

Ahrland S, Chatt J & Davies N R. The relative affinities of ligand atoms for acceptor molecules and ions. *Quart. Rev. Chem. Soc.* 12:26576, 1958.
[Akers Research Laboratories, Imperial Chemical Industries, Ltd., Welwyn, England]

Acceptors can be divided in two classes: (a) which form their most stable complexes with the first donor atom of each group, i.e., with N, O, and F, and (b) which form their most stable complexes with the second or a subsequent donor atom. The (b)-acceptors are all in a triangular area of the periodic table, with its apex at copper. [The *SC*[®] indicates that this paper has been cited over 625 times since 1961.]

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"The paper summarizes the state in 1957 of a fundamental problem which (Lewis) acids prefer which bases? The first treatise founded experimentally is Torbern Bergman's "Disquisitio de attractionibus electivis" of 1775.¹ With the advent of the Werner coordination theory, the problem could be stated more precisely. Its solution was still difficult, however, for two reasons: methods were lacking for the quantitative determination of stabilities and the bases available were mainly restricted to the halide ions and to ligands coordinating via oxygen or nitrogen. In the early 1950s, methods had been developed, but still no data existed for the heavier donors of the chalcogen and nitrogen groups Se, Te; P, As, Sb, Bi.

"As to the halides, it became evident from the 1940s that various acceptors displayed opposite affinity sequences. In 1953, I noted that the differences in stability were always especially large between the fluoride and the chloride complexes, thus either (a) $F \gg Cl >$

$Br > I^-$ or (b) $F \ll Cl^- < Br < I^-$. Even more striking, the (b)-acceptors were confined to a roughly triangular area of the periodic table, with its apex at copper.

"As a schoolboy, Joseph Chatt became interested in the rare minerals that abound in Cumberland. With good chemical sense he classified his metal ores in oxides and sulfides, just as Bergman had done in his *Sciagraphia Regni Mineralisoi* 1782.² In the late 1930s, Chatt was doing his doctoral work in Cambridge with Frederick Mann as mentor, it naturally dealt with phosphine and arsine complexes. These were found to be formed by metals occurring in nature as sulfides, never by metals occurring as oxides. Furthermore, trialkylphosphine or trialkylarsine complexes were readily formed by acceptors in the same triangular area of the periodic table as mentioned above but trialkylamines were not.

"After the war, Chatt found that olefin complexes are formed just by the acceptors readily coordinating phosphines and arsines. These acceptors evidently form strong bonds of markedly covalent character, if a congenial ligand is offered. But how to measure quantitatively the affinities involved? Surely, reliable methods had been developed, not least in Lund, but these applied to equilibria in aqueous solutions and the ligands of interest were not water soluble. The answer was to sulfonate the aromatic derivatives.

"So in 1954, we started to investigate equilibria between Ag^+ , and Cd^{2+} , and ligands coordinating via S, Se, P, As, in the laboratories run by ICI at the Frythe, north of London. Later, Norman Davies, now at the University of New South Wales, joined our group. The results allowed, with other data, the generalizations comprising all the donor groups that were stated in our review.

"In 1963, Ralph Pearson extended our classification to numerous organic acceptors, introducing the since familiar terms hard and soft acids and bases."³

1. Bergman T. Disquisitio de attractionibus electivis. *Nova Acta Regia Societatis Scientiarum Upsaliensis* 2:159-248, 1775.

2. Sciagraphia regni mineralis, secundum principia proximo digesti.

Leipzig: Bibliopolio Eruditorum. 1782. 166 p.

3. Pearson R G. Hard and soft acids and bases. *J. Amer. Chem. Soc.* 85:353-39, 1963.

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