NON-STATISTICAL APPROACH TO SOLUTIONS

Viktor Gutmann and Gerhard Resch

Department of Inorganic Chemistry, Technical University of
Vienna, Vienna 1o6o, AUSTRIA

Abstract - After a brief review of the achievements and limi-
tations of the statistical approaches to solution chemistry, a
non-statistical approach is presented. It emphasizes the ob-
vious fact that the solvent molecules within a given solution
do differ in properties. The differences are ordered with re-
spect to their local and temporal significance within the
solution and to their significance for the whole system under
consideration, including the environmental effects which are
so often neglected in scientific investigations. The various
molecules are considered to serve within a so-called "hierar-
chic" order on different levels, the level being higher the
smaller the significance of the properties of the isolated
molecules. The levels descend in the order: surface > inter-
connected inner surface areas, referred to as "channel-network"
> solute ions and molecules as well as voids which are struc-
ture modified and modifying centres ("SMM-centres") > "normal"
solvent molecules. The interrelationships and interdependencies
within a given system provide an understanding for the macros-
copic properties and their changes.

1. STATISTICAL APPROACHES

A solution is described in terms of molecules and ions. These are not directly
observable and their properties are statistically described. Statistical con-
siderations and results have contributed considerably to advances in science,
but it would be impossible to gain adequate knowledge from a single point of
view. This is because from any point of view only certain limited aspects of
a real object can be "seen", with unavoidable shifts and distortions in the
projection, so that not even a given part of the whole system can be precisely
evaluated. Statistics is based on a priori propositions, and these may lead to
idealizations. They serve as illustrations of certain aspects of nature, but
they cannot provide a complete description of nature.

As for solutions, the thermodynamic theory of solvation involves extrathermo-
dynamic equations for the concentration dependence of thermodynamic functions,
standard states of arbitrary nature and additional complications encountered
in passing from the study of solvation in solutions of non-electrolytes to
solvation in ionic solutions (Ref.1 & 2). Theories of ionic solvation again
begin with the assumption of models and deduce the thermodynamic coefficients
of solvation of hypothetical systems which correspond to the models (Ref.2).
The effects of ions on the molecular structure of the solvent are either
neglected as in Hamiltonian models or considered by interactions between the
particle ion and many solvent molecules according to specified laws of force
(function of distance or specified potential energy function) (Ref.2). Such
models must be treated by the methods of statistical thermodynamics for cal-
culating the properties of a ficticious overall system and these (Ref.3)
involve massive approximations (Ref.1). The elementary electrostatic model is
based on the idealization of the so-called "sphere in continuum" model, which
does not take into account the effects of charge transfer nor the con-
tinuous changes of the parts within the liquid system (Ref.4).

Despite the apparent wealth of experimental information, very few systematic
efforts have yet been made to characterize fully a number of aqueous systems
and few of the experimental data originating from before 1955 can be utilized
in basic studies of solution processes (Ref.5). Much of the work was performed
on fairly concentrated solutions and extrapolations to infinite dilution

frequently gave rise to incorrect values and much of the work lacks experimental precision.

The extended donor-acceptor concept provides for the comparison of the static aspects of equilibrium structures in different environments irrespective of the nature of the binding forces. A solute-solvent interaction is described in terms of charge transfer between electron donor and electron acceptor, by which a characteristic rearrangement of the charge density pattern is produced. The electronic changes, which are induced throughout the system under consideration are described by the so-called bond length variation rules (Ref.4). As negative charge is transferred from the donor atom D to the acceptor atom A the loss of electron density at D is overcompensated by an induced flow of negative charge from other parts of the donor component towards the donor atom. Its increase in negative fractional charge has been called "pile up" of negative charge at the donor atom D (Ref.6). The amount of negative charge which is transferred from the donor to the acceptor component does not remain at the acceptor atom A. Instead, it is passed on to other parts of the acceptor unit, carrying over some of the electron charge is actually increased as a result of the donor-acceptor interaction ("spill over" effect at the acceptor atom) (Ref.6). The polarities of the bonds C - D and A - B are enhanced and the internuclear distances increased (first bond length variation rule).
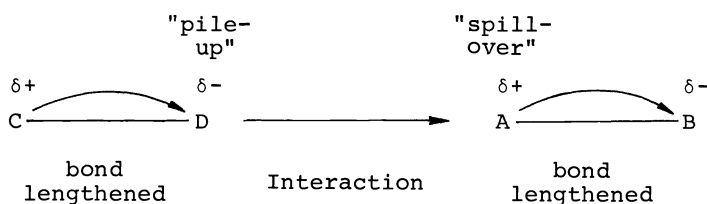
Subsequent changes in bond lengths are induced throughout the molecular system under consideration. A bond is lengthened as a result of an electron shift from a more electropositive to a more electronegative atom and shortened by an electron shift in the opposite direction (second bond length variation rule) (Ref.4 & 7). The adaptability of a given molecule to the environment provides for its variability in structure and in properties. A given bond is more readily heterolyzed,the greater its bond length, a donor atom is increased in nucleophilic and (or) reducing property as its net negative charge is increased and an acceptor atom is increased in electrophilic and (or) oxidizing property as its net positive charge is increased (Ref.4).

For the characterization of solvent effects, the parameters of the elementary electrostatic theory, such as dipole moment, dielectric constant or polarizability are unsuitable. They cannot account for the observed solvent effects, for example on ionization equilibria (Ref.8), redox-potentials (Ref.4,9 & 10), kinetic features (Ref. 4,11,12 & 13) or free enthalpies of solvation (Ref.12 & 14). For the system $Co(en)_3^{3+}/Co(en)_3^{2+}$ no relationships are found between the half wave potentials or the standard redoxpotentials in different solvents and either the dielectric constants or the dipole moments of the solvents (Ref.9)(Fig.1).

Attempts to characterize a solvent by only one empirical parameter, such as Grunwald-Winsteins Y-values (Ref.15), Kosower's Z-values (Ref.16) or Dimroth-Reichardt's E_T-values (Ref.17) were found to be limited in their applicabilities (Ref.4 and 11).

