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# Chemistry 1968. Lars Onsager

For the discovery of the reciprocal relations bearing his name, which are fundamental for the thermodynamics of irreversible processes

## PRESENTATION SPEECH

### S. Claesson, Royal Swedish Academy of Sciences

Your Majesty, Your Royal Highnesses, Ladies and Gentlemen.

Professor Lars Onsager has been awarded this year's Nobel Prize for Chemistry for the discovery of the reciprocal relations, named after him, and basic to irreversible thermodynamics. On hearing this motivation for the award one immediately gets a strong impression that Onsager's contribution concerns a difficult theoretical field. A closer study shows this indeed to be the case. Onsager's reciprocal relations can be described as a universal natural law, the scope and importance of which becomes clear only after being put in proper relation to complicated questions in border areas between physics and chemistry. A short historical review emphasizes this.

Onsager presented his fundamental discovery at a Scandinavian scientific meeting in Copenhagen in 1929. It was published in its final form in 1931 in the well-known journal *Physical Review* in two parts with the title "Reciprocal relations in irreversible processes." The elegant presentation meant that the size of the two papers was no more than 22 and 15 pages respectively. Judged from the number of pages this work is thus one of the smallest ever to be rewarded with a Nobel Prize.

One could have expected that the importance of this work would have been immediately obvious to the scientific community. Instead it turned out that Onsager was far ahead of his time.

The reciprocal relations, which were thus published more than a third of a century ago, attracted for a long time almost no attention whatsoever.

The Presentation Speech, Lecture, and Biography given here are reproduced from *Nobel Lectures, Chemistry, 1963–1970* (Elsevier, Amsterdam, 1972).

It was first after the second world war that they became more widely known. During the last decade they have played a dominant role in the rapid development of irreversible thermodynamics with numerous applications not only in physics and chemistry but also in biology and technology. Here we thus have a case to which a special Rule of the Nobel Foundation is of more than usual applicability. It reads: "Work done in the past may be selected for the award only on the supposition that its significance has until recently not been fully appreciated."

The great importance of irreversible thermodynamics becomes apparent if we realize that almost all common processes are irreversible and cannot by themselves go backwards. As examples can be mentioned conduction of heat from a hot to a cold body and mixing or diffusion. When we dissolve a cold lump of sugar in a cup of hot tea these processes take place simultaneously.

Earlier attempts to treat such processes by means of classical thermodynamics gave little success. Despite its name it was not suited to the treatment of dynamic processes. It is instead a perfect tool for the study of static states and chemical equilibria. This science was developed during the nineteenth and the beginning of this century. In this work many of the most renowned scientists of that time took part. The Three Laws of Thermodynamics gradually emerged and formed the basis of this science. These are among our most generally known laws of nature. The First Law is the Law of Conservation of Energy. The Second and the Third Laws define the important quantity entropy which among other things provides a connection between thermodynamics and statistics. The study of the random motion of molecules by means of statistical methods has been decisive for the development of thermodynamics. The American scientist J. Willard Gibbs (1839–1903) who made so many important contributions to statistical thermodynamics, has his name attached to the special professorship which Onsager now holds.

It can be said that Onsager's reciprocal relations represent a further law making possible a thermodynamic study of irreversible processes.

In the previously mentioned case with sugar and tea it is the transport of sugar and heat during the dissolution process which is of interest in this connection. When such processes occur simultaneously they influence each other: a temperature difference will not only cause a flow of heat but also a flow of molecules and so on.

Onsager's great contribution was that he could prove that if the equations governing the flows are written in an appropriate form, then there exist certain simple connections between the coefficients in these equations. These connections—the reciprocal relations—make possible a complete theoretical description of irreversible processes.

The proof of the reciprocal relations was brilliant. Onsager started from a statistical mechanical calculation of the fluctuations in a system, which could be directly based on the simple laws of motion which are symmetrical with regard to time. Furthermore he made the independent assumption that the return of a fluctuation to equilibrium in the mean occurs according to the transport equations mentioned earlier. By means of this combination of macroscopic and microscopic concepts in conjunction with an extremely skilful mathematical analysis he obtained those relationships which are now called Onsager's Reciprocal Relations.

Professor Lars Onsager. You have made a number of contributions to physics and chemistry which can be regarded as milestones in the development of science. For example, your equation for the conductivity of solutions of strong electrolytes, your famous solution of the Ising problem, making possible a theoretical treatment of phase changes, or your quantization of vortices in liquid helium. However, your discovery of the reciprocal relations takes a special place. It represents one of the great advances in science during this century.

I have the honour to convey to you the congratulations of the Royal Academy of Sciences and to ask you to receive the Nobel Prize for Chemistry for 1968 from the hands of His Majesty the King.

## THE MOTION OF IONS: PRINCIPLES AND CONCEPTS

*Nobel Lecture, December 11, 1968*

### Lars Onsager

Today I shall try to help you grasp the significance of a fairly general principle which applies to diverse types of irreversible processes. After last night it will be just as well if we do not go into all fine points of definitions or survey all possible applications. Rather, I want to talk about progress over a period of time in one field of research where much has happened (some of this relevant to the principle I mentioned) and intriguing problems still remain. Before we survey the progress in our understanding of electrolytes since the days of Arrhenius, let us take a quick look at what went before.

