

AFFINITY

TABLE DES DIFFÉRENTS RAPPORTS
deuxième partie des principes de la chimie.

Table de la Table I, page 100

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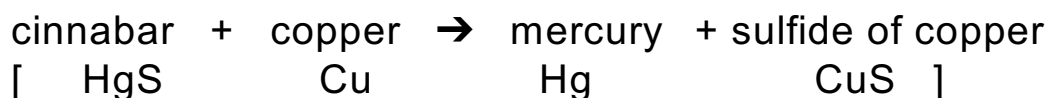
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- **affinity**:- historically the term was used to explain the selective attraction of one substance for another
- in modern chem, the whole concept has been replaced by an electron theory of bonding; in this chapter we will look at how a very successful theory was ultimately found to be unproductive and how it was replaced by more effective theories
- the early Greek ideas were very anthropomorphic, ie, the attraction of one substance for another was seen as ‘love’ and repulsion as ‘strife’
- the term “affinity” was introduced to chemistry by Albertus Magnus about 1250, and alchemists later began to attribute specific affinities to certain types of substances, eg, the affinity of acids for bases
- the alchemist Jabir, ca 1300, was one of the first to put affinities

on a scale of relative intensities, eg, for strength of combination with sulfur



- from such a scale came the idea that an element of stronger affinity for A would displace one of weaker affinity in a **displacement reaction**, eg, in vinegar



since Cu–S affinity is greater than Hg–S affinity

- thus by ca 1700, the concept of an affinity series was generally accepted, and hypotheses about the underlying cause began to appear

Affinity as an Attractive Force

- Newton had first established the concept of measurable **forces** in physics and astronomy, and extended the concept in 1708 to chemistry by postulating **quantifiable, short range forces**, both attractive and repulsive; the attractive forces were equated with affinity

- many attempts were made to measure the chemical affinity forces, especially in England, but only qualitative descriptions proved to be useful

- in 1718 **Etienne Geoffroy** collected and summarized nearly all available affinity data in his Table des Rapports (see Af-1), and larger, more complex affinity tables were constructed by others later in the 18th century

- the most complete table was published in 1775 by the Swede Torbern Bergman; it had 50 columns, some with 50 entries; in the book in which his table was published, Bergman noted

complications in affinity series due to incomplete product formation, precipitation, effects of differing quantities and whether displacements were determined in solution or mixing of solids - while Bergman's table was the most complete affinity table, it was also the last important one because it was becoming clear that chemical combination was too varied to be encapsulated in a table, however large

Affinity as Electrical Attraction

- in the 1790s, **Alessandro Volta** (1745-1827), working with Luigi Galvani, discovered that two dissimilar metals could cause an isolated frog's leg muscle to contract
- Volta concluded that the frog muscle acted as a sensor for an electrical current flowing from one metal to another
- Volta then determined that different metals gave different responses; the effect was greatest for metals furthest apart in the (affinity) series

Sn, Pb, Fe, Cu, Au, Ag

- in 1800, Volta published in the Philosophical Transactions of England an electrical storage device that consisted of a pile of coins of two different metals separated by sheets of moist salty paper, ***the voltaic pile***



Alessandro Volta

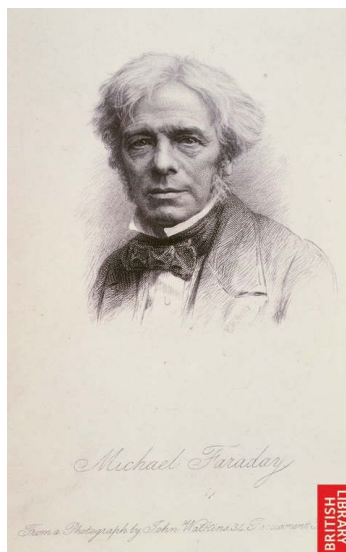


An early Voltaic pile

- the voltaic pile was a momentous discovery - it was relatively inexpensive to construct and was a nearly limitless source of electrical 'power' (and the prototype of all modern storage batteries)
- in 1802, William Nicholson used a modified pile to decompose water into hydrogen and oxygen and in 1804 Ritter noted a similarity between Volta's electrical series of metals and affinity sequences of reaction
- in 1807, Humphry Davy decomposed potash [KOH] and soda [NaOH] into oxygen and the new metals potassium and sodium with a large voltaic pile; he concluded that **electrical attraction** was the basis of chemical affinity
- in 1834, Michael Faraday measured the quantity of electricity required to decompose a fixed amount of electrolyte for different metals and equated the amount of electricity with the affinity force [whence Faraday's laws of electrolysis]



