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SOME ASPECTS OF THE PROBLEM OF IONIC SOLUTIONS

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(*Mellor Lecture,* 1953, *to Wellington Branch, N.Z.I.C.*)

The distinguished chemist whom this Branch commemorates in its annual "Mellor Memorial Lecture" was one whose interests, as Professor Monro pointed out in his 1947 Lecture, were of astonishing scope and diversity. There is hence every reason for a chemist who is honoured by your invitation to give this lecture, to speak about the particular part of our wide-ranging science, in which his own interest lies. "Electrolytic solutions" wrote T. F. Young and A. C. Jones in their contribution to Volume 3 of the Annual Review of Physical Chemistry, 1952, "are being studied with increasing vigour and success. During the last five years, problems have been solved which had resisted repeated attacks for several decades." We can agree with the authors mentioned that "we are beginning at least to understand the meaning of solvation, and we are learning more about the differences between free ions and those bound in undissociated molecules or ion-pairs." As these happen to be some of the problems in which we have been interested at Canterbury College, I am glad to have the opportunity of giving an outline of the picture of an ionic solution as it is seen today, and of considering in greater detail, one or two specific problems in the field.

It is 70 years since Svante Arrhenius presented his famous thesis to the University of Upsala. The dissertation was awarded a fourth class (*non sine laude approbatur*) and his defence a third (*cum laude approbatur*). "The award amounted to a condemnation; in view of it Arrhenius could not normally become a docent in the University of Upsala" (Walker). The original idea contained in it was the division of dissolved molecules into active and inactive. He argued as follows: A solution of ammonia exhibits a feeble molecular conductivity which increases with dilution. He explains this by progressive conversion of non-electrolyte NH_3 into electrolyte NH_4OH and proceeds: "It has been shown that pure anhydrous hydrochloric acid is a non-con-

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ductor, that is a non-electrolyte. If water is added it is converted into an electrolyte, naturally in a progressive manner. It is impossible to deny the complete analogy of this phenomenon with that occurring on the dilution of ammonia or acetic acid, although it takes place much more rapidly." He sums up "The aqueous solution of any hydrate (i.e. acid or base) is composed, in addition to the water, of two parts, one active (electrolytic), the other inactive (non-electrolytic) . . . . Probably the active part (as with ammonia) is a compound of the inactive part and the solvent."

Four years later the full theory was born—or in Sir James Walker's phrase, "crystallised from solution." The "active part" became "ions", the conductance ratio became the measure of the fraction dissociated into ions, and the Van't Hoff factor i was related to the degree of dissociation. A new journal, the Zeitschrift für physikalische Chemie, was created to publish the work of the Three Musketeers of the Ionic Theory, or perhaps one should say of Physical Chemistry, Arrhenius, Van't Hoff and Ostwald. For weak electrolytes such as acetic acid, the ionic concentrations, calculated from the conductance ratio, gave satisfactory "dissociation constants" when applied to the Mass Action equation. The strong electrolytes on the other hand, which included most salts and certain acids and bases, while providing valuable qualitative support for the ionic theory, refused to obey any of its quantitative relations. Degrees of dissociation calculated by different methods failed to agree; the law of mass action failed to hold; effects of a salt on the solubility of another and on the dissociation of weak electrolytes could not be calculated from the theory. The discrepancies were much more marked in non-aqueous solvents than in water.

Between 1905 and 1910 evidence accumulated indicating that many properties of strong electrolyte solutions vary much less with concentration than would be expected from their classical (Arrhenius) degrees of dissociation. Particularly notable were the observations of Bjerrum and of Hantzsch on optical properties. Evidence, which had been invoked to prove the existence of ions in solution, indicated that the dissociation must be complete. Parallel to such developments was the work of G. N. Lewis, directed towards putting the thermodynamics of ionic solutions on a systematic basis. The first achievement of solution thermodynamics was to show that all the mechanisms used to determine equilibria in solutions may be used to determine the same quantity (Van't Hoff). In other words, measurements of freezing and boiling point changes, vapour pressure lowering, osmotic pressure, solubility or the potentials of suitable galvanic cells may all be used to determine the chemical potential (partial free energy) of an electrolyte. It is hence usualy possible to check and confirm the results obtained by entirely different mechanisms. In thermodynamic terms the chemical theory is expressed in the equations (for a binary electrolyte)

$$G_1 = G_1^\circ + 2RT \ln \alpha c \qquad (1)$$

$$K = \alpha^2 c/1\text{-}\alpha \qquad (2)$$

where G_1 is the chemical potential of electrolyte, α is the degree of dissociation at concentration c, and K is the equilibrium (dissociation) constant. In addition Arrhenius postulated

$$\alpha = \Lambda/\Lambda_0 \qquad (3)$$

where Λ is the equivalent conductance at concentration c

Λ_0 is the limit of Λ at $c = o$.