Gay-Lussac's rule of combining volumes (1808) led Avogadro to surmise that under corresponding conditions of temperature and pressure equal volumes of different gases contain equal numbers of molecules (1811). This principle was to become the chemist's primary means to determine molecular weights, but it was long debated and not in general use until after 1860. By that time Cannizzaro could muster enough evidence for a strong argument at the first international congress in Karlsruhe, and within a few years Avogadro's principle gained wide acceptance.

We may at least speculate that contemporary developments in the kinetic theory of gases encouraged the chemists' change of attitude, although they rarely if ever admitted that; they preferred to maintain an inductive point of view in their publications. In 1860, Maxwell obtained his distribution law for molecular velocities, which implies equipartition of kinetic energy; Avogadro's principle is an automatic consequence. In the following year Boltzmann founded a more general theory of specific heats, explaining the empirical rule of Dulong and Petit; those results had to be exploited with semi-empirical modifications until the quantum theory accounted for the discrepancies much later. Guldberg and Waage (1864) formulated the mass-action law and supported it by experiments. After a while (1885) Van 't Hoff recognized a close analogy between solutions and gases, so that measurements of osmotic pressure or changes in vapor pressure or freezing point depression could substitute for vapor densities. Strangely, however, the observations on solutions of salts, acids and bases in water indicated the presence of more solute particles than there could be molecules by any reasonable interpretation of chemistry known then or now. Arrhenius(1,2) (1884) recognized that these electrolytes dissociate largely into free ions, and he could point to a pretty good correspondence between the Van 't Hoff "anomalies" and the degrees of ionization inferred from the electrical conductivity.

A greatly simplified picture of electrolyte solutions loomed. At fairly low but readily attainable concentrations solutions of readily dissociating compounds like hydrochloric acid, potassium hydroxide and a great many salts like sodium chloride would be completely dissociated and the properties of a solution would be additive, not just over molecules, but even over the constituent ions. At higher concentrations, admittedly, one would have to allow for combination to form molecules or compound ions according to the mass-action law, as suggested by Ostwald(3) (1888). Nernst developed appropriate simple theories for the diffusion of electrolytes and for the variation of an electrode potential with the concentration of the ion discharged.

Such was the simple picture presented to me as a freshman chemist in 1920. In spite of some idealization it sufficed for a great many purposes; it eased many tasks no end and we were eternally grateful for that. However, very soon the journals rather than the textbooks taught me about numerous observations which did not quite fit into the picture and of tentative explanations for the discrepancies. Whether the experimenters studied the electrical conductivities or the equilibrium properties like freezing point depressions and electromotive forces, significant deviations from the ideal additive behavior persisted to much lower concentrations than had been predicted according to the mass-action law from the measurements performed on more concentrated solutions. These phenomena became known as the "anomalies" of strong electrolytes. In many ways the anomalies displayed conspicuous regularities; if one compared salts of the same valence type like NaCl and $KNO_3$, the differences were typically small even at concentrations as high as 0.1 mole/liter. Suspicion centered on the long-range electrostatic forces between the ions.

Debye and Hückel(4) finally succeeded in predicting the effects of the electrostatic interaction from the general principles of kinetic theory. They pointed out that the electrostatic field around an ion must be screened by an average density of compensating charge. As had been found previously by Gouy (1913) in somewhat different context, the screening distance is given by the ionic strength (sum of concentrations multiplied by squares of charges), the dielectric constant of the solvent and the temperature; it varies inversely as the square root of the ionic strength. The resulting effects on the chemical potentials of electrolytes are proportional to the square root of the ionic strength; to compute the coefficient one has to know the magnitude of an elementary charge, and the measurements of Millikan(5) had already supplied that information (1917). These predictions agreed well enough with previous experiments, and the improved techniques of subsequent decades have only confirmed the agreement. The theory of Debye and Hückel was soon routinely exploited to great advantage. Those stubborn deviations from the laws of Van 't Hoff and Arrhenius and Guldberg and Waage became harmless because we could compute them, make proper allowance and extrapolate in comfort to exploit additive relations. To make matters even easier, many electrolytes turned out to be completely dissociated or nearly so.

Debye and Hückel also considered the conductivity of electrolytes, at most important source of information because the measurement is almost always feasible, and it takes only reasonable care to get accurate results. Kohlrausch had shown long since that the conductivities of strong electrolytes in water decrease linearly with the square root of the concentration. Debye and Hückel recognized that two effects contribute to this decrease. For one, while the external electric field exerts a force on the ion, an opposing force of equal magnitude is distributed over the screening cloud of compensating charge. As a result, every ion is driven against a countercurrent; the speed of this current is proportional to the charge of the central ion and independent of its own mobility. This is called the electrophoretic effect, and the theory is closely related to that of the effect so profitably utilized by Tiselius(6); but there is a significant difference between small and large particles, and the meaning of the word "electrophoresis" varies according to context. The so-called "relaxation effect" depends on distortions of the screening clouds produced by the systematic motion of the ions in the external field. As it happened, Debye and Hückel overestimated that effect and concluded that in computing the "electrophoretic force" they had extrapolated the macroscopic hydrodynamics too far.

