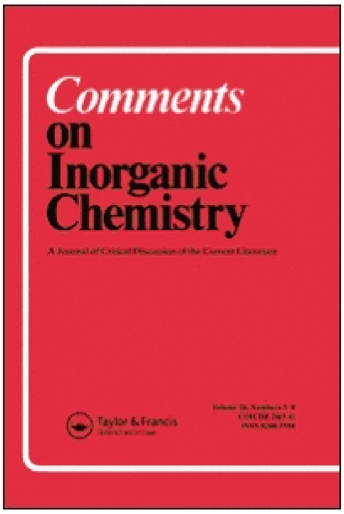

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The Impact of the Donor-Acceptor Concept

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The Impact of the Donor-Acceptor Concept

The rules of the extended donor–acceptor concept are reviewed and applied to interactions between molecules in the gas phase as well as in the solid and liquid states. The applicability of the rules to interactions in solution and at phase boundaries is pointed out. By applying these rules to phenomena in microscopic areas, the different parts of a molecular system are ordered from the point of view of their significance for the whole system under consideration. In this way the concept of "hierarchic order" has been developed and found to be universally applicable to molecular systems. The consequences for the acquisition of new knowledge in all branches of molecular science are indicated, and the continuum model of matter is states as one of the basic requirements of the hierarchically ordered relationships.

1. STRUCTURAL VARIATIONS AS RESULTING FROM INTERACTIONS BETWEEN MOLECULES

According to Lewis,[1] an acid is an electron-pair acceptor and a base an electron-pair donor. An interaction between an acid and a base is described as "resulting" in the formation of a so-called coordinate covalent bond. As these definitions were alien to existing thoughts on acids and bases, Sidgwick[2] introduced the terms electron acceptor and electron donor instead. These definitions are still in use for the description of a great number of "coordinating" interactions.

According to quantum chemistry any interaction involves the rearrangement of charge density as a consequence of charge transfer and polarization effects. This means that one of the interacting species may be considered an electron donor and the other

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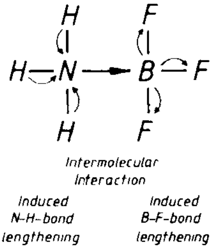
an electron acceptor. Any change in electron densities is bound to be reflected in appropriate changes in the relative internuclear positions. The rationalization of relevant observations has lead to the formulation of the so-called bond-length variation rules,[3] which have also been referred to as Gutmann rules.[4]

Rule 1

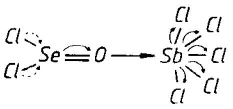
The bonds adjacent to the sites of an intermolecular interaction are lengthened. Bond lengthening may be indicated by a full bent arrow above the two atomic symbols pointing in the direction of the induced charge transfer. For a given bond, the lengthening is greater the stronger the intermolecular interaction and hence the shorter the intermolecular bond. Thus an inverse relationship is found between intermolecular and intramolecular bond lengths. For example, in amine adducts of BF_3 the B–F bonds are longer the shorter the N–B distances[5]:



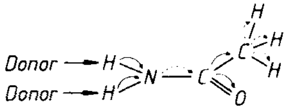
Likewise, in crystalline D_2CuX_2 complexes the intramolecular equatorial bonds are lengthened as the intermolecular axial bonds (completing distorted octahedra) are shortened, and vice versa.[6] Bond lengthening means increase in bond polarity,[7] i.e., increase in net negative charge at the more electronegative atom and increase in net positive charge at the less electronegative atom as a consequence of the electron shift from the less electronegative towards the more electronegative atom.

Rule 2

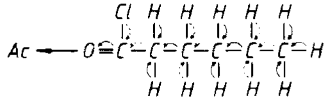
Alternating bond shortening and bond lengthening is induced throughout the system under consideration; the changes are smaller the more remote the bonds are from the site of interaction, but they are more strongly pronounced at the bonds that terminate the system.[8] Bond shortening may be indicated by a dotted bent arrow above the atomic symbols pointing in the direction of the induced charge transfer. For example, in the $Cl_2SeO \rightarrow SbCl_5$ adduct the Se–O and the Sb–Cl bonds are lengthened in agreement with the first rule, but the Cl–Se bonds are shortened[7]:



Another example is the result of donor attack on acetamide at the hydrogen atoms of the amide group: the H–H– bonds are lengthened, the N–C bond is shortened, and the C–O bond is lengthened.[9] The C–C bonds are expected to be slightly lengthened and the C–H bonds slightly shortened:



The rule may be applicable to systems that contain arrays or clusters of atoms of the same kind.[10–12] The chlorination behavior of alkylcarboxy chlorides is changed by the presence of an acceptor solvent so that alternating reactivities of the subsequent CH_2 groups are observed with greatest changes at the terminating CH_3 group[11]:

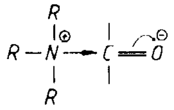


Rule 3

Increasing the coordination number of an atom leads to lengthening of the existing bonds to that atom. Correspondingly, decrease in coordination number leads to shortening of the said bonds. As the surface atoms of a condensed phase have lower coordination numbers than those within the bulk, the internuclear distances at a surface are shorter than those within the bulk.[13] As coordination numbers are increased by adsorption, the latter process leads to bond lengthening.[3,13]

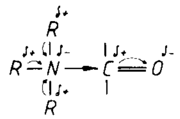
Rule 4

The electron changes at the donor atom itself lead to an increase in net negative charge ("pileup" of negative charge at the donor atom) and at the acceptor atom itself to an increase in positive net charge ("spillover" of negative charge at the acceptor atom).[14] This occurs because the original loss in electron density at the donor atom is overcompensated by the induced electron shifts within the donor component towards the donor atom. Similarly, the original gain in electron density at the acceptor atom is transferred to the other parts of the acceptor component including part of the electron density that originally resided at the acceptor atom of the free acceptor component.[3,14] These findings are in agreement with the results of quantum-chemical calculations.[3,14] Thus, the description frequently used by organic chemists, namely



$$R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N^{\oplus}}}\rightarrow\overset{|}{\underset{|}{C}}=O^{\ominus}$$

is not in agreement with the facts and should be represented by



$$\overset{\delta+}{R}\overset{\delta-}{=}\overset{\overset{\overset{\delta+}{R}}{|}}{\underset{\underset{R}{|\,\delta+}}{N}}\rightarrow\overset{|\,\delta+}{\underset{|}{C}}=\overset{\delta-}{O}$$

Thus, any molecular interaction may lead to changes within the whole molecular system under consideration. The donor properties at the donor atom of the donor component are partly distributed over the atoms on the periphery of the acceptor component which are consequently increased in donor properties. The acceptor properties at the acceptor atom of the acceptor component are partly distributed over the atoms on the periphery of the donor component which are consequently increased in acceptor properties. The interaction leads to a new system with properties which cannot be accounted for on the basis of the properties of the separated components alone.

Knowledge of solvent effects has been greatly advanced by the introduction of two empirical solvent parameters, namely the donor number (DN)[15] and the acceptor number (AN).[16] Theoretical support has been provided by the fair linear relationships that have been found between the donor number and the energy of the highest occupied molecular orbital (HOMO), as well as between the acceptor number and the energy of the lowest unoccupied molecular orbital (LUMO).[17] LFER's have also been found, for example, between the donor number and the free enthalpies of transfer for cations,[3,18] their chemical NMR-shifts and their redox potentials,[3,19] and the ionization constants of covalent substrates[3] and the rate constants of certain organic reactions.[20] Likewise, relationships exist between the acceptor number and the free enthalpies of transfer for anions,[21] the Y values, Z values and E_T solvent parameters,[3,19] the polarographic half-wave potentials for anions,[3,19] and the rates of S_N1 and solvolysis reactions.[3,21] As the solvent acceptor number is increased, the rate constant of an S_N1 reaction is increased, whereas that of an S_N2 reaction is decreased.[3,21]

With regard to choosing an appropriate solvent for a given interaction, the following rules have been proposed[12]:

(1) For interactions that involve the formation of highly reactive anions such as carbanions, a solvent of high donor number is advisable. For example, diethylether (DN = 19, AN = 4) or hexamethylphosphorictriamide (DN = 38, AN = 10), or mixtures of them are most useful for nucleophilic substitution reactions.

(2) For interactions that involve the formation of highly reactive cations such as carbonium ions, a solvent of high acceptor number and of low donor number should be used.

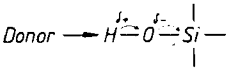
(3) Ionization equilibria involving stable (solvated) cations and stable (solvated) anions are well established in solvents of high donor number and of high acceptor number such as water.

All of these relationships are based upon the consideration of a given molecular system in different environments. Such changes are therefore independent of the interpretation of the bonding forces and, in principle, should be applicable to all molecular systems.