According to the donor-acceptor approach two empirical solvent parameters are required, namely one for the donor property and one for the acceptor property (Ref.4). The parameters are known as the donor number (Ref.18) and the acceptor number (Ref.19), respectively. Numerous quantitative relationships have been found between these solvent parameters on the one side and thermodynamic, kinetic and structural parameters on the other side (Ref.4.7 & 14). For example, the differences in free enthalpies of transfer of a cation, such as the potassium ion, are found linearly related to the differences in solvent donor numbers (Ref.4 & 14), just as the differences in free transfer enthalpies for an anion, such as the chloride ion, are linearly related to the differences in solvent acceptor numbers (Ref.4 & 14).
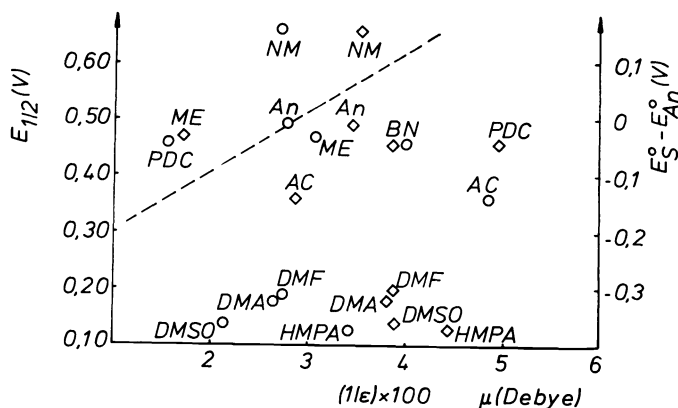
Fig. 1. System Co(en)$_3^{3+}$ (Ref.9). Left hand ordinate: half
wave potential referred to bisbiphenylchromium(I/0); AC acetone,
An acetonitrile, BN benzonitrile, DMA dimethylacetamide, DMF
dimethylformamide, DMSO dimethylsulfoxide, HMPA hexamethyl-
phosphoric triamide, ME methanol, NM nitromethane, PDC propane-
did-1,2-carbonate. Right hand ordinate: standard redox potentials
E_S^O and E_{An}^O in solvent S and acetonitrile respectively. Dotted
line: Expected relationship between standard redox potential and
dielectric constant ε as calculated by means of the Born equa-
tion. Values as related to $\frac{1}{\epsilon}$,1oo ◊ and as related to the dipole
moment μ o.

In considering the environmental effects on the static aspects of structure
and properties of a given ionic species, we have to bear in mind, that these
are modified not only by the nature of the solvent, but also by the nature of
the counter ion and by the ionic concentrations. For example, the ^{23}Na
chemical NMR shifts of a given sodium salt of the same concentration in
different solvents depend on the nature both of the solvent and of the counter
ion. A linear relationship between the ^{23}Na chemical NMR-shift and the solvent
donor number is found for the weakly donating tetraphenylborate (Ref.2o & 21),
but not for the more strongly donating iodide due to the stronger anion-cation
interactions mediated through the solvent regions.

The increase in electron density at an atomic cation as caused by the donor-
attack of solvent molecules is also found for the coordination centre in a
robust chelate complex. For trisethylenediaminecobalt(III)-perchlorate the
^{59}Co NMR-shift is linearly related to the solvent donor number (Ref.22). The
redox potential of Co(en)$_3^{3+}$ is shifted progressively to negative values, as
the solvent donor number is increased and hence a relationship exists between
the redox-potential and the ^{59}Co NMR shift (Ref.23) (Fig. 2).

Because the standard redox potential is a measure for the activity of the
redox-active species, differences in activities in different solvents are
related to differences in electron densities at the redox-active centre as
expressed by the NMR-shift. This structural interpretation of the activity
may be applied for the differences in activity for a given solute in a given
solvent at different concentrations: As the concentration is varied, the charge
densities at the redox-active centres are changed due to the changes in solute-
solute interactions as mediated through the solvent molecules. According to
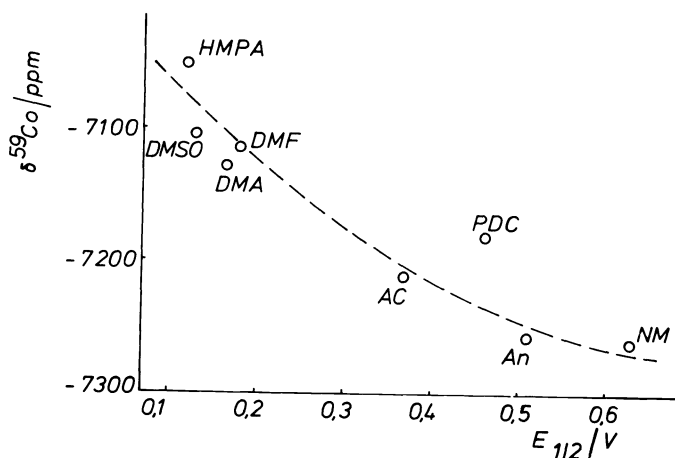
Fig. 2. Relationship between half-wave potentials (versus
bisbiphenylchromium(I/0)) and the ^{59}Co NMR chemical shifts of
Co(en)$_3$(ClO$_4$)$_3$ (referred to a 0.4 M aqueous K$_3$Co(CN)$_6$ solution
as external reference) in various solvents. NM nitromethane,
An acetonitrile, PDC propandiol-1,2-carbonate, AC acetone,
DMF dimethylformamide, DMA dimethylacetamide, DMSO dimethyl-
sulfoxide, HMPA hexamethylphosphoric triamide.

this interpretation any change in solute concentration means changes in the
nature of both solute and solvent. Such structural differences for a given
species in solutions of different concentrations are not expressed in the
familiar representation of a chemical reaction.