Fortunately, my own efforts in the summer of 1923 had produced a modest but firm result. The relaxation effect ought to reduce the mobilities of anion and cation in equal proportion. Much to my surprise, the results of Debye and Hückel did not satisfy that relation, nor the requirement that whenever an ion of type A is 10 Å West of a B, there is a B 10 Å East of that A. Clearly, something essential had been left out in the derivation of such unsymmetrical results. The model used was this: one particular ion is constrained to move at a constant speed along a straight line in the solution; neighboring ions respond to the fields in the distorted screening cloud, and in addition they mill around in random fashion according to the laws of Brownian motion. Recipe: Remove restraints on the central ion but retain an external force on it, let it execute its own thermal motion and respond to the fields of its neighbors, and recognize whatever external forces act on them. That done, the result for binary electrolytes became very simple: the relaxation effect reduces the migration velocity of every ion by a fraction which depends neither on its own mobility nor on that of the partner species (of opposite, numerically equal charge). Otherwise the effect is charge-dependent and proportional to the square root of the concentration—just like the corrections to the equilibrium properties, but with a different coefficient. As to the electrophoretic effect, it was easy to show that plausible variations of the hydrodynamics near the center of the countercurrent system driven by a widely distributed force could not matter enough to affect the limiting law; Debye and Hückel had unjustly impugned their own result.

As seen from Fig. 1, the general variation of conductivities with the concentration for 1–1 electrolytes was quite well explained; the divergence and individual variation at higher concentrations was foreseeable, but the theory was not so far developed that the significance of those features could be evaluated in detail.

Figure 2 displays the difference between a strong acid (HCl) and a weaker one ($HIO_3$). Clearly, the concept of a dissociation equilibrium was still indispensable.

In Fig. 3 we see the conductivities of a few ternary electrolytes compared with the theoretical limiting formulas.

In Fig. 4 the curves with appropriate limiting tangents are extrapolated according to the theory; previous empirical extrapolations are indicated too. The point was that the new extrapolation for $MgSO_4$ agreed

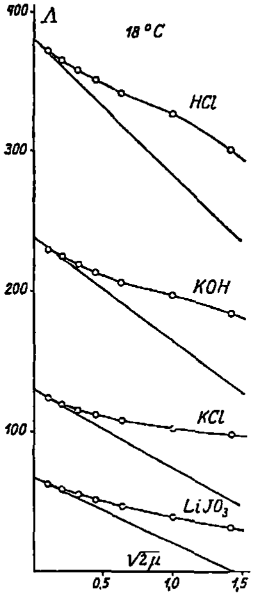

Fig. 1. Conductivities of 1-1 electrolytes in water. Λ, equivalent conductivity; μ, concentration in equiv./L. From ref. 8.

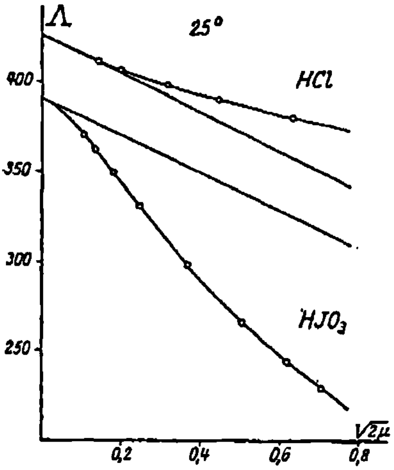

Fig. 2. Conductivities of hydrochloric acid and iodic acids in water. Same notation as Fig. 1. From ref. 8.

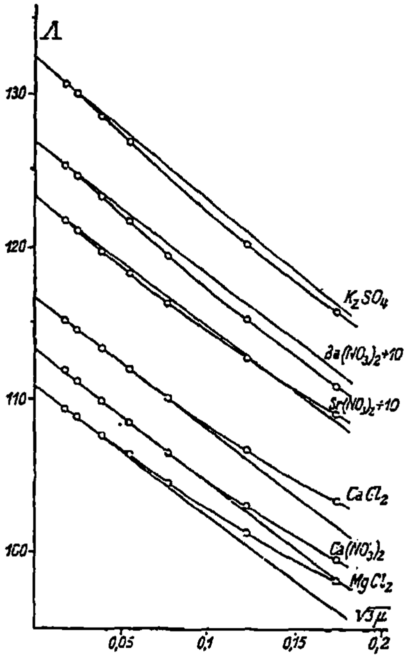

Fig. 3. Conductivities of 1–2 electrolytes in water. Same notation as Fig. 1. From ref. 8.