An example of its application to the solid state is provided by the consideration of the effects of pressure which is reflected in the so-called pressure–distance paradox.[22] The effect of pressure is considered as paralleling that of a donor–acceptor interaction between the most loosely connected atoms of the system. For example, in SiO_2 the Si–Si and the O–O distances are greatly diminished by increasing the pressure while the Si–O bonds are lengthened.

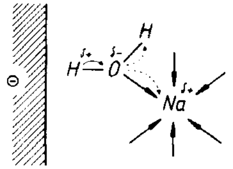
The bond-length variation rules may be applied equally well to interface phenomena. For example, the external O–H bonds of an aerosol surface are lengthened by adsorption of donor molecules, the lengthening being greater the higher the donor number of the adsorbed species.[23] Adsorption of triphenylchloromethane on barium sulfate even leads to heterolysis of the C–Cl bond in the adsorbed molecules.[24] Even weak adsorption leads to characteristic changes in structural properties. For example, UPS-measurements on palladium revealed induced adsorption variations of Pd valence band emission due to adsorption of xenon, the changes in ionization potential of Xe $p_{3/2}$ and Xe $p_{1/2}$ electrons being a function of xenon coverage.[25]

According to the donor–acceptor approach, an electrical double layer must be built up at any phase boundary[12,26]; according to the fourth rule, interface charge transfer leads to an increase in negative charge at the donor sites (pileup effect) as well as to an increase in positive charge at the acceptor sites (spillover effect). For example, the interactions of donor molecules with the external hydrogen atoms of an aerosol surface lead to increasing positive charges at the H atoms and to increasing negative charges at the donor atoms of the adsorbed donor molecules.

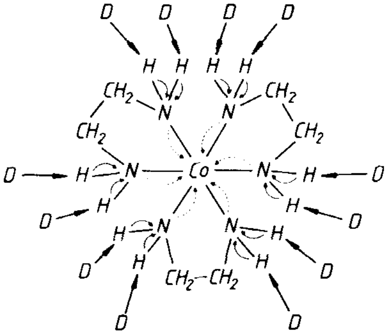


$$\text{Donor} \longrightarrow \overset{\delta+}{H} - \overset{\delta-}{O} - \underset{|}{\overset{|}{Si}} -$$

These effects are greater in the presence of ions in either phase. The acceptor properties at a phase boundary are increased by the presence of cations, while its donor properties are increased by the presence of anions, the net effect depending on the donor and acceptor properties, respectively, of the ions. This is because a certain fraction of the charges residing on the idealized gaseous ions has been distributed over the solvent molecules and piled up at the atoms or molecules terminating the phase. The electric double layer is increased by the presence of an appropriate electric field, as increase in charge at the electrode leads to increasing pileup and spillover effects, respectively. For example, in an alkaline sodium chloride solution in water, as used in electrolysis, the concentration of sodium ions may be up to 10^{12} times greater than that of the hydrogen ions. The exclusive evolution of hydrogen at the cathode may be described as due to the discharge of those hydrogen atoms which, possessing a high positive net charge near the cathode surface, are weakly bonded within the water molecules. Thus, such bonds may be easily heterolyzed with subsequent reduction of the hydrogen ions formed, whereas the hydroxide ions produced near the cathode have to remain in solution:



The donor–acceptor approach readily accounts for the structural dependence of solutes on the medium both in the solid and in the liquid states. Solute particles are modified by the solution, which is itself modified by the donor–acceptor interactions. For example, in trisethylenediaminecobalt(III) perchlorate solutions, the donor solvent interacts with the hydrogen atoms of the NH_2 groups; the N–H bonds are lengthened and the N–Co bonds shortened with a corresponding decrease in net positive charge at the cobalt center.[27] The ^{59}Co NMR shift is related to the solvent donor number. A relationship is also found between the solvent DN and the standard redox potential[28]:



This means that the redox potential is related to the electronic structure at the redox-active center as reflected in the ^{59}Co NMR chemical shift. As the standard redox potential is a measure of the activity of the redox-active species, differences in electron densities as revealed by differences in ^{59}Co NMR shifts are the structural expression of the observed changes in activities. This structural interpretation of the thermodynamic activities may also account for the observed differences in activities of a given solute in a given solvent at different concentrations. Such structural changes are not expressed in the familiar representation of a chemical reaction.[29]

The modification of the solution structure due to changes in solute composition is less readily accessible. This is because a borderline between the so-called solvation spheres and the less affected solvent molecules cannot be drawn unambiguously, and differences between the various microscopic regions within the phase cannot be measured due to the statistical character of the measurable quantities. The latter provide time and space averages over *all* solvent molecules of the solution. We can, however, obtain additional insight by applying the rules of the donor–acceptor approach to the microscopic areas. In this way, some of the information that is obscured in the statistical data may be disclosed.