Lewis expressed the deviations of actual solutions from (1) and (2) by means of the "activity coefficient" (a term which had been used by Arrhenius in a different sense). The stoichiometric activity coefficient γ of a binary electrolyte is defined by

$$G_1 = G_1^\circ + 2RT\ln\gamma c \qquad (4)$$

and this is related to the (mean) activity coefficient of the ions by

$$\gamma = \alpha f \qquad (5)$$

In 1923 Debye and Huckel succeeded in calculating f_1, the activity coefficient of an ion, by assuming that its deviation from unity is caused by the effect of interionic forces on the thermodynamic properties of solutions. Physically they pictured the distribution of positive and negative ions in solution as resulting from a balance between the coulombic potential energy, which would produce a regular lattice arrangement as in a crystal, and the kinetic energy which would produce a completely random distribution. The term "ionic atmosphere" is a good description of the non-random yet non-regular arrangement of ions. The existence of this atmosphere leads to a lowering of the energy of the ions, which in turn is revealed in the deviation of the solution from "ideal" behaviour. The testing of this theory, by the different but interrelated methods mentioned earlier, has shown quite clearly that, as a quantitative theory, it gives equations which represent the correct "limiting law" for the thermodynamic properties, e.g., the activity coefficient $-\log f_1 = A\, c^{\frac{1}{2}}$ for a $1 - 1$ electrolyte (6) Many measurements were made on simple systems "to discover the nature of the transition from solutions so dilute that the theory is exact and measurements are impossible to those so concentrated that the theory becomes too complicated but measurements are relatively easy." (Scatchard).

In addition the development by Onsager (1927) of the earlier treatment by Debye and Huckel of the irreversible phenomenon of electrical conductance, led also to a "limiting law" relating equivalent conductance to concentration, the equation again containing $c^{\frac{1}{2}}$, "the hall-mark of phenomena depending on the (Debye-Huckel) ion atmosphere." (R. P. Bell). This equation takes the form

$$\Lambda = \Lambda_0 - (x\Lambda_0 + y)c^{\frac{1}{2}} \qquad (7)$$

and has been subjected to very severe testing by conductance measurements in water over the range 3×10^{-4} to 5×10^{-3}N, and also in other solvents. Major triumphs of the theory were the explanation of the effect of high field strengths on conductance (Wien effect) and the prediction of the effect of high frequencies (Debye and Falkenhagen).

Quantitative agreement is limited to dilute solutions; below 0.01 M for 1—1 electrolytes in water and at lower ranges still for electrolytes of higher valence type, and for all electrolytes in other solvents. This agreement is however sufficient to justify the basic model—strong electrolytes must be regarded as "completely dissociated" (not significantly different from 100 per cent.), and in any ionic solution the "ion atmosphere" has observable influences on the properties of the solution.

To Arrhenius we owe the concept of dissociation, almost complete for strong and incomplete for weak electrolytes. To Debye and Huckel goes the credit for showing qualitatively in all cases and quantitatively in dilute solutions, the importance of the coulomb forces. "Complete dissociation" states Redlich, "merely meant that electrostatic interaction, which according to the conclusive deductions of Debye and Huckel must be taken into account in any case, is sufficient to represent the data without an assumption of the existence of undissociated molecules."