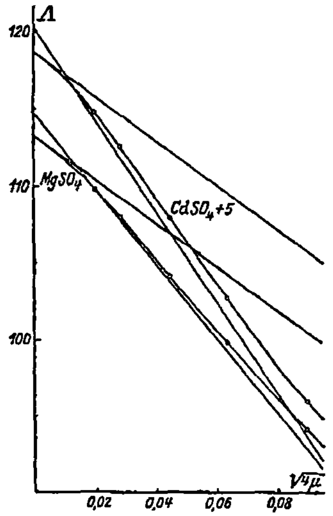

Fig. 4. Conductivities of 2–2 electrolytes in water. Same notation as Fig. 1. From ref. 8.

with the limiting value expected from the additivity rule while the old one did not. It became clear that $MgSO_4$ was incompletely dissociated (as well as $CdSO_4$), a conclusion confirmed by later studies of the chemical reaction kinetics (Eigen(9)).

In Fig. 5 we see some deviations from Kohlrausch's rule of independent mobilities, first computed by Bennewitz, Wagner and Küchler(10) (1929), then demonstrated by Longsworth (1930). Solutions containing HCl and KCl in varying proportion are compared at constant total concentration. The fast hydrogen ions are delayed as they overtake the slower potassium ions and detour around them; the potassium ions are speeded up by the same interaction. The resultant net decrease of the total conductivity had been observed in a similar case before (Bray and Hunt, 1912) and pronounced a baffling mystery.

Going back to the time when I revised the theory of Debye and Hückel, the task was by no means easy. The key was a principle of superposition applied to the ion cloud around a pair. To begin with, it was a bit confusing that the force exerted by the external field on an ion as well as the interaction between the ions were proportional to the charge. In order to gain perspective I decided to ignore the relation between the charge and the driving force, and took a look at a more general problem. One constant field of force is acting on each kind of ion; what are the effects of the Coulomb interaction? The problem is in fact equivalent to that which arises in the most general case of diffusion and electrical conduction combined; the gradients of chemical potentials are equivalents of forces:

$$k_j = -\nabla\mu_j - e_j\nabla\varphi$$

where $k_1, k_2,\ldots$ stand for forces, $\mu_1, \mu_2,\ldots$ for chemical "potentials of ions," $e_1, e_2,\ldots$ for charges and $\varphi$ for the electrostatic potential. A measure of ambiguity in the definition of $\varphi$ induces a corresponding ambiguity in

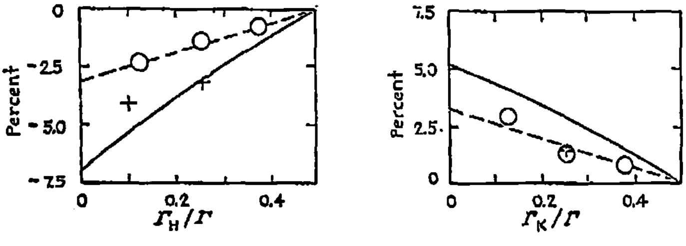

Fig. 5. The variation of cation mobilities with mixing ratio for aqueous solutions containing varying proportions of HCl and KCl at constant total concentration of 0.1 mole/liter. Measurements by Bennewitz, Wagner and Küchler(10) (1929). From ref. 35.

$\mu_1, \mu_2,...$; but the combination $(\mu + e\varphi)$, known as the "electrochemical potential," is uniquely defined for the purpose in hand. If the result of the computation was written in terms of transport $J_1, J_2,...$

$$J_j = \sum L_{ji} k_i$$

the coefficients $L_{ji}$ were invariably symmetrical. It was soon evident that this did not depend on any mathematical approximations. For the relaxation effect I could depend on Newton's principle of action and reaction; for all the complications of hydrodynamics a "principle of least dissipation" derived by Helmholtz assured the symmetry. Admittedly, I did assume some consistent scheme of Brownian motion kinetics; but even that seemed not essential. The symmetry relation itself was equivalent to a principle of least dissipation; inverting the equations:

$$k_j = \sum R_{ji} J_i$$

then

$$R_{ji} = R_{ij}$$

and the integral of the dissipation function

$$R(J, J) = \sum R_{ji} J_j J_i$$

equals the degradation of free energy, and it is a minimum in a case of stationary flow.

An unusual problem in chemical kinetics attracted my attention at the same time, C. N. Rüber was studying the mutarotation of various sugars by several precise methods: optical rotation, refractive index (interferometer) and volume changes (dilatometer). He discovered that there were (at least) three modifications of galactose, and the possibility that any one of these might transform into either of the others gave rise to a little problem in mathematics. In analyzing it I assumed, as any sensible chemist would, that in the state of equilibrium the reaction $1 \rightarrow 2$ would occur just as often as $2 \rightarrow 1$, etc., even though this is not a necessary condition for equilibrium, which might be maintained by a cyclic reaction—as far as the mathematics goes; the physics did not seem reasonable. Now if we look at the condition of detailed balancing from the thermodynamic point of view, it is quite analogous to the principle of least dissipation.

