (1743–1794) [SM49]. Lavoisier himself

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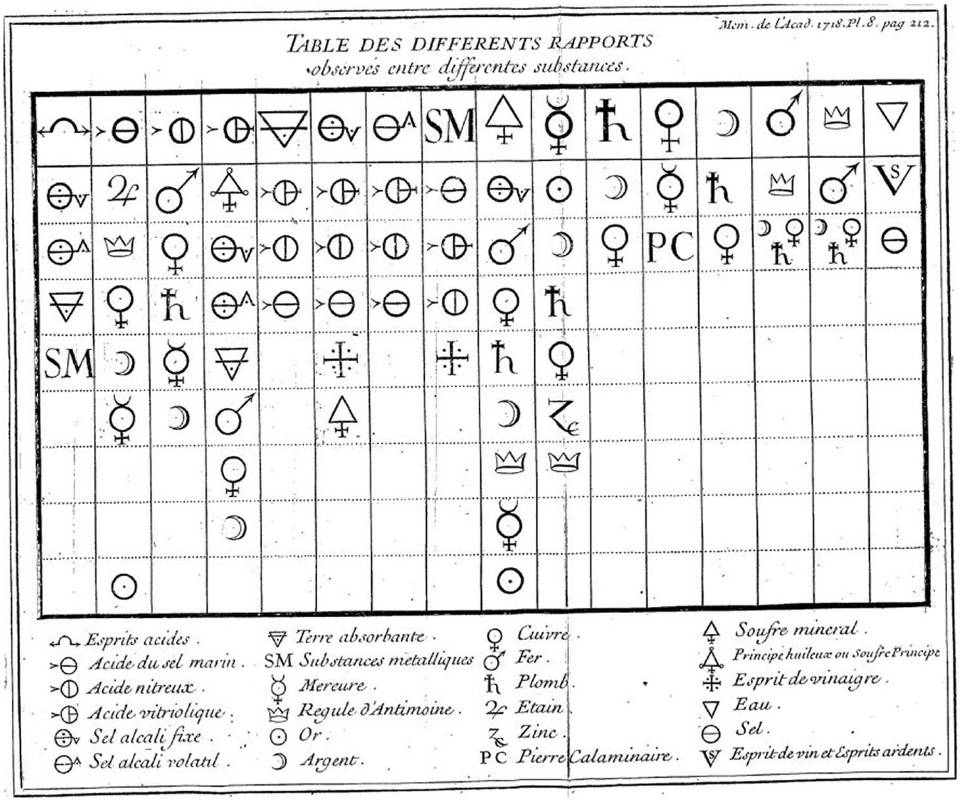
[1] Due to a huge number of references most of them were moved to the Supplementary Material.



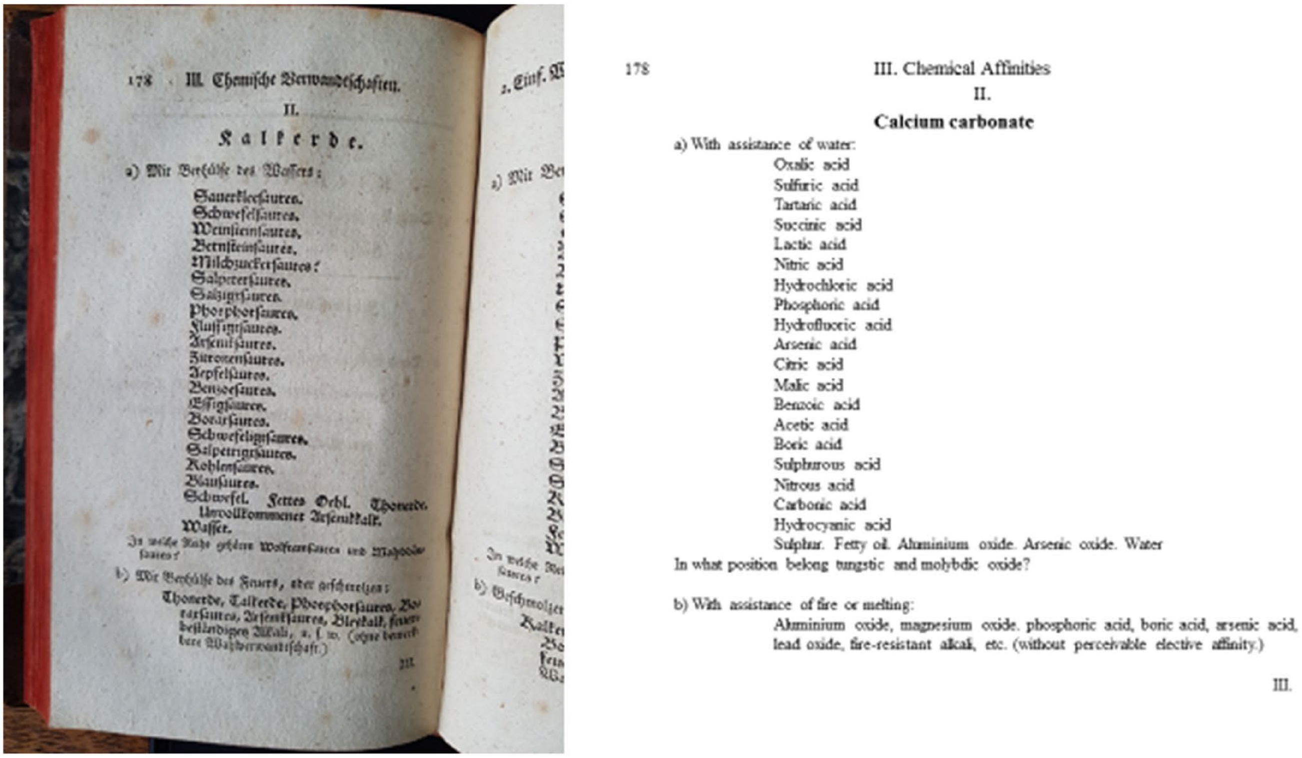
Mem. de l'Acad. 1718. Pl. 8. pag 212.

TABLE DES DIFFERENTS RAPPORTS
observés entre differentes substances.

⌒	>⊖	>⦶	>⊕	🜃	⊖v	⊖^	SM	🜍	☿	♄	♀	☽	♂	♕	▽
⊖v	♃	♂	🜏	>⊕	>⊕	>⊕	>⊖	⊖v	⊙	☽	☿	♄	♕	♂	VS
⊖^	♕	♀	⊖v	>⦶	>⦶	>⦶	>⊕	♂	☽	♀	PC	♀	☽ ♀ ♄	☽ ♀ ♄	⊖
🜃	♀	♄	⊖^	>⊖	>⊖	>⊖	>⦶	♀	♄						
SM	☽	☿	🜃		✢		✢	♄	♀						
	☿	☽	♂		🜍			☽	Ƶ						
			♀					♕	♕						
			☽					☿							
	⊙							⊙							

⌒	Esprits acides.	🜃	Terre absorbante.	♀	Cuivre.	🜍	Soufre mineral.
>⊖	Acide du sel marin.	SM	Substances metalliques	♂	Fer.	🜏	Principe huileux ou Soufre Principe
>⦶	Acide nitreux.	☿	Mercure.	♄	Plomb.	✢	Esprit de vinaigre.
>⊕	Acide vitriolique.	♕	Regule d'Antimoine.	♃	Etain.	▽	Eau.
⊖v	Sel alcali fixe.	⊙	Or.	Ƶ	Zinc.	⊖	Sel.
⊖^	Sel alcali volatil.	☽	Argent.	PC	Pierre Calaminaire.	VS	Esprit de vin et Esprits ardents.

Fig. 1 The affinity table proposed by Geoffroy [SM25, page 212]. This diagram is also freely available at https://w.wiki/8FmB. At the head of each column is a substance with which all the substances below can combine, where each column below the header is ranked by degrees of affinity. Explanation of symbols: ⌒ Acidic spirits, 🜃 Absorbent earth, ♀ Copper, 🜍 Mineral sulfur, >⊖ Acid of sea salt, SM Metallic substances, ♂ Iron, 🜏 Oily principle or sulfur principle, >⦶ Nitrous acid, ☿ Mercury, ♄ Lead, ✢ Spirit of vinegar, >⊕ Vitriolic acid, ♕ Antimony regulus, ♃ Tin, ▽ Water, ⊖v Fixed alkali salt, ⊙ Gold, Ƶ Zinc, ⊖ Salt, ⊖^ Volatile alkali salt, ☽ Silver, PC Calaminar stone, VS Spirit of wine and fiery spirits



178 III. Chemiſche Verwandtſchaften.

II.