In the concentration ranges normally of interest to the chemist, the "limiting laws" do not hold. The reasons are various. A more complex mathematical theory will no doubt be constructed—some notable attempts have been made—and will show that the fundamental model for the solution of a strong electroltye is valid at higher concentrations than can now be treated by the simple Debye-Huckel theory. But evidence exists for such variations from the fundamental model as the existence of undissociated molecules, ion-pairs (Bjerrum), triple ions (Fuoss and Kraus) and complex ions, and for the idea that the solvent plays a role other than that of only providing a dielectric medium in which the solute species can exist—in other words that ions are "solvated." The study of these variations is a complex problem. Ideally one would like to possess an experimental method of detecting and estimating each species present, and for determining whether and to what extent it is solvated; as well as an adequate theory, valid for all concentrations, of how the observable properties of the mixture of species are modified by the interionic and intermolecular forces which are known to operate. The concentrations of some species have unfortunately to be determined by difference. In the equation $\gamma = \alpha f$, while the γ is an experimental quantity no general method for determining α exists, and we have seen that the calculation of f is so far approximate only. Nevertheless progress has occurred and as Young and Jones claim some of it is worth looking into.

The classical method of determining the equilibrium constant for the dissociation of a weak electrolyte is the measurement of electrical conductance. Indeed the excellent "constants" found by Ostwald with this method played an important role in the acceptance of the Arrhenius theory. They are to some extent, however, fortuitous. Because the ionic concentrations are low, ion-atmosphere effects are small. Moreover the identification of α, the degree of dissociation, with Λ/Λ_0 the conductance ratio, which assumes incorrectly that the speed of the ions does not vary with concentration, produces a low value of α which, for water as solvent, almost exactly balances the increase in α which is produced by the ion atmosphere effect. Correction for the latter gives a dissociation "constant" (better called a "quotient") which increases with concentration. For example acetic acid at 25°C gives the following data:

m	10^5 K (classical)	10^5 K (corrected)
0.0001	1.776	1.778
0.001	1.781	1.797
0.01	1.804	1.840
0.10	1.795	1.846

The limiting value of K as m approaches zero—the thermodynamic dissociation constant—can be found by both conductance and galvanic cell methods, and is 1.754×10^{-5} (Harned). This is an important property of the acid, but so is the variable concentration quotient given in the third column.

In the hey-day of "complete dissociation" following the triumph of the Debye-Huckel theory, there was a tendency to ignore the possibility of small amounts of association (or incompleteness of dissociation) for strong electrolytes. Much credit for keeping this possibility in view should go to C. W. Davies, who on the basis of conductance measurements properly corrected for the effect of the ion atmosphere on both the speed of the ions (Onsager equation) and on the activity coefficients, published many dissociation constants for salt solutions. Some of his data are as follows:

Salt	$NaNO_3$	KNO_3	$MgNO_3^+$	$CaNO_3^+$	$PbNO_3^+$
K	3.8	1.6	strong	0.52	0.065

Salt	$NaSO_4^-$	$BaOH^+$	$MgSO_4$	$ZnSO_4$
K	0.20	0.23	0.007	0.0047

On the other hand it is by no means clear that these results demonstrate the presence of "undissociated molecules." O. Redlich has claimed for a number of years that the upper limit for the determination of the dissociation constant of an electrolyte by conductance (and allied) methods is not high. An example given by Young and Jones is noteworthy. For trifluoroacetic acid, Henne and Fox obtained 385 ohm^{-1} for the equivalent conductance at 9 x 10^{-4} M, and extrapolation gave Λ_0 as 390. These give an "Ostwald dissociation constant" of 0.07. However in the corrected method, used by Davies and others, the degree of dissociation α is equated, not to Λ/Λ_0 but to Λ/Λ_e where Λ_e is the equivalent conductance of the free ions, corrected for interionic effects. To determine Λ_e, use may be made of the fact that Λ_0 for $CF_3.CH_2COOH$ is almost the same as Λ_0 for acetic acid, and it is reasonable to assume that $\Lambda_0—\Lambda_e$ will be the same for both also. This gives Λ_e as 385.7 for trifluoroacetic acid, and a "dissociation constant" of 0.5. But if Λ_e is 0.2% smaller, or Λ (at 9 x 10^{-4} M) is 0.2% larger, K becomes infinite.

Hence "(a) the ratio Λ/Λ_0 can not be used for a determination of the dissociation constant of an electrolyte so strong as trifluoroacetic acid . . . . (b) The ratio Λ/Λ_e is useful only when Λ_e can be estimated with an uncertainty definitely smaller than the difference between Λ and Λ_e."

But how strong *is* this acid? A change in Λ_e of less than 0.2% increased the apparent value of the "constant" from 0.5 to infinity.