Gradual changes in molecular environment may at a certain stage give rise to a
drastic change in macroscopic properties. This may be illustrated by the be-
haviour of acetamide in solvents of different donor number (Ref.24). By co-
ordination of a donor solvent at each of the hydrogen atoms of the amide group,
the net positive charges at both hydrogen atoms are increased (spill-over
effect at the acceptor atoms), the H-N-bonds lengthened, the negative charge
at the nitrogen atom increased, the net positive charge at the adjacent carbon
atom increased, the N-C-distance decreased and the adjacent C-O distance in-
creased (Ref.24). The differences in net positive charge at the N-H-hydrogen
atoms has been measured by means of the ^{1}H NMR chemical shift found linearly
related to the differences in solvent donor numbers up to a donor number of
2o. The presence of one NMR signal showed equivalence of both hydrogen atoms
and free rotation of the N-C bond. In passing from tetrahydrofurane (donor
number 2o) to trimethylphosphate (donor number 23) the NMR signal is split,
as the N-C bond has been shortened to that extent that it has lost its
freedom to rotate; hence each of the hydrogen atoms has been fixed in a
different molecular environment.
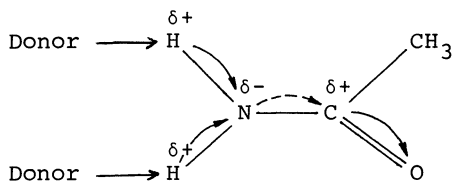
The decisive influence of the solute species on the properties of the solution
is connected with the strain to which the solute particles are subjected. The
redox potential of cations is shifted to more negative values, as the elec-
tronic strain is increased and the net positive charge of the cation is de-
creased. For anions, an increasing strain is due to solvation by acceptor

molecules, and this leads to a decrease in net negative charge, reflected in more positive values in redox potentials (Ref.4).

It is apparent that for a given solute species in different solutions the experimentally accessible mean values of the various properties are extremely useful in order to account for their <u>mean</u> modification by its molecular environment. The situation is, however, more complicated in order to account for the modification of the solvent by the solutes. Solvation structures are usually considered within limited areas around the solute particles, and <u>the actual arrangements of solvent molecules cannot be measured</u>. Measurements on solvent properties yield time averages and space averages over all solvent molecules in the solution. Molecules, which do not deviate appreciably from the statistically derived mean values, may be denoted as "<u>normal</u>" solvent molecules. "Normal" means with reference to the solution under consideration and not to a ficticious reference system, such as a "pure" solvent. It is well-known that solute-solvent interactions modify the vibrational spectra in changing the intensities by orders of magnitude, in shifting the frequencies to higher or lower values, and in broadening the bandwiths at one-half maximum absorbance.

It would be impossible to draw border lines between solvation spheres and "unperturbed" solvent regions, as all molecules in the solution are interrelated and interdependent. As interactions between solute ions or solute molecules are mediated by the "solvent molecules", the <u>structural changes have a collective character</u>, i.e. they must be connected with the correlated behaviour of the ionic complex and the solvent (Ref.25). The enormous influence of the cationic species on the first-sphere solvation of chloride ions has been shown by the results of X-ray and neutron-scattering (Ref.26 & 27), which are interpreted by tetrahedral coordination in hydrochloric acid and by octahedral coordination in solutions of lithium chloride.

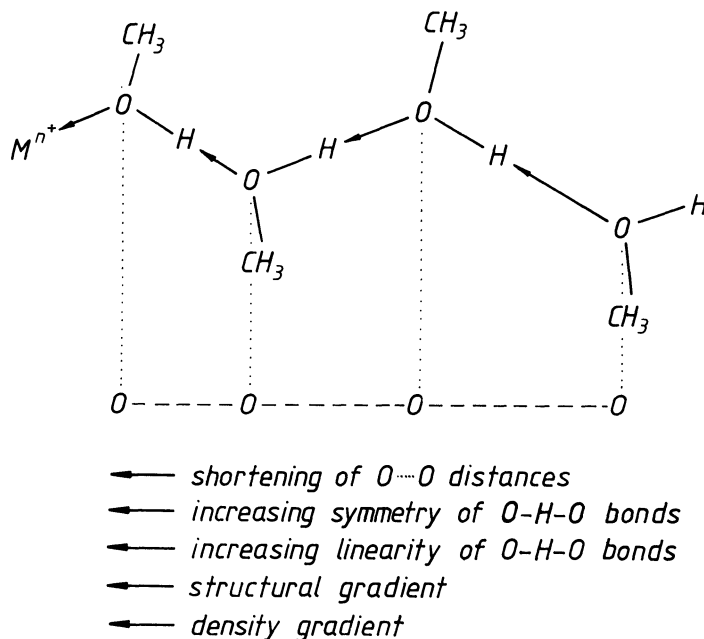## 2. DIFFERENTIATION OF THE PARTS WITHIN A GIVEN SOLUTION

<u>In choosing reality as the point of departure</u> we shall not start from hypothetical models on solvent-structures or from a hypothetically "pure" solvent (Ref.28), but rather <u>from a given real solution</u>. Because of the non-observability of the local and temporal "structural" aspects, we may attempt to illustrate the static aspects of order in terms of the extended donor-acceptor approach (Ref.4). As an example we shall describe the features expected due to the stepwise formation of solvation spheres around a metal ion in methanol. In the first solvation sphere methanol molecules are known to be coordinated to the metal ion through their oxygen atoms. Due to their donor actions toward the cation the net positive charge q_M^+ at the latter is decreased. The O-H bonds are lengthened by the coordination and hence both the negative net charge at each oxygen atom q_0^- and the positive net charge at each O-H hydrogen atom q_H^+ is increased, and even the hydrogen atoms of the methyl groups do not remain unaffected. Both the loss of positive charge at the metal ion Δq_M^+ and the gain in negative charge at the O-atoms Δq_0^- are distributed over the hydrogen atoms (Ref.6 & 28):

$$\Delta q_M^+ + \sum \Delta q_0^- = \sum \Delta q_H^+$$

Formation of a second solvation sphere leads to further cooperative charge redistributions, i.e. further decrease of positive charge at M, increase in negative charge at the inner sphere oxygen atoms, decrease in positive charge at the hydrogen atoms in the first layer (spill-over effect), increase in negative charge at the oxygen atoms and increase in positive charge at the hydrogen atoms of the second solvation sphere. Thus the inner-sphere coordinate bonds are further shortened and the net positive charge at M further decreased (the latter effect accounting to the change in activity with changing number of solvation spheres). With decrease in distance from M the O---O bonds are increasingly shortened, the hydrogen bonds increased in both symmetry and linearity and the differences in local density within microscopic areas increased as has been pointed out by Lengyel (Ref.29).