Kalkerde.

a) Mit Beyhülfe des Waſſers:

Sauerkleeſaures.
Schwefelſaures.
Weinſteinſaures.
Bernſteinſaures.
Milchzuckerſaures?
Salpeterſaures.
Salzigtſaures.
Phosphorſaures.
Flußſpatſaures.
Arſenikſaures.
Zitronenſaures.
Aepfelſaures.
Benzoeſaures.
Eſſigſaures.
Boraxſaures.
Schwefeligtſaures.
Salpetrigtſaures.
Kohlenſaures.
Blauſaures.
Schwefel. Fettes Oehl. Thonerde. Unvollkommener Arſenikkalk.
Waſſer.

In welche Reihe gehören Wolframſaures und Molybdänſaures?

b) Mit Beyhülfe des Feuers, oder geſchmelzen:

Thonerde, Talkerde, Phosphorſaures, Boraxſaures, Arſenikſaures, Bleykalk, feuerbeſtändigen Alkali, u. ſ. w. (ohne bemerkbare Wahlverwandtſchaft.)

III.

178 III. Chemical Affinities

II.

Calcium carbonate

a) With assistance of water:

Oxalic acid
Sulfuric acid
Tartaric acid
Succinic acid
Lactic acid
Nitric acid
Hydrochloric acid
Phosphoric acid
Hydrofluoric acid
Arsenic acid
Citric acid
Malic acid
Benzoic acid
Acetic acid
Boric acid
Sulphurous acid
Nitrous acid
Carbonic acid
Hydrocyanic acid
Sulphur. Fetty oil. Aluminium oxide. Arsenic oxide. Water

In what position belong tungstic and molybdic oxide?

b) With assistance of fire or melting:

Aluminium oxide, magnesium oxide, phosphoric acid, boric acid, arsenic acid, lead oxide, fire-resistant alkali, etc. (without perceivable elective affinity.)

III.

Fig. 2 The affinity table proposed by Gren [SM45, volume 4, page 178]. The translation on the right side gives the names of the acids, although Gren lists the respective adjectives. At the beginning of the book, Gren mentions that he does not regard this as essential. Highest affinities are on top

Fig. 3 The affinity table proposed by Gergens and Höchheimer [SM44, page 85]

also proposed his own variant of the elective affinity tables and at the first time used the stoichiometric coefficients in the reaction equations [SM59]. He also contributed to the modern chemistry by developing quantitative measurements and calculations [SM60, SM61].

The affinity diagrams remained the main tool for the visualization of chemical reactions till the middle of the nineteenth century [see SM62]. In 1808 the English chemist and physicist John Dalton (1766–1844) proposed individual graphical symbols for the chemical elements known at that time [SM63], and in 1814 the Swedish chemist Jöns Jacob Berzelius (1779–1848) introduced [SM64–SM68, see also SM69, SM70] the now common letters for them. This resulted in the gradual replacement of the affinity tables and diagrams by the symbolic representation of the elements and reactions [SM69].

A special place among the works of that period is occupied by the German metallurgist Karl Friedrich Wenzel (c. 1740–1793) [SM71], devoted to dissolution of various metals in acids. He also focused his attention on time in chemical reactions and placed the first stone into the fundament of chemical kinetics. However, as with the works by Homberg, his research remained unnoticed by his contemporaries.

The early nineteenth century and the mass actions

Until the end of the eighteenth century all the reactions were treated as irreversible, and the possibility or impossibility of their occurrence were determined by the chemical affinities of the starting compounds to each other. Of course, some reactions existed that proceeded, contrary to the then ideas; however, these extensions were explained by the influence of unknown extrinsic factors that can “mask” the affinities. The same views held at the dawn of the career of the French chemist Claude Louis Berthollet (1748–1822). He decided that in addition to the chemical affinities of the reagents, other reverse forces exist and that earlier or later an *equilibrium* between these forces establishes. In 1798–1801 Berthollet participated in Napoleon’s Egyptian campaign [SM72], during which he visited the shores of the lake Natron at the North of Tanzania. The sediments of chalk and soda covered the lake shores, and after studying this natural phenomenon Berthollet characterized it by the following reaction: $CaCO_3 + 2NaCl \rightarrow CaCl_2 + Na_2CO_3$.

Only then ideas on elective affinity favored the occurrence of the reverse reaction. Berthollet explained the observed phenomenon by the great excess of the initial reagents and the constant removal of the products [SM73]. After returning to Paris, he conducted a series of experiments on reversible reactions [SM74–SM76]. Based on these data he developed a new theory of chemical interactions and published it in a few books [SM77–SM79]. In this theory Berthollet did not reject the concept of elective affinity, but assumed that the affinity between two substances is not constant, but depends on *masses* of these substances. When the *mass actions* of the direct and reverse reactions become equal, the reaction reaches its equilibrium. Berthollet’s theory was not clear for the contemporaries and very slowly disseminated in the scientific community, even despite of the support of the French chemist and physicist Joseph Louis Gay-Lussac (1778–1850) [SM80–SM84, see also SM85], and Berzelius [see SM86, SM87]. Even after half a century had passed, many researchers requested a broader experimental confirmation of this theory before accepting it [SM88–SM91], or simply rejected it in favor of Bergmann’s ideas [SM92, SM93]. The major contribution to the development of Berthollet's equilibrium theory was made by the German chemist Heinrich Rose (1795–1864) [SM94–SM104] and by the Russian physicist and chemist Nikolay Nikolayevich Beketov (Николай Николаевичъ Бекетовъ) (1827–1911) [SM105–SM107]. In 1850, the Scottish chemist Alexander William Williamson (1824–1904) studied the reversible reactions during his research on ethers [SM108–SM110]. He concluded that the chemical equilibrium is dynamic, rather than static ("reactants" as well as "products" are constantly forming and decomposing in a way that the amount of all the substances involved remains constant) and that the reactions take place at the same rate in both directions, giving the impression of having stopped. The idea that equilibrium is reached when the rates of the two opposite reactions equalize, was also clearly stated almost at the same time by the Italian–French chemist Faustino Giovita Mariano Malaguti (1802–1878) [SM111, SM112]. However, neither of these persons succeeded to find a quantitative expression for the mass action.

The middle of the nineteenth century and the rise of chemical kinetics

The middle of the nineteenth century was the time when purposeful studies of the influence of time on chemical reactions started [see SM113]. Many studies were devoted to this topic [SM88, SM111, SM112, SM114–SM128]. However, all these studies were of qualitative nature and were very similar to the previous works of Homberg and Wenzel. The authors tried to express the value of chemical affinity in various reactions, based on the observations of how fast the reaction proceed of one substance with a series of others. But the necessity of finding a quantitative expression for the influence of mass action on chemical affinities was already recognized. A few scholars started to solve this problem, namely the British chemist John Hall Gladstone (1827–1902) [SM129–SM134], the English anatomist George Rainey (1801–1884) [SM135], and the French chemists Pierre Eugène Marcellin Berthelot (1827–1907) and Leon Péan de Saint-Gilles (1832–1862) [SM136–SM139]. All these authors presented their data on the influence of the composition of the reaction mixture on the reaction processing in table form, but did not succeed to find a quantitative expression. But it was already close!

However, it is not surprising that many chemists experienced serious troubles in quantitatively treating their results. Mathematics courses were included into the chemistry curriculum only after World War II. Until that time chemistry was the discipline of a primarily experimental nature. Only after several decades, chemists supplemented their experimental praxis by developing theoretical reflections and laws. It is not surprising that only with the help of mathematics the chemists managed to get the ball rolling.

In 1850 the German chemist Ludwig Ferdinand Wilhelmy (1812–1864) performed a series of experiments on the rate of the cane sugar inversion reaction [SM140, SM141]. He introduced the term *reaction rate* and for the first time provided an equation for the reaction rate and for the sugar content in solution as a function of time. For the first time he used differential and integral equations for the kinetics of a reaction of the first order. Wilhelmy's work was ahead of his time and was not understood by his contemporaries. Only several years later, when the same reaction was studied by the German chemist and philosopher Wilhelm Friedrich Ostwald (1853–1932) [SM142, SM143], the Swedish physicist and chemist Svante August Arrhenius (1859–1927) [SM144], the Irish brewer and chemist Cornelius O'Sullivan (1841 – 1907) [SM145], and the Russian and Soviet physical chemist Ivan Alekseyevich Kablukov (Иванъ Алексѣевичъ Каблуковъ) (1857–1942) [SM146], the contribution of Wilhelmy as one of the "fathers" of modern chemical kinetics was recognized.