Redlich (1946) concluded that conductance methods and those depending on colligative properties are useless for K values above about 0.2, for 1—1 electrolytes. For those of higher charge types, the upper limit is lower, and he questioned the value 0.0047 attributed to zinc sulphate by Davies. It is not just a question of the order of magnitude of K, but whether it can be distinguished from infinity.

We may now consider a method of an entirely different kind taking as example some work done at Canterbury College on the lead halides. In 1949 Garrels and Gucker called attention to the discrepancies in the published dissociation constants of $PbCl^+$. A more extensive table than theirs is as follows:

	K (25°C)	
E.M.F. (Carmody)	0.0293	
E.M.F. (Hannan)	0.0289	
Conductance (Davies, etc.)	0.0304	(18°)
Conductance (James)	0.025	
Solubility (Von Ende)	0.06	
Absorption Spectra (Fromherz)	0.0775	(22°)
E.M.F. (Guntelberg)	0.10	
Abs. Spectra (Cavigli, 1950)	0.09	
Polarography (Vasilev, etc.)	0.023	

Some of the figures (Von Ende, Guntelberg) can be discounted as of low accuracy. The main discrepancy is between electrical methods, which give K in the range 0.025—0.03, and optical methods, which give a figure 3 times greater. The optical work has been repeated, first by A. I. Biggs and then, as a part of much more extensive investigations by M. H. Panckhurst, and the earlier work has been found to be in error. Panckhurst's final figures are K = 0.0315 ± 0.002 at 18°C for $PbCl^+$; K = 0.0165 ± 0.001 for $PbBr^+$, compared with Fromherz's 0.0709; and K = 0.012 compared with Fromherz's 0.0345, for PbI^+.

We have further satisfied ourselves that the E.M.F. method, though in agreement with the conductance work and this new optical work for $PbC1^+$ is not in fact satisfactory. A new analysis of Carmody's work shows that small variations in the standard potential of his cell, within the probable error of its determination, can cause considerable uncertainty in the value of K. Panckhurst chooses K = 0.033 as the best E.M.F. value, but with no great precision. Similarly an analysis of very good E.M.F. work on $PbBr_2$ by R. G. Bates gives scattered values of K for $PbBr^+$ in the range 0.03—0.04, very different from both Fromherz's value 0.071, and Panckhurst's 0.016.

This new optical work differs from that of Fromherz and Lih essentially in the determination of the extinction coefficient of the ion $PbC1^+$. Their curves are plots of log ξ against wave length, where ξ, the extinction coefficient, as defined by the Beer-Lambert law, viz.

$$\log I^\circ/I = \xi \, cl$$

I° is the intensity the incident of light, I is the intensity of the emergent light passing through a solution of concentration c mols lit. $^{-1}$ contained in a cell 1 cms. long.

Their work established that a band with maximum absorption at 208.5 mμ can be attributed to the Pb^{++} ion, presumably hydrated (see later). A point of intersection of the curves for different concentrations of $PbCl_2$ at 216mμ, indicates the presence of a chemical equilibrium between two absorbing species, whose spectra have the same extinction at this wave length. Fromherz and Lih showed that the second species is $PbCl^+$, and that its band has a maximum at 227 mμ. To use the Beer-Lambert relation as an analytical tool to find the concentration of $PbCl^+$ in a given $PbCl_2$ solution [and hence to calculate $K(PbCl^+)$], it is necessary to find ξ for $PbCl^+$ at some wave-length. Fromherz and Lih, making certain assumptions about shape of the $PbCl^+$ band, obtained $\xi PbCl^+$ by an algebraic method. They then used the value of ξ at the maximum (227 mμ), 11,750, to solve an equation relating the observed extinction for a solution of known concentration of $PbCl_2$, to the extinctions and amounts of Pb^{++} and $PbCl^+$. We consider their value for ξ_{max} for $PbCl^+$ is much too high, and this is the essential error in the work.

First of all it has been possible to obtain the absorption curve for $PbCl^+$ in a more satisfactory way, by a method introduced by Biggs. (This method was outlined.)