I developed a strong faith in the principle of least dissipation, and recognized that it had been used somehow by Helmholtz in his theory of galvanic diffusion cells and by Kelvin in his theory of thermoelectric phenomena. Some years later in Zürich in a conversation with P. Scherrer, I found that he had been strongly impressed by the ideas of G. N. Lewis about detailed balancing. This made me put the cart behind the horse. Now I looked for a way to apply the condition of microscopic reversibility to transport processes, and after a while I found a handle on the problem: the natural fluctuations in the distribution of molecules and energy due to the random thermal motion. According to a principle formulated by Boltzmann, the nature of thermal (and chemical) equilibrium is statistical, and the statistics of spontaneous deviations is determined by the associated changes of the thermodynamic master function; that is the entropy—or at constant temperature, equally well the free energy. Here was a firm connection with the thermodynamics, and we connect with the laws of transport as soon as we may assume that a spontaneous deviation from the equilibrium decays according to the same laws as one that has been produced artificially. When this reasoning was exploited by appropriate mathematics, the long-suspected reciprocal relations did indeed appear among the results, which were first announced in 1929. In view of the very general claims I felt that concepts and conditions ought to be defined with great care, and a complete exposition(11, 12) did not appear until 1931.

One consequence of the principle is that the removal of a constraint will never decrease the rate of dissipation of energy. For example, closing an electric contact allows a current to flow; that is one way to remove a constraint. In this sense the principle was applied as a hypothesis by Kelvin in his theory of thermoelectric phenomena. By the same route Helmholtz arrived at a relation between streaming potentials and electrophoresis in capillaries (an inside-out variation of the effect utilized by Tiselius); he also derived a formula for the electromotive force of a concentration cell, which was later generalized by MacInnes and Beattie(13) (1920). The most important application of the dissipation principle not yet suggested in 1931 was a general relation between the cross-coefficients for diffusion of different solutes. This was announced for electrolytes in a joint paper with Fuoss(14) (1932), where of course the relation of MacInnes and Beattie was implied as well. By now there is a fairly extensive literature on the subject. A comprehensive review of varied applications and significant experimental tests was given some years ago (1960) by D. C. Miller(15); he concluded that the relations are generally confirmed within the limits of error of the measurements.

Possibly the most important as a tool of research is the relation of Helmholtz, MacInnes and Beattie. The thermodynamic properties of electrolyte solutions can be determined from the measurements of the voltage between electrodes reversible to both ions. Largely through the efforts of H. S. Harned, methods of preparing reversible electrodes for several kinds of anions (halide, sulfate) and cations (hydrogen, silver, alkali metals and some others) have been perfected; but for a great many ions this has not been achieved and the prospects look poor.

Following MacInnes and Brown(16) (1936), the voltage of a concentration cell is measured between electrodes reversible to the same ion, and when in addition the transference number (fraction of the current carried by one ion) is known, the free energy of dilution can be computed. MacInnes and Longsworth(17) had shown (1932) how the transference numbers can be determined quite accurately by observing the displacement of a boundary between two solutions (with one common ion) by the passage of an electric current.

In 1932 Fuoss and I(14) computed the effects of the interaction between the ions on transport processes (conduction and diffusion, even viscosity) in mixtures of general composition. The algebraic techniques which enabled us to cope with a complicated system of equations were improved many years later (Onsager and Kim,(18) 1957). Precision methods for the study of diffusion were not developed until the decade 1940–50. Then Kegeles and Gosting(19) (1947) showed that Gouy's optical fringe method gives excellent results when the principles of physical optics are properly applied; meanwhile Harned and co-workers(20, 21) developed a relaxation method which depends on measurements of electrical conductivity for analysis *in situ*. The two methods supplement each other very nicely: at low concentrations of electrolytes, where Gouy's method fails for lack of fringes, the resistivities of the solutions suffice for easy measurement. Thus at long last Nernst's relation between the coefficient of diffusion and the electrolytic mobilities was verified to about 0.1 %.

I have indicated already that the theory of long-range interaction by no means eliminated the need to consider a mass-action equilibrium with undissociated species. As was pointed out by Bjerrum(22) (1927), when the ions are highly charged or very small, or where the dielectric constant is not 80 but just 20 or less, the electrostatic interaction at close range will be so strong that pairs of ions will stay together for a long time and act pretty much like ordinary molecules. For that matter, recent kinetic studies have revealed (Eigen,(9) 1967) that replacements in the innermost shell of solvent molecules and anions around a cation may be fairly infrequent—once in a microsecond, say, or even longer—so that molecules are reasonably well defined in the sense of chemical kinetics. However, even when the recombination kinetics is too fast for a sharp definition, it is often convenient to distinguish between "free ions" and "associated pairs" by some arbitrary but reasonable convention. Bjerrum(21) suggested (1927) that we draw the line at a distance where the work of separation against the Coulomb force is twice the thermal energy ($kT$) per molecule; in water that distance is

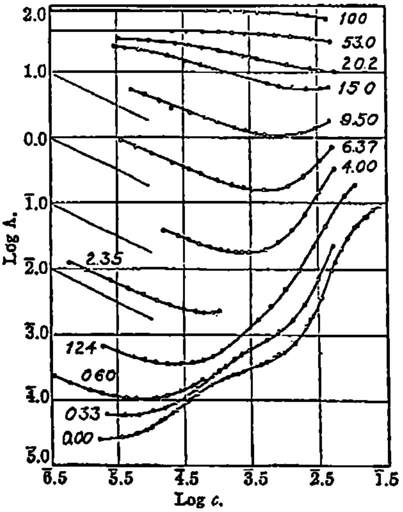

Fig. 6. The equivalent conductivity $\Lambda$ of tetraisoamylammonium nitrate in mixtures of water and dioxane, as a function of the salt concentration $c$. From ref. 23.