3. STRUCTURAL VARIABILITIES IN MICROSCOPIC AREAS

Differences between the various parts and the structural inhomogeneities within a phase have been illustrated.[30-34] The next step was the evaluation of these findings with regard to the significance of the different parts within the whole system and with regard to their significance for the whole system under consideration with the aim of gaining an understanding of the system *in* its multiplicity rather than *from* its multiplicity.[30]

The structural inhomogeneities in any real system are influenced by the so-called thermal motions, but they are not destroyed by them. They appear chaotic only from the statistical point of view. In order to describe the ways in which *the structural inhomogeneities are dynamically maintained*, the distinction may be made between so-called "regular" building units within the solid material under consideration and the so-called "defects".[30-34] The former are situated near the so-called regular lattice points and they differ from each other only slightly in properties, i.e., in energy and in relative range of positions. The number of regular building units exceeds by many orders of magnitude the number of the units arranged around the so-called defects, such as solute particles, holes, dislocations and phase boundaries. The contributions by the latter units to the average pattern are statistically rather insignificant. Hence the statistical information on a crystal structure is virtually independent of the presence of defects. For a solution a similar distinction may be made between "normal" solvent molecules and those with properties which deviate more considerably from the statistically accessible mean values. Normal solvent molecules are but slightly affected by the strain fields originating from solute particles and from phase boundaries.

In liquid water solvent molecules are characteristically arranged around a cation,[35,36] which is decreased in positive net charge by the electron transfer from the water molecules, so that the O–H bonds of the solvent are lengthened. Such effects extend in principle throughout the whole system under consideration. However, the differences in properties between the various water "layers" become smaller with increasing distance from the cation. With decreasing distance to the cation the intermolecular $O \cdots O$ bonds of the solvent are increasingly shortened and the "intramolecular" O–H bonds lengthened. This means that the hydrogen bonds become more symmetrical and approach linearity more closely as they approach the cationic coordination center.[29] Local gradients in densities are known to exist[37] and, because of the phenomenon of preferential solvation in solvent mixtures, even gradients in local analytical composition.[29]

The consideration of the linear relationships between energy of activation and entropy of activation have led to the conclusion that the solvent transmits any changes in the states of its molecules, so that even weak interactions extend over large ensembles.[38] Solute particles therefore appear to exert a decisive influence on the solution structure. As the solute particles are themselves modified by the solution, it has been proposed that they be considered as structure modified and structure modifying centers ("SMM centers"). The differentiation of solute molecules within a given solution is well-known from kinetic studies. Whereas thermodynamic parameters represent mean values for all particles of the same kind in the solution, the activation parameters refer to those of the reacting species as they are in preferred states for the considered reaction. The activation parameters are also known to be particularly sensitive to changes in environment.

The structural inhomogeneities within a phase are characteristically reflected in surface inhomogeneities. Bond contractions around SMM centers cause additional bond contractions at the surface,[33] and this is reflected in the lowering of the vapor pressure of the system by the solutes.[29] A surface is microscopically highly differentiated and continuously interacting both with its own phase and with the contacting phase.[26] Any phase boundary is known to have a twofold function, namely to separate the phases and at the same time to connect them.[39]

All of the so-called defects are known to migrate according to gradients in chemical potential which never vanish. Their maintenance at different sites at different times serves for maintenance of the ***dynamically coexisting microstates,*** which are hardly measureable,[40,41] and which are required for the maintenance of a system at equilibrium.[40] Displacement reactions are known to occur continuously in any real solid material. Their ordered sequences are required for the system in order to maintain its configuration under constant conditions and to exert its integral operation in a changing environment. This means that the parts within the system must influence each other to different extents so that their motions must be ordered* according to a certain pattern of sequences. In these ways ***the static aspects of the structure are dynamically maintained*** and this has been illustrated recently by means of a so-called Rubik cube.[42]

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*The conceptual difficulty that may arise at this point is due to the definition of order as accepted both in solid state physics and in thermodynamics. This is based on the static aspects of order as represented by the nonexisting ideal crystal. However, order always has both static and dynamic aspects and may be defined by the establishment of regularities between before and after, as it is also understood in biology, in social and political sciences, and in everyday life.[26,30]

4. THE CONCEPT OF THE HIERARCHIC ORDER AND THE HIERARCHIC SYSTEM ORGANIZATION

The execution of the "dynamic order"* requires differences in domination for the various parts of the system, as they are characteristic for a so-called "*hierarchic order*" and the "*hierarchic organization*" (HO) of the parts.