Secondly use was made of the fact that in solvents of decreasing dielectric constant (methanol-water mixtures), while the band moves to longer wave-lengths, its shape and height remain the same. The proportion of $PbCl^+$ increases greatly, so that in 98% methanol there is little Pb^{++} present at all in the concentration range used. It has thus been possible to find ξ_{max} for $PbCl^+$, and Panckhurst's final value of 6400, little more than half that of Fromherz and Lih, leads to the value of $K(PbCl^+)$ 0.031, mentioned earlier. Similarly ξ_{max} for $PbBr^+$ is 6800, and this value is a little more accurate than the chloride figure. For PbI^+ the position is less satisfactory. The absorption curve is complicated by the existence of a second band for all species containing I, with almost complete overlapping in some cases. Pankhurst estimated ξ_{max} at about 9000. (The value 10,200 has been determined since the lecture was delivered by Miss M. M. Smillie.)

With both the bromide and the iodide new bands appear on the long wave length side of the PbX^+ bands, in high methanol solvents. For example 0.00179 $PbBr_2$ in 98% CH_3OH gives a well-defined band with a maximum at 273 mμ. As this develops with increasing concentration of the salt the band for $PbBr^+$ decreases in height. As the $PbBr_2$ concentration is decreased, the new band decreases in height and that of $PbBr^+$ increases. Points of intersection indicate the presence of two species in equilibrium. Fromherz has developed a band at 304 mμ for $PbBr_2$ in water with addition of excess Br^- and attributed it to $PbBr_4{}^=$. Accepting this it seems clear that the new band is that of $PbBr_2$ It is not possible, however, to determine its dissociation constant, nor that of PbI_2, desirable though such results are.

The determination of these constants involves no assumption about the nature of the complex, nor about the nature of the absorbing process which gives such high extinction coefficients, which are of the order of those of organic dyes. (The question was discussed whether the complex ions are ion-pairs or molecular ions.)

Some consideration of solvation is now necessary.

It has long been generally accepted that ions are "solvated" and with the growth of understanding of co-ordination and of ion-dipole interaction, the concept has become much clearer. The habit of representing the important hydrogen ion in water as H_30^+ (or better OH_3^+ by analogy with NH_4^+) and other ions as M^+ or X^-, rather obscures the fact that most ion species are probably complexes. Unfortunately quantitative estimates of "hydration numbers" for ions in aqueous solution show little more than that some properties of the solutions (e.g., mobility) appear to reveal a much greater range of influence of the ion on the water molecules than other properties (e.g., partial molal volumes). Bockris reviewed some 12 different methods of estimating hydration numbers and those attributed to the Na^+ ion at infinite dilution range from one (partial molal volume) to about 700 (polarimetry).

Bockris hence suggested division of the total solvation number into "primary" and "secondary" solvation. The former is the number of solvent molecules which constitute, together with the ion, a mechanical unit that moves during electrolytic transport as a single entity—the solvent molecules having lost their own translational degrees of freedom. "Secondary" solvation refers to all "electrostatic interactions which are not included" in the primary solvation. It would seem that secondary solvation must remain a hazy concept, varying with the particular property of the solution upon which interest is focussed. Primary solvation numbers on the other hand may be expected to be small and relate to the number of solvent molecules which can form an immediate sheath round the ion. For this reason a theoretical approach such as that initiated by Bernal and Fowler (1933) seems to be the most promising. Their theory of the structure of liquid water has been improved upon by Lennard-Jones and Pople but their picture of ionic hydration is still useful.

The internal electric field of liquid water is controlled by the electrostatic field of the dipoles of the water molecules. Introduction of charged ions will modify the field, the effect being roughly proportional to the polarising power of the ion, as measured by the charge/radius ratio. Thus large monovalent cations (Cs^+) will have the least effect: small polyvalent cations (Al^{+++}) will have large effects. It is known that the mobilities (speeds) of large ions (K^+ Rb^+ Cs^+ Cl^- Br^- I^-) are about the same, while small ions