The development of the mass action law

The persons whose contribution to the development of chemical kinetics and the theory of equilibrium are hard to overestimate include the British chemist Augustus George Vernon Harcourt (1834–1919) and the British mathematician William Esson (1838–1916) [see SM147–SM150]. Harcourt performed kinetic studies of the reactions of potassium permanganate with oxalic acid and of hydrogen iodide with hydrogen peroxide and Esson helped him to present the results in form of differential equations [SM151–SM159]. They presented the kinetic equations for the reactions of different orders. These equations are now included in every university practice course on formal kinetics. They introduced the term "*rate constant*" and proposed a first equation for its temperature dependence. The reaction between H_2O_2 and HI is now called the Harcourt–Esson reaction. In the years following the publications of Harcourt and Esson, a number of papers appeared which were based directly on their concept of the rate of chemical changes. Various authors [SM90, SM91, SM145, SM160–SM163] tried to implement the kinetic equations to various chemical reactions.

Another pair of outstanding scientists that made a key contribution to physical chemistry was the Norwegian mathematician and chemist Cato Maximilian Guldberg (1836–1902) and the Norwegian chemist Peter Waage (1833–1900) [see SM164, SM165]. Following the works of Berthelot and Saint-Gilles [SM136–SM139], they studied the esters hydrolysis reaction; following the work of Rose [SM166], they studied the reaction of decomposition of carbonates; and following the work of the English chemist Sir Benjamin Collins Brodie (1817–1880) [SM167], they studied the reaction of barium peroxide with hydrochloric acid. They intended to find a mathematical representation for the influence of masses on chemical affinities of the substances and for the "chemical force" that drives the reactions. Their first papers were written in Norwegian [SM168–SM171], then they republished their results in French [SM172–SM174], and, finally, in German [SM175, SM176]. They introduced the term "*active mass*" for the quantity that is now known as "*mass concentration*" and assumed that active masses represent chemical affinities of reactants. They stated that the chemical forces that give rise to a combination of reagents are proportional to active mass product of the reactants, and the state of equilibrium results from an equality of chemical forces of the forward and reverse reactions, and they managed to propose an equation that later became known as the *Law of Mass Action*. Guldberg and Waage went a step further in the correct direction introducing suitable formulae for equilibrium and rate expressions but did not have the theoretical instruments to justify and interpret them correctly. They examined a huge number of different chemical systems falling in the old trap of getting general laws from the many experiments rather than the good experiment. However, the names of these two Norwegians will always remain in the history of physical chemisry as two founders of the theory of chemical equilibrium.

In 1867 the Austrian physicist Leopold Pfaundler von Hadermur (1839–1920) tried to explain the chemical equilibrium in terms of the kinetic theory developed by the German physicist and mechanicist Rudolf Julius Emanuel Clausius (also known as Rudolf Gottlieb) (1822–1888) and the Scottish physicist James Clerk Maxwell (1831–1879). He assumed [SM177, SM178] that not all molecules are in the same state of motion at a given temperature, and only a small amount of collisions between the molecules are effective to produce both forward and reverse chemical reactions. Eventually, a balanced molecular chemical equilibrium is achieved. In their last paper [SM176], Guldberg and Waage referred to Pfaundler's theory to explain their equation. Pfaundler's ideas were also used by Marcelin Berthelot in his thermal theory of affinity [SM179].

The heat theory of affinities and the Thomsen–Berthelot principle

The law of mass action proposed by Guldberg and Waage aroused considerable interest in the evaluation of the affinity coefficients and in finding the quantitative values of the chemical forces [SM180]. In the fortieth years of the nineteenth century, the Swiss and Russian chemist Germain (Herman) Henri (Heinrich) Hess (1802–1850) conducted a series of thermochemical studies [SM181–SM193], and as a result he formulated a rule, which is now called the *Hess law* [see SM194, SM195]. A short time after, Clausius formulated a statement [SM196–SM199] that was later called *the first law of thermodynamics* and showed that the Hess law is its partial case. Another person, who formulated the same law, but from different background, was the Scottish mechanical engineer William John Macquorn Rankine (1820–1872) [SM200, SM201]. These studies caused many chemists to think that the heat evolved in the chemical reaction is due to the operation of the chemical forces and, therefore, is the true measurement of the affinities. A *heat theory* of affinities dominated among the chemists during the next three decades, before it was disproved by the German physicist Hermann Ludwig Ferdinand von Helmholtz (1821–1894). Under the influence of this theory, the Danish chemist Hans Peter Jørgen Julius Thomsen (1826–1909) [SM202–SM207] and Marcellin Berthelot [SM179, SM208–SM210] independently formulated a principle that all chemical changes are accompanied by the production of heat and that processes which occur will be those in which the largest amount of heat is produced. Now this hypothesis is known as the *Thomsen–Berthelot principle* [see SM211, SM212]. Even despite this principle was erroneous, it contributed to the fact that chemists' views regarding chemical equilibrium shifted toward chemical thermodynamics. For example, these views were supported by Nikolay Beketov [SM213].

Berthelot and Thomsen actively disputed and challenged each other for the right to be renowned as the founders of this principle—neither recognized a contribution of the other one. These debates resulted in a series of publications [SM210, SM214–SM220], in which they accused each other in the inaccuracy of their statements and tried to claim their own right for the principle. This correspondence—both in French and in German—attracted the attention of other scientists to that problem. One of these persons was the Dutch physical chemist Jacobus Henricus (Henry) van't Hoff (1852–1911).

The late nineteenth century and the rise of modern physical chemistry

Van't Hoff's advantage over the previous researchers, who tried to find the quantitative values of chemical affinities, was that he was equipped with the very powerful tool of chemical thermodynamics. In fact, our present concept of chemical equilibrium differs only a little bit from the form presented by him in his treatise entitled "Études de dynamique chimique" [SM221, SM222]. He developed the law of mass action independently of Guldberg and Waage and from a different basis [SM223]. Van't Hoff assumed that the *rates* of the forward and reverse reactions are equal in equilibrium rather than the "the chemical *forces*."

In the seventieth years of the nineteenth century, the *second law of thermodynamics* was already formulated by the French mechanical engineer and physicist Nicolas Léonard Sadi Carnot (1796–1832) [SM224], Rudolf Clausius [SM225–SM227], William Rankine [SM228, SM229], and the British physicist and engineer William Thomson, 1st Baron Kelvin (1824–1907) [SM230–SM233]. Van't Hoff was familiar with this law, and he stated that a *maximum work* done by a chemical process rather than its heat is the measure of chemical affinity. He defined it as "the work, which can be done by the force of affinity, which brings about a chemical reaction." Van't Hoff also recognized from the second law of thermodynamics that a maximum amount of work is produced in a chemical reaction when the process is carried out isothermally and reversibly. He pointed out that the law of mass action is valid only for constant temperature conditions and that the influence of temperature on the equilibrium constant can be determined from considerations involving the second law of thermodynamics. Later Svante Arrhenius developed the equation for the dependency of the rate constant on temperature [SM144, SM234] that is consistent with van't Hoff's equation.

In 1876 the American physicist Josiah Willard Gibbs (1839–1903) published his epic papers on chemical thermodynamics [SM235, SM236] in which he introduced the thermodynamic potential, which is now known as the *Gibbs free energy*. A few years later Hermann von Helmholtz [SM237–SM239] introduced another thermodynamic potential, which is now known as the *Helmholtz free energy*. The significance of these potentials for the theory of equilibrium was recognized far later. However, van't Hoff's greatest achievement in the field of chemical equilibrium was the relation that is now known as the "*isotherm of chemical reaction*"—the relation between the equilibrium constant and the Gibbs free energy. Along with Helmholtz, van't Hoff did much to stimulate the great interest on the potential measurement method of determining the maximum work.

The implementation of the second law of thermodynamics to the study of equilibria in chemical systems was also performed by the German chemist August Friedrich Horstmann (1842–1929). He studied the processes of thermal dissociation of the various substances. He gave a correct thermodynamic derivation of equilibrium conditions for the dissociation of NH_4Cl [SM240], $CaCO_3$ and PCl_5 [SM241], and $NH_2CO_2NH_4$ [SM242], including the temperature dependence, treating the vapors as ideal gases. Horstmann developed a theory of thermal dissociation and his findings are applicable to any other equilibria involving perfect gases.