The anions, acting as donor, may compete with solvent molecules in "outer-sphere"-coordination and hence contribute to the solvation structure according to their donor properties and relative positions. As these are continuously changing, solvation features around any given particle are dynamically changing. The individual migrations cannot be observed and appear therefore chaotic. They follow gradients in chemical potential and hence they must be considered as being ordered. <u>The static aspects of this order at a given time may be described by a pattern of inhomogeneities established throughout the</u>

whole liquid system.

────▶ shortening of O⋯O distances
────▶ increasing symmetry of O-H-O bonds
────▶ increasing linearity of O-H-O bonds
────▶ structural gradient
────▶ density gradient

In solvent mixtures inhomogeneities even in local analytical composition must exist. For example, in a water-methanol mixture water molecules will be enriched near an ion, whereas alcohol molecules will be found enriched in regions more remote from an ion. An experimental indication for the extension of such effects up to 2 μm is the solubility of quartz in water provided in capillaries of extremely small cross-sections (Ref.3o). Resolution of data into solvation and excess properties reveals that the latter do not vanish at $c \approx 1o^{-6}$, which means a mean sphere of influence of each ion of about 1oo nm (Ref.31) corresponding to abut 4oo solvent layers!

The consideration of the linear relationships between activation energy and entropy of activation, which has been called the compensation effect, lead Likhtenstein (Ref.32) to a similar conclusion, namely that the solvent transmits the change in the state of solvent molecules caused by the cooperative interactions of the reactants with the solvent, to adjacent solvent molecules and from there to further molecules etc. In this mechanism, also weak interactions extend over large ensembles and make a considerable contribution to the system parameters, in particular to the energy and entropy terms. Experimental evidence indicates that the far-reaching effects are of even greater importance the lower the solute solubility (salting-out effects, for example for CO_2 or SO_2).

The macroscopic properties of a solution are changed even by small external changes, such as pressure or temperature and hence actions must be in operation, which extend through the whole solution. Dissolution of a small amount of a solute may cause measurable changes in physical properties, such as vapor pressure, surface tension, viscosity or density, which are characeristic for the whole solution. The actions of the solutes are therefore not confined to limited areas and in particular they must reach the phase boundaries. This means, that a solute ion or molecule, which has been shown to be modified by the solvent, is also modifying the whole liquid system under consideration; it is therefore a structure modified and modifying centre for which the abbreviation "SMM-centre" may be used.

Any liquid is known to contain "empty" space, usually referred to as "voids" or "holes". In most liquids the extent of such voids and their mobilities is greater than in the solid state. Molecules immediately surrounding such "inner-surface areas" are under strain and more strongly bonded to each other than in the absence of inner- or outer-surfaces (Ref.33), as has been illustrated for the static aspects in water in an idealized two dimensional way (Fig.3).
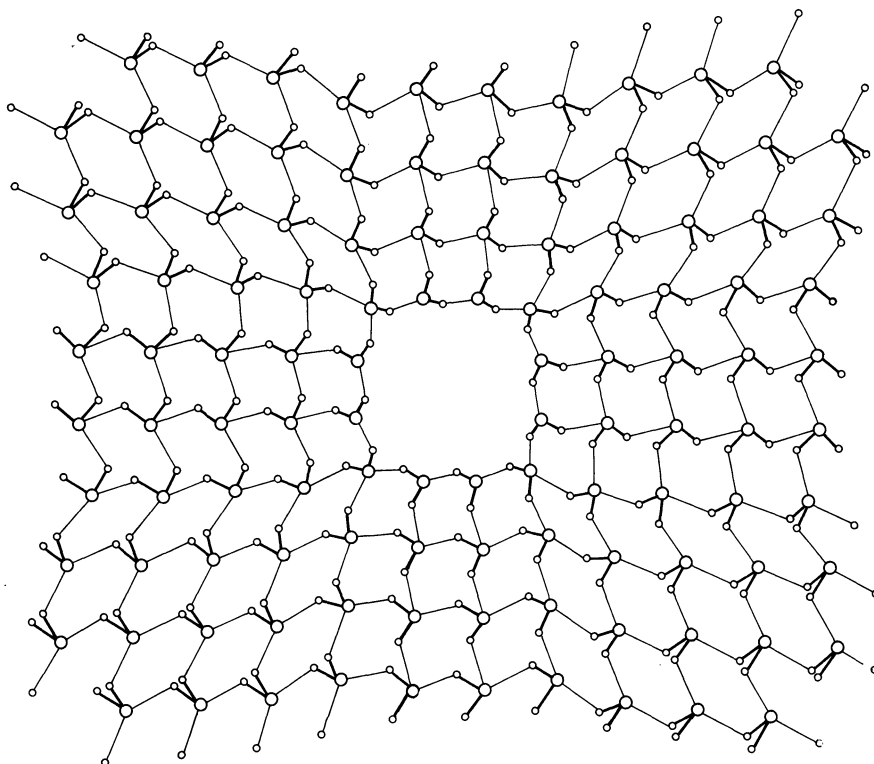
Fig. 3. Illustration of the static aspects of order of water
molecules surrounding an idealized hole of dimension as found
in clathrates.

Like a vacancy in a solid (Ref.34 to 36), a void in a liquid is therefore a
SMM-centre. SMM-centres irrespective of their nature, are not independent
within a solution, but rather interrelated with each other. This means, that
part of the information contained in solute ions and solute molecules, has
been transferred to the voids and vice versa.