(Li^+ Mg^{++}) move much more slowly. The latter are almost certainly much more hydrated. Bernal and Fowler considered that the simplest and most accurate method of estimating hydration is by the densities of ionic solutions, which lead to the result that, in dilute solutions, the increase ΔV in volume caused by adding a mol of electrolyte to the dilute solution is constant, and additive for the ions, i.e., $\Delta V = V_+ + V_-$. Further the increase is roughly proportional to the size of the ions. To divide ΔV between the cation and anion some arbitrary assumption is needed, e.g., that V_{CsCl} can be divided in the ratio of the ionic volumes in the solid $V_{Cs^+} : V_{Cl^-} = 27 : 37$. It then turns out that for all anions except OH^- and F^-, and for large cations such as Rb^+ and Cs^+, the apparent volumes in solution are close to the volumes in solid. Presumably the hydration is zero. For other ions V_+ is either negative or much less than the volume in the solid. Hydration seems the likely reason, since it will disturb the open structure of liquid water. Hydration will be complete when the hydration number is equal to the co-ordination number for the ion in the crystal, e.g., 4, 6 or 8 according to the ionic radius. The theory leads to the idea that ions such as Na^+ K^+ F^- are permanently hydrated with $n = 4$. Larger ions such as Cs^+ or Cl^- also show 4 co-ordination but are not permanently hydrated, moving in the solution exchanging water molecules. Bernal and Fowler use their theory to calculate hydration energies, which are readily calculated also from experimental data. The agreement is reasonably good.

Among the methods published for determining hydration numbers is one by R. H. Stokes and R. A. Robinson, depending on the variation of activity coefficients with concentration for relatively strong solutions. Their values are higher than seem likely for primary solvation and the assumption that the Debye-Huckel theory is applicable in their concentration range, apart from hydration effects, seems rather doubtful. Typical parameters of their equation are as follows:

HCl 8 $HClO_4$ 7.4 $LiCl$ 7.1 $NaCl$ 3.5 KCl 1.9
$RbCl$ 1.2 $MgCl_2$ 13.7 $CaCl_2$ 12.0

These numbers, in the author's words are numbers "introduced to allow for the average effect of ion-solvent interactions where these are largely compared with **k**T and may well contain contributions from solvent molecules outside the 1st layer."

We are endeavouring at Canterbury College to consider the relation of ionic hydration to the standard potential of certain galvanic cells. The cell

H_2 (g) | HCl (m) solvent | $AgCl$ (s) | Ag

is usually stated to allow the reaction

$$\tfrac{1}{2} H_2 (g) + AgCl (s) = H^+ (m) + Cl^- (m) + Ag (s)$$

to proceed. If, however, the ions are hydrated to the extent of (x + y) water molecules per HCl, the reaction is

$$\tfrac{1}{2} H_2 (g) + AgCl (s) + (x + y) H_2O = H^+xH_2O(m) + Cl^- yH_20 (m) + Ag (s)$$

and the free energy change obtainable from the E.M.F. of the cell must refer to this second reaction. Dr. F. A. Johnson derived an equation from which (x + y) could be obtained from the measurements of the standard potential of the cell which have been made over several years in a series of mixed solvents (methanol-water). It is necessary to assume that, for solvents not too high in methanol, the ions are preferentially hydrated—a reasonable assumption.

The results appeared to support x + y = 1, which agrees with the concept that the hydrogen ion is singly hydrated, and the chloride ion unhydrated. The theory has since been tested using the cell

$$Na_xHg \mid NaCl \text{ (solvent)} \mid AgCl (s) \mid Ag$$

The results are not, however, at all decisive.

I have reviewed the current position with regard to degrees of dissociation, the "ion-pair" concept, and ionic solvation. One thing is very clear, the importance of adequate theory. Despite the insight of Bjerrum, especially into the idea of "complete dissociation" and the systematic work of the school of G. N. Lewis in the thermodynamics of ionic solutions the whole field was to some extent languishing till Debye and Huckel revived it with a brilliant theory. There is nothing unique in this. The business of science, as I understand it, is the development of theories—explanatory theories of increasing breadth of application—tested by experiment, which has the last word, not the first as inductivists believe. The experimenter can say "this theory is wrong" and that it must be either modified or abandoned. It is doubtful whether he can ever say "this theory is true" in any absolute sense—some other experiment, equally well founded, may later refute him. In novels of crime detection, to which I am somewhat addicted, I am always impatient with the investigator who, allegedly, declines to theorise until he has more "facts." What is a fact and how can it have significance except in relation to a theory?