The various parts are found to serve the system on successively graded levels. A level is hierarchically higher the greater its significance for the whole system, the greater the energy content per part, and the greater the adaptability of the parts towards changes. Forces operating on a higher level regulate and control the properties of the parts serving on one of the lower levels. The various levels are dynamically in coexistence according to the requirements of the ordered relationships by which the characteristic "motion pattern" is established. This pattern is independent of the actual positions of the individual particles, the properties of which are highly influenced by the dynamic order of the system. This order is, however, lost by the physical or by the mental dismemberment of the system under consideration.[43] It is therefore impossible to learn about the dynamic order from the properties of the isolated parts and their mutual interactions alone.[29]

The surface provides the first line of defense and the communication area of the system with its environment. It regulates the exchange and the redistribution of matter, energy and information between and within the phases under consideration.[26,42] The surface contains also the historical information of the system.† Surface particles are under constrained conditions and in states of high energy per part. The forces acting on the surface control the properties of all of the other building units and hence the surface provides the highest hierarchic level.[29–33]

Solute particles and holes (SMM centers) are under less constrained conditions and in states of smaller energy per part. They

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† The decisive role of the conditions under which an alloy has been produced and the paramount influence of its mechanical and thermal pretreatment is well known in material science and technology.

are known to influence each other (for example, ion–ion interactions as mediated through normal solvent molecules) and to play a decisive role for the static and dynamic aspects of the regular units. They therefore serve on a level inferior to the surface but superior to that of the regular building units.[29-33] The latter are under the decisive influence of the forces acting on the SMM level and, consequently, they are serving the lowest level within the HO of the system under consideration.

Within a given phase the following hierarchic levels may be distinguished:

1. Phase boundaries (highest hierarchic level)
2. SMM centers, such as solutes, holes and vacancies
3. "regular" building units or "normal" solvent molecules, respectively (lowest level).

In the various levels the parts are further differentiated. They serve the system in an "optimal" way. Particles in the lowest level contribute mostly to the statistical results; they have "great freedom" but small influence on the system properties. On the other hand, the properties of the parts in a high level hardly influence the statistical results, but they have great influence on the system properties, although "less freedom."

As the HO cannot be observed directly, changes in macroscopic properties caused by changes in environment must be related to the inferred changes in the HO of the system. Relationships are expected to exist between changes in temperature, pressure, irradiation, fields, molecular environment and actions of mechanical forces on the one side, and changes in macroscopic properties such as vapor pressure, surface tension, redox potential, viscosity, density, conductivity, mechanical, chemical, kinetic, thermodynamic and structural properties on the other side.

As will be presented in more detail elsewhere, one of the most fundamental findings concerns the redistribution of energy within the system under consideration. Any change in energy is distributed over the parts in the different levels acording to their relative resistances against changes (LeChatelier-Brown principle). The latter are smallest for the parts in the highest hierarchic level and greatest for the parts in the lowest hierarchic level. *Thus, the energy content of a part is changeable to a greater extent the higher the hierarchic level the part is serving.* As the energy content of a phase is increased, its energy pattern becomes more differentiated because the parts in higher energy states will gain more energy per part than those in the low energy states. For example, the crystal structure of a given metal may remain nearly unchanged on increasing the temperature, whereas surface properties and mechanical properties may undergo considerable changes. The observed increase in ductility with increasing temperature requires an increase in internal elasticity and this becomes greater the greater the internal differentiation within the system.

5. FURTHER CONSEQUENCES

Like the second law of thermodynamics, the concept of the HO is based on observations and not on *a priori* propositions. The following postulate is derived from the examination of the wealth of observations: ***Any real system requires a hierachic system organization.*** This requires continuous relationships between all of its parts. In other words: ***the continuum state of matter is a requirement for the existence of any real system.*** It will be shown in a forthcoming paper that the ***particle aspects and continuum aspects of matter are not antithetical*** but rather are mutual requirements both for the existence and for the observability of matter.[44]

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