Chemical equilibria and affinities were the subjects of the early studies of one more classic in the field of physical chemistry, namely Wilhelm Ostwald [see SM243]. When he began to study chemistry, the problem of comparing and measuring chemical affinities had only recently been expressed by Guldberg and Waage and much remained to be learned about the affinity coefficients for individual reactions. Ostwald's earliest research, conducted while he was still a student, addressed these problems, and it determined the direction in which his subsequent work in physical chemistry has developed. In a series of different investigations, conducted throughout the late 1870s and early 1880s [SM244–SM249], he sought to show that quantitative changes in different physical properties, such as specific volume, refractive index or viscosity, could all be used to measure the extent of a chemical reaction, and thus provide information about the affinity coefficients of the reactants. At the same time he began to study the reaction kinetics more carefully and by the mid-1880s, Ostwald's work had significantly advanced the study of chemical affinity [SM175, SM250–SM255]. He had managed to collect a large body of experimental evidence, mostly for acid–base reactions, showing that different reactions could be characterized quantitatively by affinity coefficients, which depend on the nature of the acids and their degree of dilution. He also established that such coefficients could be measured with tolerable accuracy by various physical methods, both statically and dynamically. Later, when Ostwald was introduced to Arrhenius' experiments on the dependence of the electrical conductivity of acidic solutions on the concentration [SM256], he realized the significance of these studies and launched his own series of electrochemical studies, in which he linked the affinity coefficients in various reactions with the electrical conductivity of the solution [SM257–SM263].

It is worthy to notice that, for their great contribution to the development of equilibrium theory, chemical thermodynamics, and kinetics, van't Hoff, Arrhenius, and Ostwald are often called the "three musketeers of physical chemistry."

The solution theories and the pH concept

The development of the first solution theories were also affected by the concept of affinity. The first physical theory of solutions was developed by van't Hoff, Arrhenius, and Ostwald. In 1844, an attempt to find a numerical value for a quantity connected to the affinity had been made by the German chemist Eilhard Mitscherlich (1794–1863) [SM264], who tried to measure the attractive force of water on hydration in hydrate salts by controlling the decrease of the vapor tension in these crystals. When van't Hoff read Mitscherlich's book, he was surprised by the very low value of the hydration force, convinced that even the weakest chemical forces should be much stronger. This work led him to the interest in the phenomenon of the osmotic pressure. The osmotic pressure was discovered by the French clergyman and physicist Jean Antoine Nollet (1700–1770) in 1748 [SM265, SM266, see also SM267] and used intensively by the botanists. Van't Hoff learned about it from the Dutch botanist Hugo Marie de Vries (1848–1935), whom he met in a street in Amsterdam, and immediately recognized the importance of osmotic pressure measurements for the evaluation of chemical affinity. He decided to use a cell of the type invented by the German botanist and plant physiologist Wilhelm Pfeffer (1845–1920) [SM268] to test his ideas. Using a diluted solution of cane sugar in water, van't Hoff was able to show that the attraction between water and sugar was about 100 times larger than that measured by Mitscherlich between the sulfate and the hydration water. From these measurements he further deduced a much more important and general result, i.e., that in diluted solutions the particles of the solute behave like the particles of an ideal gas and therefore that the osmotic pressure is proportional to the absolute temperature as the pressure in the gas phase. Later these studies resulted in van't Hoff's theory of solutions, in which he presented his view on the chemical physics of diluted solutions [SM269–SM274], establishing a perfect formal parallelism between ideal gases and diluted solutions. Ostwald also proposed an expression, which was later recognized as the *Ostwald dilution law*. In fact, it was an implementation of the mass action law to the process of dissociation of weak electrolytes.

At the same time Svante Arrhenius studied a dependency between the relative strength of acids and their electrical conductivity [SM256]. He explained this phenomenon in the way that the acids in the solution produce charged species (ions). This idea was supported by Ostwald, who realized that the electrical conductivity could be connected with the chemical affinity. With the support of Ostwald, Arrhenius published a paper in which he formulated a theory of electrolytic dissociation [SM275]. In this paper he also provided a physical meaning of the van't Hoff factor (a coefficient in the relation between the osmotic pressure and concentration) [SM274]. Opposition to Arrhenius' proposal was immediate and intense, but its explanatory value was so great that, despite some notable exceptions, resistance was rather quickly overturned. The main crusader of the ionic dissociation theory was Wilhelm Ostwald, whose adoption and spirited defense were crucial in winning general acceptance for the new ideas. In numerous works written during the late 1880s and early 1890s [SM276–SM283], he persuasively argued the great value of those ideas for connecting various experimental regularities that had not previously been clearly associated.

The solution theory proposed by van't Hoff, Arrhenius, and Ostwald assumed that the interactions between the particles of the solvent and the solute are of purely physical nature, similar to those between the molecules in gases. This theory describes the properties of dilute solutions satisfactory, but it does not work for concentrated solutions.

Another solution theory was developed in the sixtieth years of the nineteenth century by the Russian chemist Dmitriy Ivanovich Mendeleev (Дмитрій Ивановичъ Менделђевъ) (1834–1907) [SM284]. He studied the properties of mixtures of water with ethanol, the dependence of the specific volumes of these mixtures on the solution composition [SM285, SM286], and determined the dependency of various physical properties of the mixtures on the content of alcohol [SM287, SM288]. His studies led him to the conclusion that the interactions between the particles of a solvent and a solute are of chemical nature. The molecules of a solvent surround the molecules of a solute, interact with them forming coordination bonds, and form a solvation shell. This shell is so strong that even after removing the solvent the molecules of a solute remain bound and form a crystal hydrate. According to Mendeleev, the formation of a solution results from interactions between the particles of all components. Interaction was understood in a broad sense as an "active binding force of varying strength in solution." It was emphasized that "definite chemical compounds are merely particular cases of indefinite chemical compounds" [SM286, SM288–SM291]. Hence it followed that "the difference between proper solutions and other types of chemical compounds lies in different degrees of stability." Mendeleev's chemical theory of solutions is based on the idea on the dominant role of solvation of solutes. Mendeleev considered that various chemical interactions could take place during dissolution, namely the formation of compounds with different degrees of stability, substitutions or decompositions of the components of solutions, and decompositions of solutes by solvents [see SM292]. Mendeleev's hydrate theory was used to explain the anomalous results of freezing point measurements on electrolyte solutions by the German chemist Friedrich Rüdorff (1832–1902) [SM293, SM294] and the Swiss chemist Louis Casimir de Coppet (1841–1904) [SM295–SM297].

Another person, who contributed to the topic of solution theory, was the American physical chemist Harry Clary Jones (1865–1916). He worked both with Ostwald, Arrhenius, and van't Hoff and was one of the followers of ionization theory. Jones and his students gathered a tremendous amount of experimental data on solutions, and to explain these data he developed a solvation theory [SM298–SM304]. He specially noticed that Mendeleev's hydrate theory had no relevance or connection to his own one. While Mendeleev's theory predicted the formation of a few definite compounds of solute with water, Jones suggested the formation of a complete series of hydrates. The amount of hydrated water varies in a wide range depending on the solution concentration and temperature. His theory involved all possible solvents, not just water.

In the late nineteenth century and early twentieth century, a hot debate arose concerning these two theories [see SM305, SM306] between "ionists" and "anti-ionists." It was believed that dissociation and association were contradictory to each other.

The modern representation of the solution theory combines these two approaches [see SM307]. In 1889–1891, Ivan Kablukov worked with Ostwald and Arrhenius at the University of Leipzig. As a student of Mendeleev, Kablukov was unable to accept Arrhenius' idea that ions in solution do not interact in any way with the solvent. He discovered an abnormal electrical conductivity of the nonaqueous solutions of electrolytes and an increase of the conductivity of alcohols upon addition of water to them. This led him to the conclusions that the ions in solution are also solvated. Kablukov contended that there is no inherent contradiction between ionic dissociation and ionic hydration and assumed that both these theories will merge in the future. Independently from Kablukov, the same conclusions were discovered by another Russian and Soviet physical chemist, Vladimir Aleksandrovich Kistyakovskiy (Владиміръ Александровичъ Кистяковскій) (1865–1952) [see SM308]. He argued that ions must interact with the surrounding solvent molecules and thought that this interaction was the only possible source of the energy needed for dissociation to occur. These two scientists combined the physical and chemical approaches to the solution theory [SM146, SM309–SM311] and gave rise to its presentation in the modern form. Later Jones also came to the same conclusions.