A further contribution to the liquid structure is provided by the constrained
conditions for the boundary units. Just as on a surface of a solid the atoms
are more strongly bonded to each other than in the bulk (Ref.37) the mean
bond distances between solvent molecules near the surface must be shorter than
in other regions of the solution. The effects of "solvent contraction" within
the boundaries have far-reaching effects, as will be shown in the following
section.

The complicated and locally changing interrelationships between the various
parts of the solution cannot be reached from the statistical point of view
alone. Because the individual dynamic processes cannot be measured or pre-
dicted, they appear chaotic from this point of view. Any individual motion
requires, however, a driving force, i.e. a local gradient in chemical potential
and hence it is directed. As the continuous motions take place, the system
maintains its configuration and integral operation in an essentially constant
environment, and it responds to alterations in the environment in such a manner
as to counter the change in the direction of optimal preservation of its inte-
grity. This means that all motions within the macroscopic system have to occur
according to ordered relationships in favour of the whole system under consi-
deration. Because the ordered relationships cannot be found by using the
idealizations, as they may be derived from statistical results, we must
attempt to build a wider frame.

3. THE SIGNIFICANCE OF THE PARTS FOR THE WHOLE SOLUTION

We may take the unusual attitude of choosing an alternative point of view from
which enquiries may be made about the significance of the various parts for
the whole solution under consideration (Ref.34). In using the common abstract
description by means of the constituent molecules and ions, full consideration
must be given to the actual differentiation of the parts within the complex

relationships of the whole system (Ref. 34). Emphasis on the statistically derived mean values for the energies and exchange rates of solvent molecules have lead to consider the observed deviations as insignificant. In fact, the constituent parts are interrelated and interdependent, by no means isolated (see Note a), but rather penetrating each other (by their electron "shells"). The continuous and variable connectivity between the various parts of the system means that at any given time the state of any given unit is to be considered as perturbed with regard to its ficticious isolated state. At any given time each part is subjected to a somewhat different local environment and hence it has properties within the complex system, which would not be found in the idealized state of complete isolation. By the mental process of transferring a solvent molecule from given solution into an "isolated" state, many of their properties are actually lost. The recognition of the differences between the parts is possible by comparing the properties in both states. The differences may then be ordered with respect both   their temporal and local significance within and to their significance for the real liquid solution under consideration.

According to the local and temporal significance within the system various groups of parts may be distinguished, namely "normal" solvent molecules, solute ions or molecules, voids and molecules at surfaces. In each of these groups the parts serve the whole solution in different ways, namely on different levels, which influence each other in different intensities. The different dominations in the mutual interrelationships allow to recognize successively graded levels as they are characteristic for a so-called "hierarchic" order, which has also been proposed recently for the solid state (Ref.34 to 36). The level is hierarchically higher, the greater its significance for the whole system. Forces of a higher level control and regulate the properties of the parts serving the lower levels. All of the motions within the system should be consequent and illustrative of the concerted action of dynamic forces, which are not directly observable. Non-observables are accepted for example in thermodynamics and in quantum mechanics (Ref.38). Unobservable is also a field, which is recognized barely by its interaction with matter. Likewise, the "plan" may be recognized by observing the reaction behaviour to changes in temperature, pressure, composition, irradiation, molecular environment, action of fields or mechanical forces and hence by observing changes in macroscopic properties. From this point of view, we may describe how the "plan" uses the parts of the system in its favour for example in approaching or maintaining its optimal state in energy. From this point of view the properties of the ficticiously isolated parts are of extremely low significance.

If one establishes a hierarchy of significance among the molecules of a solution, the surface molecules must certainly be appropriated a prime position, because of their major role in providing the "first line of defense" and showing greatest adaptability towards changes and greatest resistance against changes. Surface molecules are more strongly bonded to each other than within bulk areas. Each molecule at the surface is under great strain and it is in a state of high energy. The mean higher energy states of surface molecules as compared to those of molecules in the bulk is reflected in the surface tension which is the difference of free energies in the bulk and the interface. Surface tension determinations for liquid/gas systems are extremely affected by the gas content of the liquid phase and consequently depending on interface ageing and this means that it has at least a trace of a kind of primitive memory.

Whereas in the interfacial region significant changes in composition and structure occur, the bulk liquid remains less affected by them. This shows the extraordinary great adaptability of the boundary areas. Extra energy may be passed on to molecules of lower energy or it may be stored at the surface by appropriate motions of its constituents. Alternatively the free surface area may be enlarged by increasing the number of surface molecules over which the energy may be redistributed.

Energy redistribution within the various parts of the liquid is controlled and regulated by the forces acting on the surface. Likewise, exchange of matter (adsorption, desorption) and redistribution of matter ("diffusion") is under the control of surface forces. Interactions between surface and other parts of the liquid are continuously and dynamically taking place. The strong forces at the surface serve the macroscopic system in its favour in approaching the minimum state of total energy. This requires ordered relationships between the surface and the various other parts of the liquid system. Each point at the surface must contain informations about the static and the

---

Note a. Complete isolation of a part would not allow its observation.

dynamic aspects of order in other parts of the system, as "seen" from the
point under consideration. Likewise any point within the system contains in-
formations of other parts, as "seen" from the said point. Hence fluctuations
at the surface are representative for fluctuations within the system.