3.5 Å for KCl, 7 Å for $MgCl_2$, 14 Å for $MgSO_4$, etc., and in a solvent of dielectric constant 20 at room temperature the "Bjerrum distance" is 14 Å for KCl. In solvents of very low dielectric constant only the salts of big complex ions dissolve and exhibit appreciable conductivity. Figure 6 exhibits the effect of the dielectric constant. Fuoss(23) (with Kraus, 1933) measured the conductivities of solutions of tetraisoamyl ammonium nitrate over a wide range of concentrations in mixtures of water and dioxane, covering a range of dielectric constants from 78 to 2.25.

The descending branches of the curves represent a mass-action equilibrium between neutral pairs and individual ions. The minima and the increasing branches indicate that at higher concentrations the current is carried mostly by charged aggregates of several ions in mass-action equilibrium with smaller neutral aggregates and simple pairs, inflexions in the rising branches suggest ring-shaped neutral aggregates. Tentative estimates indicated that the Coulomb forces could be held largely responsible for the variations of the various equilibrium constants. The long-range effects entail relatively small corrections compared to the enormous range of variation displayed in Fig. 6. Similar results are found quite often in solvents of low dielectric constants, but by no means always; we know a good many examples where strong specific interactions of the ions with each other or with the solvents are indicated. The accumulation of more and better data have motivated efforts to refine our original computations.

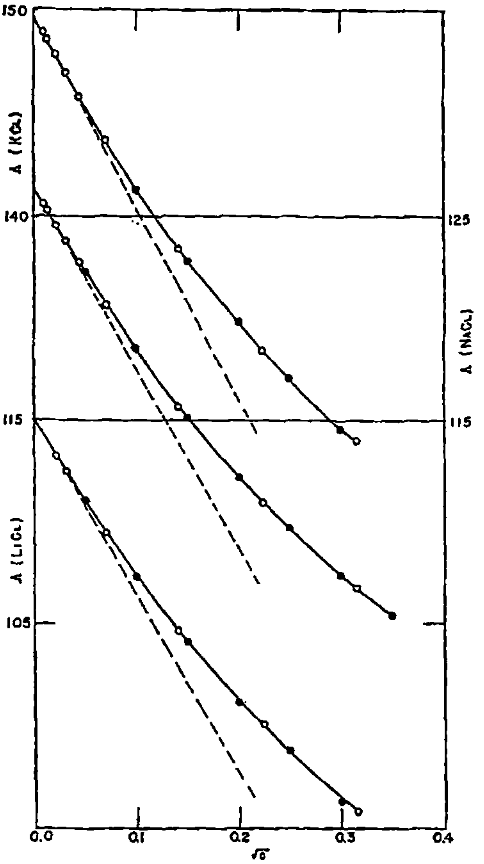

Fig. 7. Conductivities of chlorides in water. Measured points by Shedlovsky(25) (1932), computed curves by Onsager and Fuoss(24) (1955).

Fuoss and I undertook such a computation(24) (1955); in Fig. 7 the predictions are compared with Shedlovsky's excellent measurements(25) (1932). In form our computed results agreed substantially with those of Pitts(26) (1953); but certain differences in the models entail differences of interpretation in terms of short-range interactions. In this context we might seek at least a partial answer to the question how closely the effects of short-range interactions on the conductivity may correspond to the effects on the thermodynamic properties in the sense of Arrhenius. That task begins to look feasible.

The theoretical developments of the nineteen twenties inspired a search for additional symptoms of long-range interaction, and several were

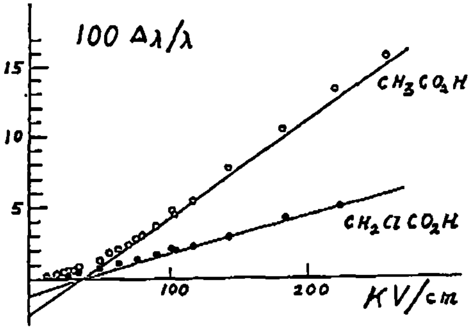

Fig. 8. Deviations from Ohm's law in aqueous solutions of weak acids. Points from Schiele.(32)

found. For example, in a rapidly alternating field the ion can be caused to change its direction of motion before the relaxation force is fully developed. As a result the conductivity increases somewhat through a range of frequencies which corresponds to the (Maxwell) relaxation time, and the phase of the voltage lags a little behind that of the current. Alternatively, a very strong field causes an ion to move so fast that a screening cloud of the normal type has no time to form; in the limit of high speeds the screening is performed by a deficiency of other ions moving with the same speed (M. Wien; Onsager,(29) 1934; Wilson,(30) 1936; Eckstrom and Schmelzer,(31) 1939). Attempts to exploit this effect as a means to eliminate the complications of long-range interactions for weak electrolytes met with a surprise (Schiele,(32) 1932).