In the first decade of the twentieth century, the Danish chemist Søren Peder Lauritz Sørensen (1868–1939), who was the head of Carlsberg laboratory in Copenhagen, studied the effect of ion concentrations on proteins. Because the concentration of hydrogen ions was particularly important, he denoted it as p_H [SM312–SM314]. He introduced the pH scale, founded the basics of pH-metry, and proposed two methods of measuring pH, namely potentiometry using a hydrogen electrode and colorimetry using a set of various acid–base indicators. This scale found the immediate acceptance among biochemical researchers, but chemists were unaware of it until the German biochemist and physician Leonor Michaelis (1875–1949) published a book on hydrogen ion concentration [SM315]. However, only after more than 10 years by initiative of the editorial office of the *Journal of Biological Chemistry* the concept of pH was standardized and brought to the contemporary view [see SM316, SM317]. Later on, the symbol "*p*" ubiquitously became the symbol of the negative decimal logarithm operator [see SM318, SM319]. An important step in the development of the pH concept was the rejection of the definition $\mathrm{pH} = -\log_{10} c_{\mathrm{H}^+}$ in favor of the more correct thermodynamic meaning $\mathrm{pH} = -\log_{10} a_{\mathrm{H}^+}$ [SM320]. In 2010 the introduction of pH was recognized as the most valuable achievement in solution chemistry and in biochemistry [SM321–SM323].

For many years after Guldberg and Waage presented their law, the nature of electrolytes remained fuzzy, and it was not clear how the principles of equilibrium could be applied to ionic species. In 1908, 1 year before Sørensen presented the concept of pH, the American chemist and biologist Lawrence Joseph Henderson (1878–1942), whose early studies were devoted to the study of blood and its respiratory function, recognized a simple relationship between a weak acid, its salt, and the hydrogen ion concentration. It was already known at that time that blood can resist changes in acidity and basicity due to its bicarbonate buffering system, but Henderson expressed a clear relationship between the composition of a buffer, its buffering capacity, and the hydrogen ion concentration [SM324, SM325]. A total of 10 years later, the Danish physician Karl Albert Hasselbalch (1874–1962), who also described how the affinity of blood for oxygen was dependent on the concentration of carbon dioxide, converted the Henderson equation into the logarithmic form and used it to study the metabolic acidosis [SM326]. In this form it is known as the *Henderson–Hasselbalch equation*. This equation founded the basis for the quantitative description of chemical equilibria in aqueous solutions [see SM327–SM329].

The electrode potential and equilibria in electrochemical systems

The ability of some chemical elements to displace another one from aqueous solutions was known already by medieval alchemists [SM14, SM15]. However, only at the second half of the eighteenth century, after the discovery of electrochemical elements, scientists started to think about the electrochemical nature of the redox transformations in solutions and tried to propose a measurable quantity for the displacement ability of various elements.

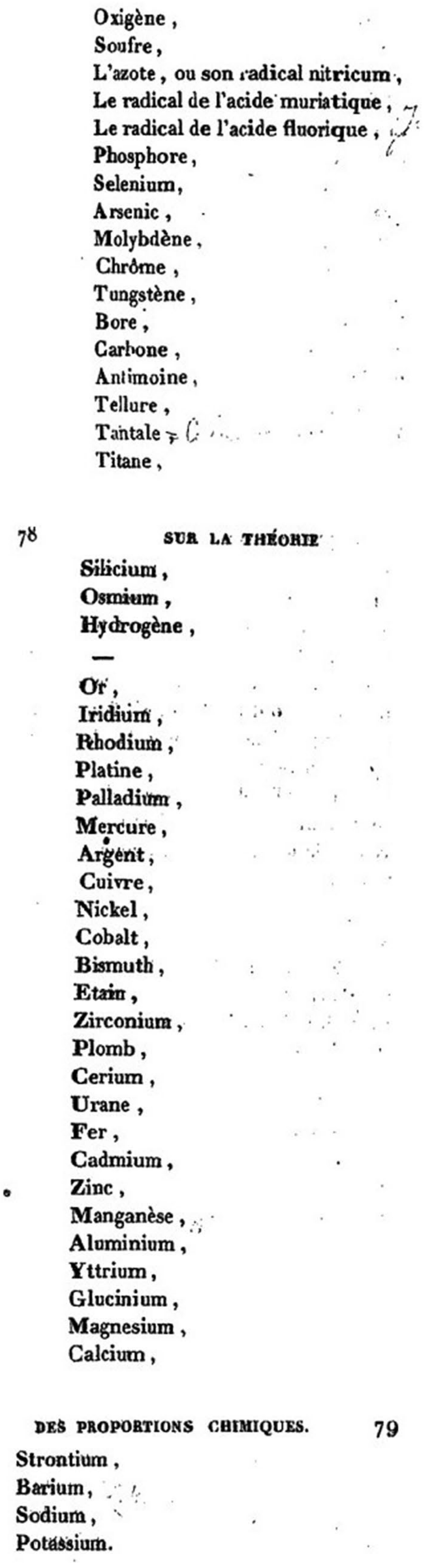
In the late eighteenth century the Italian physicist and biologist Luigi Aloisio Galvani (1737–1798) discovered the phenomenon that when two dissimilar metal strips were touching the nerves of a severed frog's leg and each other, the muscles of the leg violently contract [SM330]. Galvani assumed that the bodily fluids of the living or recently deceased animal generate an electrical stimulus that causes the muscles to contract. He raised the theory of *animal electricity*. After reading Galvani's book, another Italian physicist and chemist Alessandro Giuseppe Antonio Anastasio Volta (1745–1827) rejected this theory and assumed that the contact of dissimilar metals itself produces the electricity and the bodily fluids act only as the conductors. He started a series of experiments in which he put various metals in contact and observed the electrical effects. He composed the following series of metals: Zn, Pb, Sn, Fe, Cu, Ag, and Au—and concluded that, for metals in contact, the farther one was from another in this series, the higher was the "power" of electricity. This was the so called *Volta's law of the electrochemical series* [SM331]. In fact, it was the prototype of the contemporary electrochemical series. During his experiments, Volta invented the first electrochemical battery—now known as a *voltaic pile* [SM332]. However, Galvani remained unconvinced, and for several years a debate over the nature of current electricity raged between the supporters of animal electricity, on the one hand, and the supporters of Volta's metal contact theory, on the other side [see SM333]. A few years later the German physical chemist and one of the fathers of modern electrochemistry, Johann Wilhelm Ritter (1776–1810), proposed another theory. According to Ritter, electricity is produced due to a chemical reaction rather than to a simple metallic contact. Ritter conducted several experiments with electrochemical cells and linked the electrochemical series of metals with the series of metals arranged by the increase in their relative chemical affinity to oxygen [SM334–SM337]. These studies found further development in the works of Nikolay Beketov, who paid much attention to the study of the displacement reactions and proposed a "displacement metal series" in its modern view [SM338].

In 1800, shortly after Volta's announcement of his discovery of the voltaic pile, the English scientist and civil engineer William Nicholson (1753–1815) and the English surgeon Sir Anthony Carlisle (1768–1840) reported on its ability to decompose water [SM339], and the Scottish military surgeon and chemist William Cruickshank (around 1740 or 1750–1810 or 1811) reported on its ability to decompose aqueous solutions of various salts, acids, and alkalis [SM340]. These results raised a question of the mechanism by which electric current can electrolyze the liquids and solutions. A flurry of electrochemical experimentation and speculation among chemists was initiated, and at least ten different chemists proposed their own speculative theories of electrolysis and the relationship between electricity and chemical affinity. One of these persons was the British chemist Sir Humphry Davy (1778–1829); one more influential person was Jacob Berzelius. They both accepted Ritter's theory of electricity and they both assumed that there was a correlation between the chemical affinities of the various solution components and their ease of electrolysis.

Davy suggested that chemical affinity was the result of electrical attractions between opposite charges induced on the atoms when they came into physical contact, and that electrolytic decomposition was the result of the charged atoms or particles being more strongly attracted to the charged poles of the electrolysis cell than to each other [SM341, see also SM1, SM342–SM344]. On the other hand, Berzelius proposed an electrical theory of heats of reaction. He assumed that the atoms and molecules of matter already contained unequal amounts of positive and negative electrical fluid prior to combining and that these were concentrated at opposite poles on their particles. Particles attracted to the negative pole during electrolysis had an excess of positive over negative fluid, whereas those attracted to the positive pole had an excess of negative over positive fluid. When atoms combined to form molecules, their oppositely charged electrical fluids reacted with each other to form free heat and the residual unneutralized electrical fluids then redistributed themselves at opposite poles of the product molecules [SM345, see also SM1, SM346, SM347]. He also attempted to arrange all of the then known chemical elements in a continuous "electrochemical" series, with the most electronegative (oxygen) at the top and the most electropositive (potassium) at the bottom (see Fig. 4). This was in many ways a relic of the affinity tables popular in the eighteenth century, since the resulting electronegativity scale was, in effect, measuring the relative affinities of the various atoms for the two electrical fluids. According to Berzelius, the greater the difference in the electronegativities of the reacting atoms, the greater their chemical affinity, and the greater the heat evolution produced when their oppositely charged fluids combined. Although these assumptions implied a direct correlation between affinity and heats of reaction, Berzelius never quantitatively followed up their thermochemical implications. Instead, he applied his theory to the classification and naming of chemical compounds and to establishing restrictions on what atoms and groups could displace one another in chemical reactions.

