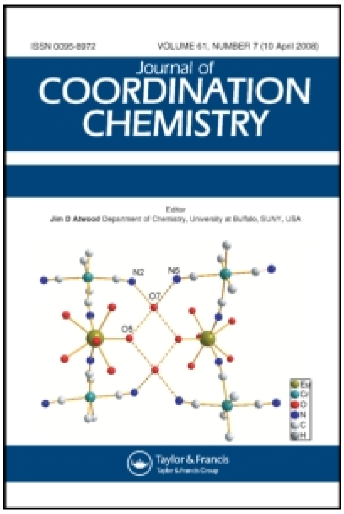

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A review of: "Chemische Funktionslehre, by V. Gutmann. Springer-Verlag Wien-New York, 1971. 159 pp. (in German)."

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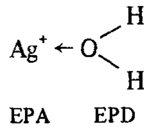
Book Reviews

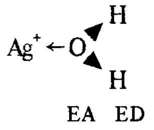
Publishers are invited to submit, via the editors, books for review in this journal. Any newly published book dealing with a subject relevant to the field of coordination chemistry will be welcome; this includes clear ancillary experimental or theoretical relationships, e.g. from chemistry, biochemistry, biophysics, etc. All books received will be acknowledged in print.

CHEMISCHE FUNKTIONSLEHRE, by V. Gutmann. Springer-Verlag Wien–New York, 1971. 159 pp. (in German).

When two or more molecules, atoms or ions intend to react with each other, they must collide, form an intermediate activated complex, shift electrons and produce products. Chemical kinetics describe and interpret the actions up to a successful, product forming collision, but does not dwell on the electronic rearrangements occurring within the intermediate complex. Dr. Gutmann has focussed his attention on exactly these electronic changes in his "Theory of Chemical Functions". The stated purpose of his book is the development of ideas about the dynamics of the electronic changes taking place after the reactant molecules have collided. The chemical function of an ion, atom or molecule is determined by its electron population, which is defined as the totality of the electrons in the ground state of the species in question and expresses the relative availability of electrons. A species possessing an ideal electron population does not enter into any chemical reaction. Therefore all elements with exception of helium and neon, and all compounds and ions have a non-ideal electron population. If the electron population of a certain chemical species is high relative to the molecule, ion or atom it reacts with, an electron shift towards this species of lower electron population will take place. Chemical species strive to equalize their electron populations in reactions. Such an equalization can be achieved by functioning as an electron donor, electron pair donor, electron acceptor or electron pair acceptor. It is characteristic of the electron population to be very sensitive to even small changes of the electron cloud, leading to a reversal of the initially assumed functions. Two examples should clarify this change of chemical function.

Hydrated Ag^+ ions are weak protonic acids in aqueous medium. The oxygen atom of the water molecule serves initially as the electron pair donor, the silver ion as the electron pair acceptor. The electron population of the oxygen atom has been reduced in this reaction, allowing the oxygen atom to act now as an electron acceptor and thus polarizing further the O–H bond. The electron shift towards the oxygen facilities deprotonation of the coordinated water molecule.





(The further polarization of an existing covalent bond is defined as an electron acceptor – electron donor function).

The formation of an iron(0)-carbon monoxide bond is initiated by the donation of an electron pair of CO to the iron(0), which serves as electron pair acceptor. The reduction of the electron population of CO and the concomitant increase of the electron population of Fe cause reversal of the initially exhibited functions. Carbon monoxide becomes now an electron pair acceptor, the iron atom an electron pair donor (of the π-type). Donation of an electron pair from the iron d-orbitals into π-orbitals of CO leads to back-bonding and reversal of the functions. Carbon monoxide is again an electron pair donor, iron(0) an electron pair acceptor. Such repeated reversals of functions with the associated electron shifts decrease the iron-ligand distance, increase orbital overlap and thus stabilize iron carbonyls.

Following the introductory chapter, the author applies these concepts to redox potentials in aqueous and non-aqueous solutions, to ion solvation and solubility problems, to ionization of polar covalent compounds through interaction with the solvent, to complex and auto complex formation in solution, to the kinetics of fast reactions in coordinating solvents, to charge-transfer complexes, to reaction mechanisms in organic chemistry, to the formation of chemical bonds and to catalysis.

Everyone interested in gaining a unifying bird's eye view of such diverse topics as redox reactions, complexation, bond formation, catalysis, kinetics and solvent-dependency of chemical reactions should read Dr. Gutmann's book. The reader will be forced to think about established chemical facts in new, refreshing and unifying ways, which might first appear strange. The theory of chemical function nicely explains – in at least a qualitative manner – experimental observations, which cannot be understood otherwise, e.g. degree of ionization of covalent compounds in solvents possessing the same dielectric constant.

It is unfortunate that no quantitative measure of the electron population exists. There does not seem to be a chance to find a suitable scale derived from atomic or group properties for the millions of known molecules, which would allow the prediction of the directions and magnitudes of the electronic shifts occurring in the many possible activated complexes.

The book contains a few errors. There is a misspelled word in the quotation on page 11. A number of sentences of improvable design have been found throughout the text, which yielded their meaning only after numerous readings. These sentences should pose formidable difficulties for the reader whose German is not excellent. The names (p. 75) "arsorane" and "stiborane" for pentavalent compounds of arsenic and antimony of the type R_3MX_2 is incorrect and should be replaced by arsane and stibane. The discussion of the conditions for successful polarography in non-aqueous medium (p. 21–24) are extraneous to the subject of the book. Some of the arrows in Figure 8 point into the wrong direction. The enthalpy of dissolution of an ionic compound in a solvent, labeled to be only endothermic in Figures 20, 24 and 32, can be exothermic as well as endothermic. The energy associated with the conversion of a solid metal to the gaseous state is mislabeled in Figure 32.

Dr. Gutmann's book "Theory of Chemical Functions", in conjunction with the reactivated knowledge of the German language, a good dictionary and the corrections mentioned above, should prove valuable to those readers interested in acquiring a qualitative overview of a very large area of chemistry.

KURT J. IRGOLIC