Figure 8 actually displays the excess field effects for two weak acids over the field effect for a strong one (HCl). The straight lines represent my own computations(29) (1934). The field disturbs the dissociation equilibrium because it helps pairs of ions to separate for good once they have reached the fringes of the Coulomb field. The assistance is nearly proportional to the absolute value of the field. The negative intercepts represent mainly a decrease in the rate of recombination by the screening clouds of ions, effective in the absence of a strong external field. In the light of such analysis, the Wien effect seemed to hold promise as a good tool for the study of fast recombination kinetics; recent work—particularly by Eigen and DeMaeyer—has shown that this was not a vain hope (Eigen(9)).

Many solids exhibit electrolytic conduction, and symptoms of reaction kinetics, Wien effect and so forth have been observed. Impurities and other defects often play a decisive role, and these factors are none too readily controlled, so that the standard of precision has to be rather modest; but it is often possible to divine the mechanism. Arrhenius had to fight for his faith; but those days are long past. We now realize quite clearly that it takes excess charges moving somewhere to produce an electrolytic conductor. In a salt crystal such an excess charge can be an additional ion in an abnormal "interstitial" position (Frenkel defect) or a vacancy (Schottky defect) at a place normally occupied by an ion. The position of the vacancy is changed whenever a neighboring ion moves in to fill it. In KCl, for example, Schottky defects predominate as "ions" of both signs; but in AgCl some silver ions leave their normal sites for interstitial positions to produce positive Frenkel and negative Schottky defects. Schottky defects of opposite signs can combine to form neutral vacancy pairs, and various complications which involve more extensive defects can occur too. In any event, in well-ordered crystals we generally expect that the ions will carry undivided elementary charges.

Nevertheless, we have come to realize that in certain disordered crystals elementary charges can be transported in installments by point defects. We don't have to go far. Ice is a good example! In that solid almost all current is carried by mobile protons—excess or defect. First, let me explain the essentials of the structure. Each molecule is surrounded by four neighbors at a distance of 2.76 Å. Each hydrogen is placed near the line through the centers of two oxygens and closer to one than to the other; the distances are about 1 Å and 1.76 Å. Two neutrality rules are normally satisfied: each oxygen carries two near hydrogens, so that the water molecules are intact and neutral. The other neutrality rule requires that one and only one hydrogen connects any two neighboring oxygens: the hydrogen bonds are intact. Any violation of either neutrality rule produces an electrically active defect.

(Animated cartoon)

A chance rotation of a molecule produces a pair of bonding defects; these separate and move through the crystal by successive rotations of the participating molecules. Other bonding defects enter the picture and wander through it. A chance transfer of a proton from one molecule to its neighbor produces a pair of ionic defects: positive hydronium $H_3O^+$, negative hydroxyl $OH^-$. The positive ion moves by donating a proton, the negative by stealing one. The motion of the ions leave molecules oriented against the field; the drift of the bonding defects turns them into the field again.

(End of cartoon)

Estimates of the ionic mobilities vary over a considerable range; but in any event the positive ionic defect is much more mobile in the solid than in the liquid, and its mobility varies very little with the temperature. The mobilities of the bonding defects are more like those of ordinary ions in

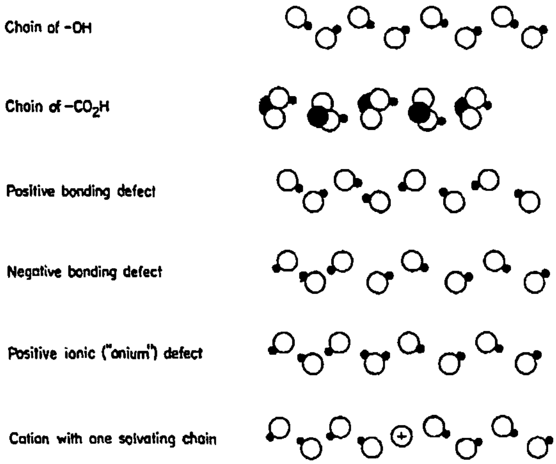

Fig. 9. H-Bond chains and electrically active defects.

the liquid, and the temperature coefficients are similar. Nevertheless, the bonding defects determine the direction of polarization in pure ice, because they are much more numerous, possibly several pairs for each million molecules. As to the task of transporting a direct current, that is about equally distributed between bonding and ionic defects; each type carries about half an elementary charge. One kind of current may get out of step with the other for a short time; but this produces a polarization which equalizes the number currents.

If you apply the principle of least dissipation to this kind of coupling you may be stretching some thermodynamic concepts just a little bit; but it is a good safeguard against greater errors, Jaccard(33) (1964) found it quite helpful.