A very important stage in the history of electrochemistry was the discovery of the laws of electrolysis by the English physicist and chemist Michael Faraday (1791–1867) [SM348–SM352]. Faraday conducted a huge number of electrochemical studies; he introduced our modern electrochemical nomenclature and clearly distinguished between the intensity and the quantity of electric current. Using his "law of definite electrolytic action" he tried to determine the equivalent weights of all the elements known at that time. The same law was proposed at the same time by the Italian chemist Carlo Matteucci (1811–1868) [SM353, SM354], although it is not clear whether he did it independently of Faraday or not [see SM355]. This was the first quantitative expression in the topic of electrochemical processes. It is interesting that Berzelius rejected Faraday's findings, opposed his theory, and stated that Faraday's determinations of the equivalent weights of the elements are not consistent with his own [SM356]. Later the term of electrochemical equivalent was introduced [see SM357–SM359]; and the numeric value of the electric charge per 1 mol of electrons was called the *Faraday constant* (*F*).

With the discovery of the energy conversation law it became evident that electrochemical cells are devices for



Oxigène,
Soufre,
L'azote, ou son radical nitricum,
Le radical de l'acide muriatique,
Le radical de l'acide fluorique,
Phosphore,
Selenium,
Arsenic,
Molybdène,
Chrôme,
Tungstène,
Bore,
Carbone,
Antimoine,
Tellure,
Tantale,
Titane,

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Silicium,
Osmium,
Hydrogène,
—
Or,
Iridium,
Rhodium,
Platine,
Palladium,
Mercure,
Argent,
Cuivre,
Nickel,
Cobalt,
Bismuth,
Etain,
Zirconium,
Plomb,
Cerium,
Urane,
Fer,
Cadmium,
Zinc,
Manganèse,
Aluminium,
Yttrium,
Glucinium,
Magnesium,
Calcium,

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Strontium,
Barium,
Sodium,
Potassium.

Fig. 4 The electrochemical series proposed by Berzelius [SM345, pages 77–79]. The electronegativity decreases from the top to the bottom in the following order: oxygen, sulfur, nitrogen on his nitric radical, radical of muriatic acid, radical of fluoric acid, phosphorus, selenium, arsenic, molybdenum, chromium, tungsten, boron, carbon, antimony, tellurium, tantalum, titanium, silicon, osmium, hydrogen, gold, iridium, rhodium, platinum, palladium, mercury, silver, copper, nickel, cobalt, bismuth, tin, zirconium, lead, cerium, uranium, iron, cadmium, zinc, manganese, aluminum, yttrium, glycinium, magnesium, calcium, strontium, barium, sodium, and potassium ▶

the mutual conversion of chemical and electrical energy, and in the fiftieth years of the nineteenth century, the models of Davy and Berzelius had been replaced by the proposition that the chemical affinity of the reaction in an electrochemical cell should correlate in some manner with the electrical cell voltage [see SM360, SM361]. The first thermodynamic treatments of cell potential were made by Helmholtz [SM362] and Thomson [SM363]. These treatments were based on Berzelius electrical theory of heat and the first law of thermodynamics. They assumed that a cell potential correlates with the enthalpy change of the cell reaction. This assumption played the same role in the development of chemical thermodynamics, as the Berthelot–Thomsen principle. However, exactly like the Berthelot–Thomsen principle was replaced by the concept of free energies, the statement of Helmholtz and Thomson was also replaced by the assumption that the free energy is the quantity that determines the cell potential. This dependence was firstly proposed by Helmholtz [SM237–SM239] together with the Helmholtz free energy and the variation of *Helmholtz–Gibbs equation*. After the fundamental works of Gibbs [SM235, SM236] and van't Hoff [SM221] the Gibbs free energy was accepted as the measure of the chemical affinity in reaction, and the relation between ΔG (the change of free energy) and E (the cell voltage) was established, $\Delta G = -n \cdot F \cdot E$ (n: number of transferred electrons) [SM364]. Later this equation was called a *basic equation of electrochemical thermodynamics* [see SM365–SM368].

It was the German physical chemist Walther Hermann Nernst (1864–1941), who made the final refinement to the theory. He related the cell voltage to the osmotic pressures of the reactants, and finally, to the equilibrium constant of the cell reaction [SM369–SM371]. The original equation proposed by Nernst described only the reaction between the metal and its ions in solution (which proceeds on the electrodes of the first kind). At the same time, the American physical chemist Wilder Dwight Bancroft (1867–1953) proposed the quantification of the potential of the redox reaction proceeding on the inert electrodes [SM372], although he failed to find the concentration dependency. The quantitative expression for the potential of redox electrodes was proposed by the German chemist Rudolf Peters (1869–1937), a PhD student of Wilhelm

Ostwald [SM373, see also SM374]. This fact is not widely known, and the generalized equation for the cell potential is now called the *Nernst equation* [see SM375, SM376], although in some German-language literature it bears the name “Peters equation” [see SM377]. In 1897 Nernst further suggested the use of the hydrogen electrode as the zero-point standard for reporting cell potentials [see SM378]. This proposal was experimentally implemented by the Australian chemist Norman Thomas Mortimer Wilsmore (1868–1940), who determined the hydrogen scale half-cell potentials for 31 elements, and was also adopted by the first reference work dealing with the tabulation of cell potentials [SM379]. Later many researchers used the electromotive force measurements to determine the Gibbs free energies and entropies of the various species [SM380, SM381].

The concept of activity

In 1907 the American physical chemist Gilbert Newton Lewis (1875–1946) introduced the concepts of activity and fugacity [SM382, SM383] that replaced the concepts of concentration and pressure in the rigorous definition of chemical equilibrium [see also SM384]. Using fugacities and activities allowed to use the law of mass action and other thermodynamic relations for an exact description of the behavior of species. The concepts of activity and fugacity were devised to take into account the fact that mass action generally does not vary linearly with concentration, as was assumed by earlier workers. Lewis also defined the term “*free energy*” instead of “*the maximum work*” [SM385]. When a system at constant temperature passes spontaneously from one state to another, the maximum useful work that becomes available represents the decrease in the free energy of the system. This decrease can be taken as a measure of the affinity of the chemical process. In 1923, after Lewis and the American physical chemist Merle Randall (1888–1950) published their now classic “Thermodynamics” [SM380], the term “free energy” completely replaced the term “affinity” for the driving force of chemical reactions.

Later the concept of activities was developed by the English physical chemist Edward Armand Guggenheim (1901–1970) [SM366]. He argued that activities of the single ions in solutions are unmeasurable and even physically meaningless and favored the usage of the *mean ionic activities* and *activity coefficients* that were proposed by the Dutch–American physicist and chemist Peter Joseph William Debye (1864–1966) and the German physicist and chemist Erich Armand Arthur Joseph Hückel (1896–1980) [SM386, see also SM387]. However, chemists have never been able to give up the idea of single ion activities, and by implication, single ion activity coefficients. The attempts to define a single ion activity in terms of purely thermodynamic quantities and the proposals of a measuring single ion activity coefficients method based on purely thermodynamic processes are still present [SM388]. Later the concept of activities of the components of alloys were also introduced [SM389].