Humphry Davy



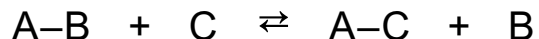
- Berzelius said polar atoms were surrounded by spheres of +ve and -ve electricities; his views were extended by Ampère who in 1814 proposed that charged atoms were surrounded by electrical

fluids of opposite sign, and combination of two oppositely-charged atoms was really due to combination of the electrical fluids, ie,

- the interpretation of affinity as electrical attraction had moderate success in explaining the formation of inorganic compounds with significant ionic character, but the theory ruled out diatomic elements and could not explain the affinity forces in non-polar organic cmpds
- as the 19th century advanced, electrical attractive forces were gradually replaced by more sophisticated models of “bonding”; the term affinity remains today only in the term “electron affinity”

Equilibrium Concepts

- **Claude-Louis Berthollet** used affinity tables to explain the direction of reactions, but he concluded that simple affinity forces were not the only factor affecting reactions
- for a reaction like



Berthollet proposed that the total affinity of C for A increases as the amount of C increases; Berthollet introduced the term **chemical mass**, where

chemical mass

= affinity force x substance weight

- Berthollet was the first to suggest that the mass of a reagent could have an effect on the amount of product formed



Claude-Louis Berthollet

- in the mid 19th century both Malaguti and Gladstone independently studied reversible reactions in solution and verified Berthollet's ideas; they concluded that the balance between reactants and products depended on an **equilibrium** between forward and reverse reactions

- in 1862-63 Berthelot and Saint-Gilles studied the equilibrium amounts in organic esterification reactions, ie,



- they observed that i) the equilibrium quantities depended on the quantities of reagents and/or products and ii) the same equilibrium amounts were obtained starting from either the reagent or the product side

- the Danes Guldberg and Waage extended equilibrium ideas even further. They proposed:

1. Equilibrium was a balance between forward and reverse reactions
2. The crucial chemical mass was the amount of substance in solution
3. The initial rate of a reaction in one direction was proportional to the concentrations of reacting species

- in 1867 they concluded that for a system such as



rate of the forward reaction = rate of the reverse reaction

and $k [\text{A}] [\text{B}] = k' [\text{C}] [\text{D}]$

and therefore $K_{\text{eq}} =$

- K_{eq} determined equilibrium concentrations quantitatively, but in a way completely free from affinity concepts

Thermochemical Concepts

- in late 18th century Lavoisier collaborated with the physicist Laplace to measure the heat released by a reaction (by measuring the amount of ice melted by a reaction)
- they worked on the premise that the heat released by a reaction was a measure of the change in affinity forces between reagents and products

- in 1840 Hess discovered that the amount of heat released by a reaction was a constant and independent of the route by which reactants were converted to products [our Hess' law]

- in 1873 Berthelot proposed that every chemical reaction moved spontaneously to give the products that released the most heat, and therefore he concluded that only exothermic reactions were spontaneous

- chemists recognized that there were several exceptions to Berthelot's proposal, ie,
 1. A few endothermic reactions proceeded spontaneously, and grew cooler as a result
 2. The whole notion of equilibrium conditions required the reverse reaction to be endothermic
 3. The heat evolved by exothermic reactions varied with the reaction temperature

The Thermodynamic Answer

- several chemists/physicists in the early 19th century studied the relationship between heat and work, an interrelationship that **became known as *thermodynamics***

- in 1869 Horstmann suggested that an additional factor affected the position of equilibrium in a chemical reaction, and that was **entropy**, the amount of disorder in a chemical system [see Thermodynamics later, if covered]

- about 1885 Helmholtz (Germany) and Gibbs (USA) independently derived equations which related the “free energy” of a chemical system (ie, the amount of energy chemicals could release that could become available for external work) to enthalpy (heat) and entropy (disorder) terms

- Helmholtz’ equation was valid for reactions at constant volume

$$\Delta A = \Delta H - T\Delta S \quad (\text{external work} = 0)$$

Gibbs’ equation was valid for reactions at constant pressure, ie, most lab reactions

$$\Delta F = \Delta H - T\Delta S \quad (\text{external work} \neq 0)$$

- about the same time, van’t Hoff (Holland) realised that the total affinity differences between reactants and products must include both enthalpy (ΔH) and temperature-dependent entropy ($T\Delta S$) terms. Only at absolute zero does the entropy term become =0 and then the equilibrium position depends entirely on enthalpy - thus enthalpy is a measure of affinity at absolute zero, but above absolute zero both entropy and enthalpy terms play a role

- consequently in the 19th century affinity disappeared as an explanation for reaction driving force; it was replaced near the end of the century by **free energy** [our ΔG] and, as we shall see in **Bonding**, the use of affinity as a binding force was replaced by bonding theory

- the concept of affinity had evolved and become extinct