Many of the things I have told you have a bearing on problems in biology. For example, how do ions get through in cell membrane? Observations on poisoning suggest fixed facilities for such transport. Let me just toss on the screen what I think might be an essential element of such a facility (Onsager,(34) 1967; Fig. 9).

This is a speculation, but one which is not yet refuted by observations and seems generally compatible with physical principles. The hope that it might be right adds interests to the exploration of ice and other protonic semiconductors.

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## BIOGRAPHY

Lars Onsager was born in Oslo, Norway, November 27, 1903 to parents Erling Onsager, Barrister of the Supreme Court of Norway, and Ingrid, née Kirkeby. In 1933 he married Margarethe Arledter, daughter of a well-known pioneer in the art of paper making, in Cologne, Germany. They have sons Erling Frederick, Hans Tanberg, and Christian Carl, and a daughter Inger Marie, married to Kenneth Roy Oldham.

After three years with the experienced educators Inga and Anna Platou in Oslo, one year at a deteriorating private school in the country and a few months of his mother's tutoring, he entered Frogner School as the family returned to Oslo. There he was soon invited to jump a grade, so that he was able to graduate in 1920.

Admitted to Norges tekniske høgskole in the fall of that year as a student of chemical engineering, he entered a stimulating environment; the department had attracted outstanding students over a period of years. Among the professors particularly O. O. Collenberg and B. Holtsmark encouraged his efforts in theory and helped him in the evaluation of background knowledge.

After graduation in 1925 he accompanied Holtsmark on a trip to Denmark and Germany, then proceeded to Zürich, where he remained for a couple of months with Debye and Hückel and returned the following spring, for a stay of nearly two years. There he organized his results in the theory of electrolytes for publication, broadened his knowledge of physics and became acquainted with a good many leading physicists.

In 1928 he went to Baltimore and served for the spring term as Associate in Chemistry at Johns Hopkins University. The appointment was not renewed; but C. A. Kraus at Brown University engaged him as an instructor, and he remained in that position for five years. During this time he gave lectures on statistical mechanics, published the reciprocal relations and made progress on a variety of problems. Some of the results were published at the time, one with the able assistance of R. M. Fuoss; others formed the basis for later publications. In 1933 he accepted a Sterling Fellowship at Yale University, where he remained to serve as Assistant Professor 1934–1940, Associate Professor 1940–1945 and Josiah Willard Gibbs Professor of Theoretical Chemistry 1945–1972. Incidentally, he obtained a Ph.D. degree in Chemistry from Yale in 1935; his dissertation consisted of the mathematical background for his interpretation of deviations from Ohm's law in weak electrolytes.

Over the years, the subjects of his interest came to include colloids, dielectrics, order–disorder transitions, metals and superfluids, hydrodynamics and fractionation theory. In 1951–1952 he spent a year's leave of absence as a Fulbright Scholar with David Schoenberg at the Mond Laboratory in Cambridge, England, a leading center for research in low temperature physics. In the Spring of 1961 he served as Visiting Professor of Physics at the University of California in San Diego. Of his sabbatical leave 1967–1968 he spent the first three months as Visiting Professor at Rockefeller University and the last three as Gauss Professor in Göttingen. In 1962, at the suggestion of Manfred Eigen, he joined Neuroscience Associates, a small interdisciplinary group organized by F. O. Schmitt in Cambridge, Massachusetts.

Lars Onsager holds honorary degrees of Doctor of Science from Harvard University (1954), Rensselaer Polytechnic Institute (1962), Brown

University (1962), Rheinish-Westfählische Technische Hochschule (1962), the University of Chicago (1968), Ohio State University (Cleveland, 1969), Cambridge University (1970) and Oxford University (1971), and Doctor Technical from Norges tekniske høgskole (1960).

In 1953 he received the Rumford Medal from the American Academy of Arts and Sciences, in 1958 the Lorentz Medal from the Royal Netherlands Academy of Sciences, in 1966 the Belfer Award in Science from Yeshiva University, in 1965 the Peter Debye Award in Physical Chemistry from the American Chemical Society, in 1962 the Lewis Medal from its California Section, the Kirkwood Medal from the New Haven Section and the Gibbs Medal from the Chicago Section, in 1964 the Richards Medal from the Northeastern Section.

In 1969 he received the National Science Medal, and he became an honorary member of the Bunsen Society for Physical Chemistry. During Spring 1970 he was Lorentz Professor in Leiden (the Netherlands).

Onsager is a Fellow of the American Physical Society and the New York Academy of Sciences, a member of the American Chemical Society, the Connecticut Academy of Arts and Sciences, the National Academy of Sciences, the American Academy of Arts and Sciences and the American Philosophical Society, a Foreign Member of the Norwegian Academy of Sciences, the Royal Norwegian Academy of Sciences, the Norwegian Academy of Technical Sciences, the Royal Swedish Academy of Sciences and the Royal Science Society in Uppsala, an an Honorary Member of the Norwegian Chemical Society.