However, in a complex field, such as the one I have been discussing, really significant theories such as those of Arrhenius and of Debye and Huckel do not grow in a vacuum. In a sense the experimenter must wait on the theorist. Kohlrausch's long and arduous labours in measuring the conductances of ionic solutions led him only to the Law of Independent Migration of Ions, which is strictly valid at $c = 0$, and an empirical relation which required Debye and Huckel's theory to explain it. Nevertheless systematic experiments, properly related to the broad principles of a science, can both lead to useful empirical relations, such as that of Kohlrausch or Lewis and Randall's Ionic Strength Principle, and provide hints to the theorist on lines for profitable exploration. In chemistry the principles of thermodynamics are a safe guide in the formulation of questions and the expression of results. The determination of the values of the thermodynamic functions for ionic reactions is always a fruitful procedure for the experimenter. From this standpoint the system Metal—amines has been studied during the last five years at Otago University by Mr. W. S. Fyfe. The papers which he has published in the Journal of the Chemical Society summarising his extensive results and his interpretation are a credit to New Zealand work in pure chemistry. Among other studies he has determined the heats of ammination of certain metal ions, and by combining them with the free energy data of J. Bjerrum, has obtained the entropy changes. Fyfe considers, rightly, I think, that his observations refer to the reaction.

$$[M(H_2O)m]^{z+} + n\,NH_3 = [M(NH_3)n]^{z+} + m\,H_2O$$

That is, he assumes that ions are hydrated in aqueous solution and that the formation of the ammine complex involves displacement of H_2O by NH_3. Some of his data are as follows:

Ion	n	$-\Delta H$	$-\Delta S$	$-\Delta S'$
H^+	1	12.4	-0.5	3
Ag^+	2	13.5	12.4	6
Cu^{++}	4	21.1	16.2	12
Zn^{++}	4	15.9	13.7	12
Ni^{++}	6	18.9	27.7	18

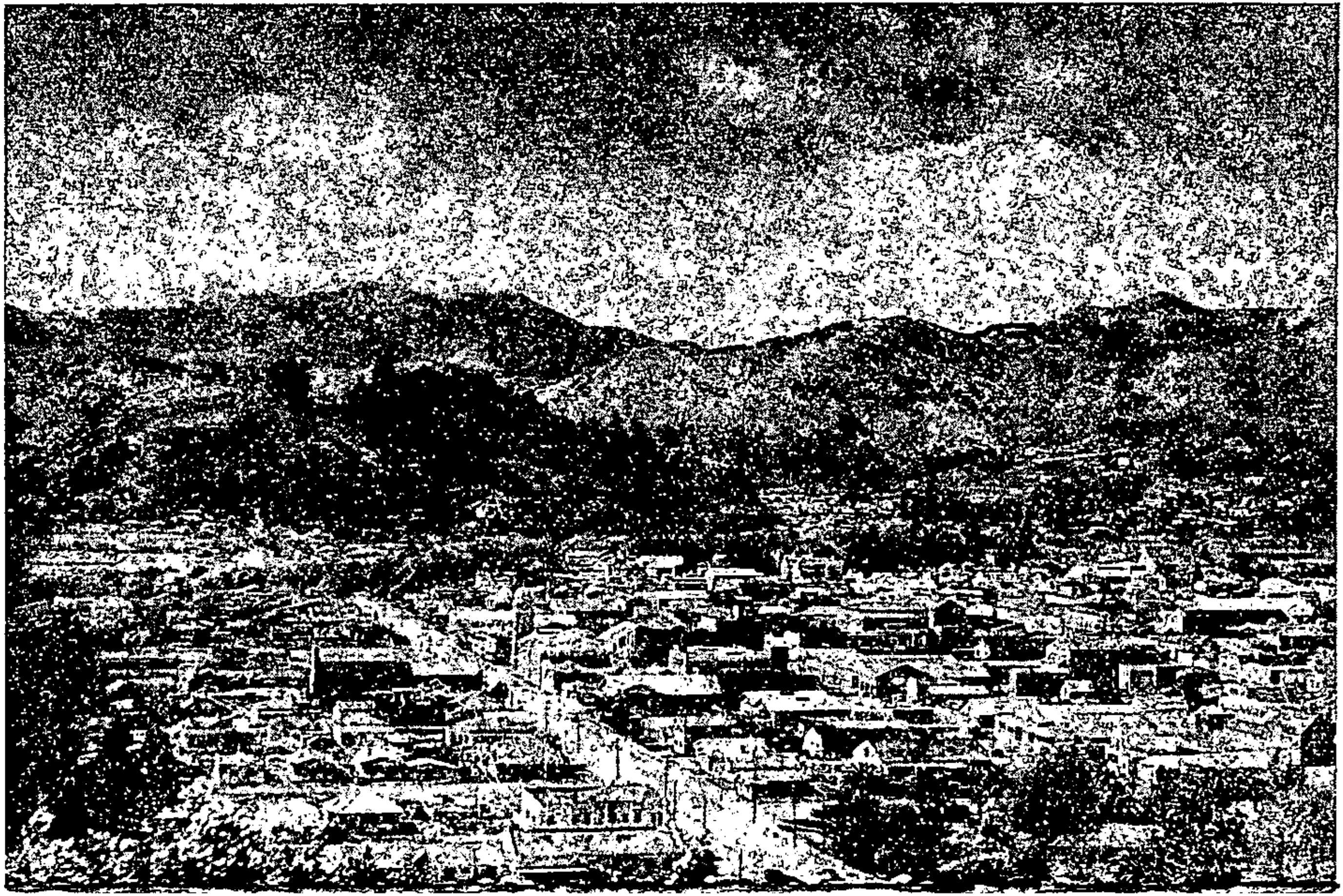
Fyfe discussed his results in terms of a theory put forward by Ulich. The latter considered the entropy of hydration of gaseous ions and the entropy difference between hydrated salts and the corresponding non-hydrated salts. The results suggested that when a water molecule becomes bound to a cation, the average entropy change is about the same numerically as the entropy of fusion of water at 25°C viz. 6 cal mol^{-1} $deg.^{-1}$. Hence he obtained hydration numbers by dividing the entropy of hydration of the gaseous ion by 6. This is an oversimplification, since it assumes that all water molecules are bound by all ions to the same extent. Ulich's value would be a minimum figure, and if the true value is about 10 cal mol^{-1} $deg.^{-1}$, reasonable hydration numbers are obtained, e.g., $n = 6$ for the transition metal ions, $n = 2$ for Ag^+.