In a solid material the network of dislocations is important for the redistri-
bution of energy, matter and information. Dislocations provide inner-surface
areas by which different points of the surface and within the bulk are inter-
connected. The existence of interconnected parts of the "empty" space within
the liquid may be proposed. They may be considered as mobile channels, which
do not end somewhere, but form either closed loops or reach the surface at
both ends. Just as in a solid the points of intersection between dislocation
and surface provide craters (Ref.34 to 36), the points of intersections
between a channel and the surface may provide "funnels". Due to the strong
curvatures, funnels are expected to represent areas of great local surface
energy (see Note b). Matter, energy and information from the surface may be
"channelled" into the bulk and vice versa. In analogy to the existence of
intersections of dislocations in solids (Ref.41), channels in the liquid may
intersect each other to provide a mobile network of channels with nodes and
intersecting points. Gradients in local surface energy in the areas between
the funnels facilitate the transfer of matter and energy towards the funnels,
from where they may be sucked in and directed by the channel-network to be
stored at appropriate regions in the liquid. Funnels are connected to each
other both through the surface area between them and through the channels. In
these ways closed loops of alternating inner and outer-surface areas are pre-
sent and in operation with pulsating gradients in local surface energies
according to which matter may be readily transported (Ref.42). The operations
of the channel network are under control of and regulated by the forces acting
on the surface. The actions of forces in opposite directions lead to modifi-
cations of the surface by the channel network, but the surface maintains its
main information, despite changes in the channel network. Hence the properties
of the units in the channel network are subject to regulation by the surface
requesting that the channel-network is hierarchically inferior to the surface.

Both surface and channel-network may produce or annihilate holes i.e. SMM-cen-
tres at the areas of changing curvatures of the outer- and inner-surface areas
respectively. As SMM-centres are formed, part of the strain is passed from the
higher levels to the SMM-centres, which are serving a level that is inferior
to that of the channel-network. The greater number and the higher mobilities
of the voids in a liquid as compared to those in a solid explains, why the
surface of a liquid is curved and rarely exhibits a macroscopically plane sur-
face.

SMM-centres under highly constrained conditions may be promoted to serve on a
higher level. The lower the solubility of a solute, the more constrained are
its parts and the greater their tendencies to reach less constrained condi-
tions by entering a higher level with strengthening the bonds between the mole-
cules serving this level. It is therefore expected that hardly soluble solutes
will be enriched in the inner- and outer surface regions. Solute segregation
into an interface leads to reduce the total free energy of the matrix and to
greater resistance and greater adaptability of the boundaries.

The driving forces for migrations in the liquid are gradients in chemical po-
tential. As a migration is taking place a new gradient in chemical potential
is produced, so that another migration is always to follow. The thermodynamic
or macroscopic state is known to represent a great number of dynamically co-
existing (fluctuating) microscopic states, which are hardly distinguishable
from each other (Ref.43). By the changes in microregions a characteristic
motion pattern must be maintained, which is independent from the actual po-
sitions of the units in any of these higher levels, namely those at inner- and
outer surface areas and SMM-centres. Neither the local arrangement of the parts,
nor the local analytical composition remains constant, but rather regularities
in dynamic character in the whole system. As such regularities
are established, we may speak of a dynamic order.

Like a field, the dynamic order cannot be observed directly, but it may be in-
directly inferred from its reactions, i.e. the macroscopic properties, as they
are maintained or changed. It is impossible to learn about the order by purely
analytical methods, because the order is lost by either the physical or the
mental dismemberment of the complex system (Ref.44). As has been stated above,

---

Note b. It has been suggested that the surface tension of a droplet should de-
        crease with increasing curvature (Ref.39 & 4o)

the elimination of a particle involves the loss of its significance within the complex relationships. It is therefore not necessarily useful to learn more and more about smaller and smaller parts with the aim to gain an understanding of the ordered motions within the system under consideration.

The dynamic order provides the framework for the conditions, under which the parts are in proper relation to each other, irrespective of their actual positions. We may therefore describe how the dynamic order makes use of the various parts within the complex relationships of the system. The temporal and local features of most of the solvent molecules are determined by the ordered motions of the surface, the channel-network and SMM-centres, i.e. of solute ions, solute molecules and voids. The overwhelming majority of constituents of the solution are most significant for statistical considerations and considered as "normal" solvent molecules.
Because the internuclear distances around an SMM-centre are not equal, the vibrations of the atoms in the normal solvent molecules will differ from each other even, if the SMM-centres were considered at fixed positions and a certain pattern of oscillations would be found reflected in a characteristic pattern of frequencies. The shorter the bond between two given atoms, the higher is the frequency and the smaller the amplitude. It is this pattern that is stable and not the individual motions between given atoms. When the SMM-centre absorbs energy and when it is moved, all of the oscillation frequencies will be altered. Because the SMM-centres are under the influence of the forces acting on the higher levels, their properties are determined not only by the temperature, but also by other environmental influences, such as pressure, irradiation, fields, mechanical forces, drop size, etc. What is termed "thermal vibrations" is actually a complicated dynamic pattern with a character all   its own that reflects the energetic influence by the environment including that of temperature as mediated through the units in the various hierarchical levels. This means that "normal" solvent molecules are under the decisive influence of the forces operating in the higher levels and hence they serve the lowest level of the hierarchic order within the solution under consideration.

It is virtually impossible to learn about the properties of the parts on a higher level from knowledge of those on a lower level. Statistical information alone is therefore inadequate to account for the behaviour of SMM-centres and of molecules at boundaries. On the other hand, the consideration of the dynamic order is in agreement with the statistical results. Quantum-chemical approaches remain useful in approximating a system on statistical grounds, although in the absence of knowledge of the elements of the dynamic order, to which the parts have to yield, such approaches are bound to be confined to idealized systems.

As the various levels are not isolated from each other, but continuously and dynamically interacting, any given molecule within the solution is by no means bound to be fixed to a certain level. Even within one and the same level molecules will differ in energy and properties, just as molecules serving different levels may be found in states of similar energy. For example, molecules at flat surface regions may be in lower states of energy than those at regions of intersecting channels. Overlap in energy states for constituents in different levels is a requirement for the execution of the hierarchic order.