The twentieth century, Le Châtelier–Braun principle and the nonequilibrium thermodynamics

However, with the replacement of affinity by the free energy, the former was not thrown into oblivion and made its contribution to the rise of nonequilibrium thermodynamics. When van’t Hoff proposed his equation [SM221], he managed to qualitatively explain how the changes in temperature can shift the equilibrium [SM390]. This was the first mention of the “*principle of the mobile equilibrium*” that was later generalized by the French chemist Henry Louis Le Châtelier (1850–1936) [SM391–SM393] and theoretically substantiated by the German physicist Karl Ferdinand Braun (1850–1918) [SM394–SM396]. Le Châtelier acknowledges that he was inspired by the works of van’t Hoff in chemical equilibrium, the Franco-Luxembourgish physicist and inventor Jonas Ferdinand Gabriel Lippmann (1845–1921) [SM397], and the Russian physicist Heinrich Friedrich Emil Lenz (1804–1865) [SM398] in the field of electricity. Later this principle was reformulated as the “*principle of moderation*” [see SM399, SM400], the “*principle of action and reaction*” [SM401], the “*principle of ability of adaptation*” [SM402], and the “*principle to preserve the status as much as possible*” [SM403], and now it is known as “*Le Châtelier–Braun principle*.” The statement initially formulated by Le Châtelier was crude and unclear and its applicability was very limited. Very soon the French physicist Camille Raveau (1867–1953) [SM404] and the Austrian–Dutch physicist Paul Ehrenfest (1880–1933) [SM405, SM406] pointed out that numerous processes proceed in contradiction with this statement. The applicability of this principle in studying and teaching the chemical equilibria was the subject of numerous debates that do not cease until today [see SM399, SM400, SM407–SM472]. Several researchers (including Le Châtelier himself) later tried to improve the formulation of this principle [see SM400, SM405, SM421, SM473–SM487].

One of these researchers was the Belgian mathematician and physicist Théophile Ernest de Donder (1872–1957), who is now well-known as the “father of irreversible thermodynamics.” He introduced the term “*extent of reaction*” (ξ) [SM488] and developed the free energy definition of chemical affinity [SM489–SM492, see also SM493]:

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{T,p}.$$

This definition is now accepted by the International Union of Pure and Applied Chemistry (IUPAC) [SM494].

De Donder also showed that for a mixture of chemical species with the possibility of chemical reaction, the chemical affinity is linked with the corresponding *Gibbs energy of reaction* [see also SM495–SM497]:

$$A = -\Delta_r G.$$

The example of the usage of affinity in modern geochemistry is discussed in the Appendix.

His ideas on irreversibility were later further developed by his famous student, the Russian–Belgian physical chemist Ilya Romanovich Prigogine (Илья Романович Пригожин) (1917–2003). Prigogine discovered that importation and dissipation of energy into chemical systems could reverse the maximization of entropy rule imposed by the second law of thermodynamics. He is best known for his definition of dissipative structures and their role in thermodynamic systems far from equilibrium [SM498–SM501]. Both de Donder and, later, Prigogine proposed the formulations of Le Châtelier–Braun principle based on new concepts of affinity and extent of reaction [SM488, SM498, SM501]. This new formulation is now accepted [see SM400, SM466].

In the twentieth century, Le Châtelier–Braun principle found its application not only in physics and chemistry, but also in biology [SM502–SM504], economics [SM505–SM521], history [SM522–SM528], and social and human science [SM529–SM536]. Prigogine's irreversible thermodynamics, in its turn, found their application in theory of life and evolution [SM537–SM540] and in sociological studies [SM522, SM541, SM542].

The concept of chemical affinity played a pivotal role in the development and establishment of a rapidly emerging field of *human chemical thermodynamics*—a branch of human chemistry that tries to implement the concepts of chemical thermodynamics, such as affinity, entropy, and Gibbs free energy, to the study of human existence, experience, and social function. In this field a human is defined specifically as a reactive chemical species or powered animate molecule, and a social system is considered as a system of reactive chemical entities [SM543]. In the year 1809 the great German writer Johann Wolfgang von Goethe (1749 – 1832) presented a novel entitled "*Die Wahlverwandtschaften*" ("Elective affinities") [SM544], in which he tried to characterize the social relationships such as friendship and love in terms of affinities. Several chemists, historians, and philosophers still discuss how strongly the chemical affinity theory of that time influenced Goethe [SM545–SM551]. It was the first, but not the last, turn of chemical thermodynamics to the social sciences. In the twentieth century, several researchers independently proposed similar views [SM533, SM540, SM552–SM558], and many theories arose.

Conclusion

The history of chemical affinity made a full circle and returned to the starting point, the relationship between chemistry and social sciences, although on a much higher level. During the movement along this circle the affinity concept contributed to the development of chemical thermodynamics and kinetics, electrochemistry, solution theory, and organic chemistry, formed many related terms, such as "electrophile," "nucleophile," "dienophile," "affinity to electrons" and others [SM559] (which are briefly discussed in the Appendix), and now it stands at the beginning of the new turn of the wheel. No one knows what kind of theories will rise due to the further development of chemical affinity.

Further reading

More information on the topic could be found in the works [1–27].

Appendices

The example of the usage of the chemical affinity in geochemistry and metallurgy

According to the IUPAC definition [SM560], the driving force (or affinity) of chemical reaction is the decrease in Gibbs energy on going from the reactants to the products, $A = -\Delta_r G$. However, the Gibbs energies of different reactions are usually not directly comparable with each other due to the different stoichiometries. This problem is usually overcome by converting the different equations to the same stoichiometry, or by using the related properties independent of stoichiometry. In geochemistry and pyrometallurgy the metal oxidation reactions are of particular importance. Let us consider the reaction of metal Me with oxygen, which results in the formation of the lowest oxide Me_aO_b, normalized to the single oxygen atom:

$$\frac{a}{b}\mathrm{Me(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \frac{1}{b}\mathrm{Me}_a\mathrm{O}_b\mathrm{(s)}.$$

Accordingly, the *chemical affinity M of the metal to oxygen* [SM561] is determined as the quantity:

$$M_{\mathrm{Me}} = -\Delta_r G = -\frac{\Delta_f G_{\mathrm{Me}_a\mathrm{O}_b\mathrm{(s)}}}{b}.$$

Table A1. The standard Gibbs energies of formation, the affinities to oxygen, and the equilibrium oxygen partial pressures for fourth period transition metals [SM562]

Metal	Lowest oxide	$\Delta_f G^o_{298}$, J/mol	M_{Me}, J/mol	$p_{O_2(g)}$, bar
Sc	Sc_2O_3	–1,819,200	606,400	$3.35 \cdot 10^{-213}$
Ti	Ti_6O	–517,200	517,200	$5.88 \cdot 10^{-182}$
V	VO	–404,200	404,200	$2.36 \cdot 10^{-142}$
Cr	Cr_2O_3	–1,058,100	352,700	$2.62 \cdot 10^{-124}$
Mn	MnO	–362,800	362,800	$7.58 \cdot 10^{-128}$
Fe	Fe_3O_4	–1,014,200	253,550	$1.45 \cdot 10^{-89}$
Co	CoO	–205,100	205,100	$1.34 \cdot 10^{-72}$
Ni	NiO	–211,400	211,400	$8.47 \cdot 10^{-75}$
Cu	Cu_2O	–147,800	147,800	$1.63 \cdot 10^{-52}$
Zn	ZnO	–320,600	320,600	$4.63 \cdot 10^{-113}$

If both the metal and the oxide are the pure bulk substances, their thermodynamic activities are assumed equal to unity, and the expression of the equilibrium constant becomes:

$$K_p = \frac{1}{p_{O_2(g)}} = \exp\left(-\frac{\Delta_r G}{R \cdot T}\right) = \exp\left(\frac{M_{Me}}{R \cdot T}\right),$$

from which follows the relation between the chemical affinity of the metal to oxygen and the equilibrium partial pressure of oxygen:

$$p_{O_2(g)} = \exp\left(\frac{\Delta_r G}{R \cdot T}\right) = \exp\left(\frac{\Delta_f G_{Me_aO_b(s)}}{b \cdot R \cdot T}\right) = \exp\left(-\frac{M_{Me}}{R \cdot T}\right).$$

Both, the affinity to oxygen and the equilibrium oxygen partial pressure might be used to compare the tendency of different metals to oxidize. Table A1 shows the data on chemical affinities of the fourth period transition metals to oxygen at standard temperature [SM562]. A clear trend can be seen, as with the increase of the metal atomic number (except zinc), their affinities to oxygen decrease, and the equilibrium partial pressures of oxygen increase, thus indicating the lesser tendency of heavier metals to oxidize.

Similarly, the *chemical affinity of metal to sulfur* is defined [SM561] to express the tendency of different metals to form sulfide minerals.

Terms related to chemical affinity

Here the other terms related to the concept of chemical affinity that are present in the modern chemistry curriculum are briefly introduced. A detailed discussion of these terms and their evolution falls outside the topic of this lecture.

Electronegativity, ionization potential and affinity to electrons

Electronegativity is the power of an atom to attract electrons to itself, although, there are several definitions of this quantity. An *ionization energy* is the minimum energy required to eject an electron out of a neutral atom or molecule, or, more generally, the *n*th ionization energy is the energy to eject the *n*th electron. An *electron affinity* is the energy released when an electron is attached to an atom or molecule, or more generally, the *n*th electron affinity is the energy released with the attachment of the *n*th electron [SM560]. The history of development of these three terms is closely intertwined with the history of chemical affinity [see SM563–SM565]. The modern quantitative scales of electronegativity were proposed by the American chemist and chemical engineer Linus Pauling (1901–1994) [SM566] and the American physicist and chemist Robert Sanderson Mulliken (1896–1986) [SM567].