The evaluation of the parts of a solution with regard to their significance for the whole system leads to the following levels (in descending order):

        1. Molecules at boundaries
        2. Molecules at interconnected inner-surface areas ("channel-network")
        3. SMM-centres (solute ions or molecules, small holes)
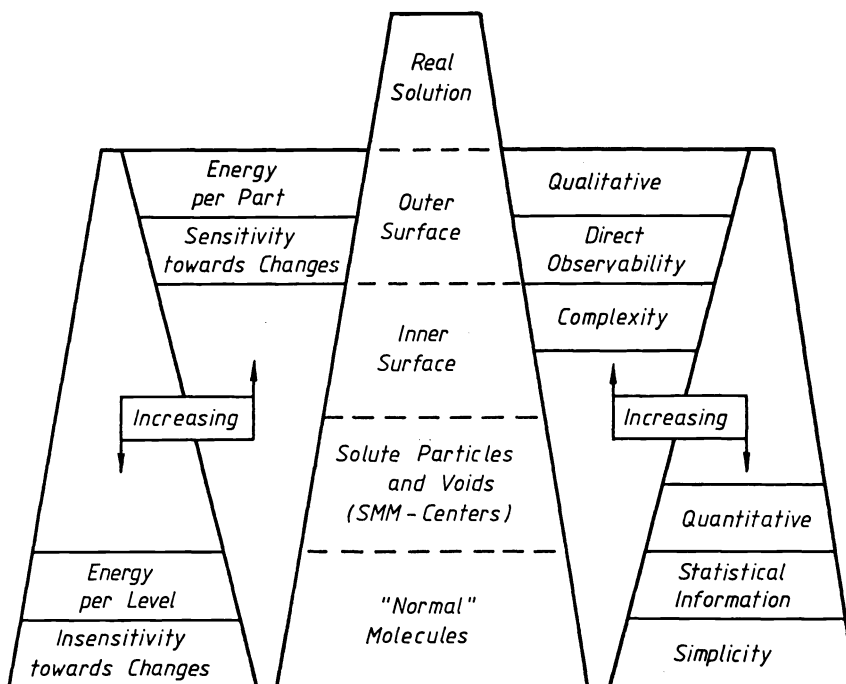   4. "Normal" solvent molecules.

Fig. 4. Illustration of the "hierarchic levels" within a
solution.

The same order is usually found by ordering the parts with respect to their
number within the system (increasing), to the consideration of the energies
per part (decreasing) and to the relative resistance and the relative adapta-
bility toward changes (decreasing). The higher the level, the greater is its
significance for the whole system,the smaller its dependence from the local
motions of the parts, the greater the range of influence, the greater the in-
formation storage capability and the greater the adaptability toward changes.
Figure 4 provides an illustration of the various levels as stated above.

4. ENERGY DISTRIBUTION AND RELATION TO MACROSCOPIC PROPERTIES

Because the dynamic order cannot be observed as such, we have to gain an un-
derstanding by starting from observable macroscopic properties, and to test
the concept by relating changes in macroscopic properties to defined changes
of forces acting upon the system.

This requires knowledge of the energy distribution within the system under
consideration. Microscopically the system contains fluctuating patterns of
charge densities and hence such patterns of density and of energy. Solute
units are in higher states of energy than solvent molecules, and areas of
high local density (with corresponding gradients) are found around such
SMM-centres. The boundary regions are areas of even higher local density
(with appropriate gradients) and hence the mean energy per part is greater the
higher the hierarchic level on which it is to serve.

On the other hand the energy per level is highly influenced by the number of
parts serving the respective level. Because the number of "normal" molecules
exceeds that of all of the others (usually by many orders of magnitude), the
energy stored in the lowest level is greatest, but the energy per part is
smallest. The number of solute units (SMM-centres) is usually smaller than
that of "normal" molecules and hence the energy content of the SMM-level is
smaller, although the energy per part is greater in the SMM-level as compared
to the lowest level. Unless extremely small droplets are considered, the
number of units at the surface is smaller than that in the other levels and,
although the energy per part is greatest in this level, the energy stored in

this level is smaller than in other levels. The relative amounts differ for different systems: In a concentrated solution (high number of SMM-centres) the energy storage capability in the SMM-level will be greater than in a more dilute solution. For extremely small drops the energy storage capability of the surface level will be greater than for large drops.

Outer Surface	Outer Surface
Inner Surface	
Solutes and Voids (SMM-Centers)	
	Inner Surface
"Normal" Molecules	Solutes and Voids (SMM-Centers)
	"Normal" Molecules

<div align="center">
Energy Storage Capability per Level   Energy per Part in the Various Levels
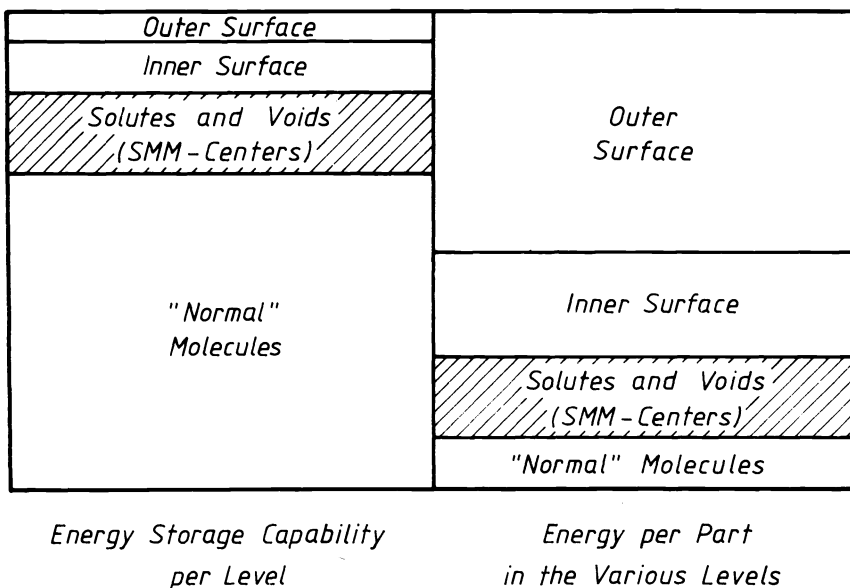</div>

Fig. 5. Illustration for the Energy Distribution within a Solution.

The most important question is, however, the response of the various levels to changes in energy of the system, i.e. the redistribution of energy. Of course, the redistribution occurs in agreement with the LeChatelier-Braun principle. The extent of energy adsorbed within a given microregion will be greater the greater the local density, and hence the greater the energy content per part. The increase in total energy of the system is distributed over the various levels that in the highest level the energy per part is increased to a greater extent than in the lower levels, whereas due to the greater number of parts the small gain in energy per part in the lowest level leads to a relatively great increase in energy for that level.