Electrophilicity and nucleophilicity

A *nucleophile* (or nucleophilic reagent) and an *electrophile* (or electrophilic reagent) are two reaction partners that form a chemical bond, where the nucleophile donates and the electrophile accepts both bonding electrons. Consequently, the *electrophilicity* and the *nucleophilicity* are the relative reactivities of an electrophilic or nucleophilic reagents, usually measured by relative rate constants for reactions of different reagents towards a common substrate [SM560]. In 1925, the Scottish chemist Arthur Lapworth (1872–1941) proposed the terms *anionoid* and *cationoid* [SM568], which were replaced by the terms electrophile and nucleophile in 1933 by the British chemist Sir Christopher Kelk Ingold (1873–1970) [SM569]. Several methods exist to rank electrophiles according to their reactivity [see SM570]. In 1999 the American theoretical chemist Robert Ghormley Parr (1921–2017) proposed an *electrophilicity index* linked with electronegativity and *chemical hardness* [SM571]. The attempts to quantify relative nucleophilic strength include the *Swain–Scott equation* [SM572], the *Edwards equation* [SM573], the *Ritchie equation* [SM574], the *Mayr–Patz* equation [SM575], and the unified equation [SM576].

Hydrophilicity and hydrophobicity

Hydrophilicity is a characteristic of materials exhibiting an affinity to water, and the tendency of a molecule to be solvated by water. *Hydrophobicity* is the physical property of a molecule that is seemingly repelled from a mass of water, and also the association of nonpolar groups or molecules in an aqueous environment which arises from the tendency of water to exclude nonpolar molecules [SM560]. This concept

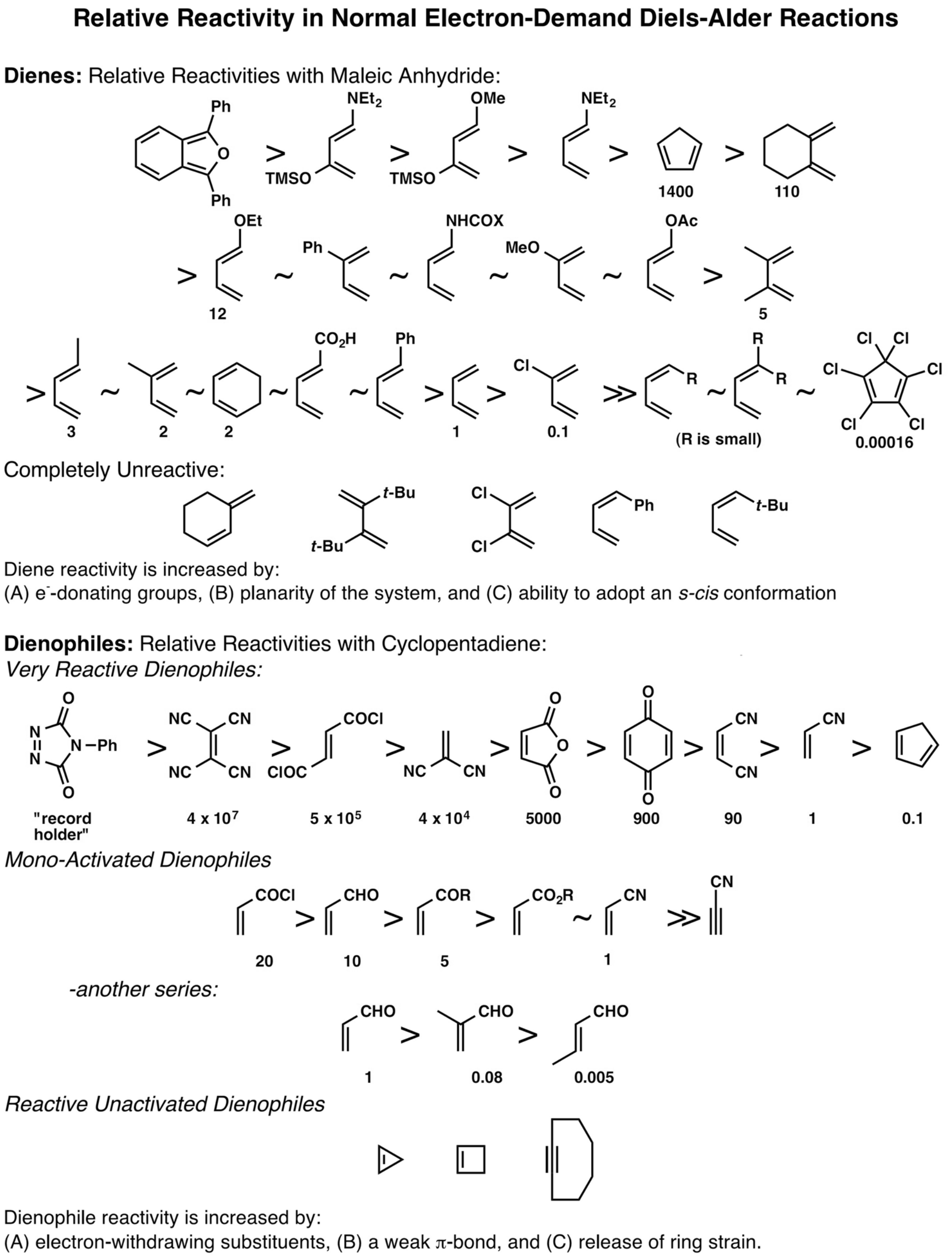

Fig. 5 The reactivity diagram of various dienes and dienophiles in the Diels–Alder reaction. The image is freely available at http://may.chem.uh.edu/teach-files/DA%20Reactivity.pdf

is extremely important for the studies of proteins, and therefore, several *hydrophobicity scales* were proposed for amino acid residues [SM577–SM581].

Lipophilicity and lipophobicity

Lipophilicity represents the affinity of a molecule or a moiety for a lipophilic environment, and the ability of a chemical compound to dissolve in fats, oils, lipids, and nonpolar solvents such as hexane or toluene [SM560]. *Lipophobicity* is a property of chemical compounds which makes them badly soluble in lipids or other nonpolar solvents. Lipophobic compounds badly absorb fats.

Lipophilicity of any compound is commonly measured by its distribution behavior in a biphasic system, either liquid–liquid (partition coefficient in octan-1-ol / water) or solid–liquid (retention on reversed-phase high-performance liquid chromatography or thin-layer chromatography system). It plays a critical role in drug discovery and design, because lipophilicity is a key physicochemical property for the determination of absorption, distribution, metabolism, and excretion properties and the overall suitability of drug candidates [SM582, SM583].

Dienophile

A chemical reaction between a conjugated diene and a substituted alkene to form a substituted cyclohexene derivative was discovered by the German chemists Otto Paul Hermann Diels (1876–1954) and Kurt Alder (1902–1958) [SM584] and is now called a *Diels–Alder reaction*. The alkenes with an electron-withdrawing group that readily react with dienes are now called *dienophiles*. Several studies were devoted to arrange the relative reactivity of dienes and dienophiles depending on their properties, and several reactivity series were produced. These series were reminiscent the historic affinity diagrams for a single specific reaction. An example of the diene–dienophile reactivity diagram is presented in Fig. 5.

Affinity of hemoglobin to oxygen

The delivery of oxygen to the cell depends on the affinity with which hemoglobin binds oxygen or releases it from erythrocytes for use by the other cells of the body. Numerically, the *affinity of hemoglobin to oxygen* may be expressed by the p_{50} value, which is defined as the partial pressure of oxygen in blood at which 50% of the hemoglobin is saturated with oxygen at a temperature of 37 °C and pH equal to 7.4, expressed in millimeters of mercury [SM585]. Various factors may alter the hemoglobin affinity, namely temperature, pH, carbon dioxide and carbon monoxide levels, 2,3-diphosphoglycerate, and other organophosphates, presence of methemoglobin or abnormal hemoglobins [SM586]. Hemoglobin affinity to oxygen was first described in 1904 by the Danish physician Christian Harald Lauritz Peter Emil Bohr (1855–1911), Karl Hasselbalch, and the Danish physiologist Schack August Steenberg Krogh (1874–1949), who discovered the S-shaped form of the oxyhemoglobin dissociation curve [SM587].

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Declarations

Conflict of interest The authors declare no competing interests.

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