The following rules have been presented for the distribution of extra energy in a solid material and these may apply to matter irrespective its state of aggregation and hence also to a solution (Ref.34 to 36):

    1. The amount of energy that can be absorbed by a system is greater the lower the temperature and the smaller the macroscopic size of the liquid system.

    2. Unless extremely small droplets are considered, the increase in energy within a level will be greater the lower the level, but the energy increase per part will be greater the higher the level.

In order to apply this concept to observable changes in macroscopic properties, we have to learn to understand (i) in what ways the parts in the various levels contribute to a given macroscopic property, (ii) in what ways the extra energy is distributed in the system and (iii) in what ways the energy contents per part and the number of the parts are varied as the total energy of the system is changed.

In as far as such knowledge will be gained, it is expected to provide within a given system an understanding of the changes of a given property, for example surface tension, viscosity, density, ionic mobility, relaxation times, as a function of environmental changes, such as those in temperature, pressure, fields, irradiation, concentration, electrode material, or mechanical forces acting on the system. We hope to be able to report on these problems in the near future.

REFERENCES

1. D. Eisenberg and W. Kauzmann, The Structure and Properties of Water, Clarendon, Oxford (1969).
2. H.L. Friedman and C.V. Krishnan, Water, A Comprehensive Treatise, Ed. F. Franks, Vol. 3, p. 1, Plenum, New York (1978).
3. S. Golden and C. Guttmann, J. Chem. Phys. 43, 1894 (1965).
4. V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum, New York (1978).
5. J.S. Rowlinson, Water, A Comprehensive Treatise, Ed. F. Franks, Vol. 2, p. 1959, Plenum, New York (1963).
6. V. Gutmann, Rev. Chim. Roum. 22, 619 (1977).
7. V. Gutmann, Electrochim. Acta 21, 661 (1976).
8. V. Gutmann and U. Mayer, Mh. Chem. 1oo, 2o48 (1969).
9. U. Mayer, W. Gerger, V. Gutmann and P. Rechberger, Z. Anorg. Allg. Chem. 464, 2oo (198o).
1o. G. Gritzner, K. Danksagmüller and V. Gutmann, J. Electroanal. Chem. 9o, 2o3 (1978).
11. U. Mayer, Pure Appl. Chem. 51, 1697 (1979).
12. A.J. Parker, U. Mayer, R. Schmid and V. Gutmann, Org. Chem. 73, 1843 (1978).
13. V. Gutmann and R. Schmid, Coord. Chem. Revs. 12, 263 (1974).
14. U. Mayer, Mh. Chem. 1o8, 1479 (1977).
15. E. Grunwald and S. Winstein, J. Amer. Chem. Soc. 7o, 846 (1948).
16. E.M. Kosower, J. Amer. Chem. Soc. 78, 57oo (1956); 8o, 3253, 3261, 3267 (1958).
17. K. Dimroth, C. Reichhardt, T. Siepmann and F. Bohlmann, Liebigs Ann. Chem. 661, 1 (1963).
18. V. Gutmann and E. Wychera, Inorg. Nucl. Chem. Lett. 2, 257 (1966).
19. U. Mayer, V. Gutmann and W. Gerger, Mh. Chem. 1o6, 1235 (1975).
2o. R.H. Erlich and A.I. Popov, J. Amer. Chem. Soc. 93, 562o (1971).
21. M. Herlem and A.I. Popov, J. Amer. Chem. Soc. 94, 1431 (1972).
22. G. Gonzalez, U. Mayer and V. Gutmann, Inorg. Nucl. Chem. Letters 15, 155 (1979).
23. A. Kotocova, U. Mayer, W. Gerger and V. Gutmann, J. Electroanal. Chem. 1oo, 875 (1979).
24. G. Gonzalez, Inorg. Chim. Acta, to be published.
25. G. Maisano, P. Migliardo and F. Wanderlingh, J. Chem. Phys. 69, 676 (1978).
26. R. Triolo and A.H. Narten, J. Chem. Phys. 63, 3624 (1975).
27. A.H. Narten, F. Vaslow and H.A. Levy, J. Chem. Phys. 58, 5o17 (1973).
28. V. Gutmann and G. Resch, Proceedings of the 5. Int. Conf. Solute-Solute-Solvent Interactions, Florence, 198o.
29. S. Lengyel, Acta Chim. Hung. 37, 87 (1963).
3o. D. Schuller, Naturwiss. 6o, 145 (1973).
31. J. Barthel, Private Communication.
32. G.I. Liktenshtein, Russ. J. Phys. Chem. (English transl.) 44, 1o79 (197o).
33. V. Gutmann and G. Resch, Z. Chem. 19, 4o6 (1979).
34. G. Resch and V. Gutmann, Z. Phys. Chem. (Frankfurt) in the press.
35. G. Resch and V. Gutmann, Abh. Braunschw. Wiss. Ges. 3o, 38 (198o).
36. V. Gutmann and G. Resch, Rev. Inorg. Chem. in the press.
37. Review article: V. Gutmann and H. Mayer, Rev. Inorg.Chem. 1, 51 (1979).
38 I. Prigogine, Angew. Chem. 9o, 7o4 (1978).
39. R.C. Tolman, J. Chem. Phys. 17, 333 (1949).
4o. R. Defay, I. Prigogine, O. Bellmans, D.M. Everett, Surface Tensions and Adsorption, Wiley, New York (1966).
41. W. Bollmann, Crystal Defects and Crystalline Interfaces, Springer, New York (197o).
42. G. Resch and V. Gutmann, to be published elsewhere.
43. P. Glansdorff and I. Prigogine, Thermodynamic Theory of Structure, Stability and Fluctuations, Wiley-Interscience, London, New York (1961).
44. P.A. Weiss, The Science of Life, Futura, New York (1973).