In a preliminary way, Fyfe compares his entropy of ammination figures with the difference between the entropies of fusion of NH_3 and H_2O, viz. 3 cal mol^{-1} deg^{-1}. The column $\Delta S'$ in the table are the calculated figures. The figures are parallel and suggest that the ions carry no more water molecules than ammonia. If they did, the experimental figures would be more positive than those calculated. Actually they are more negative.

A more detailed analysis does not change the picture and Fyfe's results support the concept of small (primary) solvation numbers.

It is the privilege of a member of a university staff to be associated with intelligent and energetic young people, and to have some of the very best of them working on any problems in which he may be interested. I am certain that the quality of research students in the University which gave Joseph Mellor his first training remains high. Indeed, I doubt if it has ever been higher than it is today and I believe some of the products of each of the chemistry departments of the four colleges, who have already done fine work as research students, are destined to follow Mellor's lead as mature investigators, teachers and writers.

NELSON: A view of the vicinity of the Cawthron Institute, our hosts at this year's Conference.



NEWS AND NOTES

Dr. G. A. Nicholls has returned to New Zealand after lecturing for two years at the University of Rochester, U.S.A., and subsequently doing research in England. Dr. Nicholls has joined the staff of New Zealand Forest Products Ltd. as a research chemist.

At the April meeting of the Auckland Branch we were privileged to discuss a variety of subjects with Dr. Leslie Lampitt, who is combining some work with the pleasure of a world tour. Dr. Lampitt discussed the work of the International Union for Pure and Applied Chemistry and it is hoped that salient features of the Union will be published at a later date. During the evening Dr. Lampitt also expressed his opinions on the relationship between management and the Chief Chemist, observing that in his own case the management gave him a completely free hand in all matters. He employs a staff of over 200 and divides the laboratory working hours into three, one-third is for control analysis, one-third for applied research and the other third for pure research, the only restriction on the latter being that the subject can be related to the food industry, a very wide field.

Dr. V. Armstrong, who is to be appointed Scientific Adviser to the New Zealand Government in England when Dr. Marsden returns shortly, has been spending some time back here. During March he addressed the Wellington Branch on "Applied Research in the U.S.A., with particular reference to problems associated with coal and fuel research."

At the April meeting of the Wellington Branch, Dr. J. W. Lyttelton, of the Grasslands Division, Palmerston North, spoke on "Fractionating of Protein Mixtures."

Mr. O. H. Keys, Government Analyst, Dunedin, has left for a four months' visit to France, the United Kingdom and U.S.A. During this visit he intends gathering as much information as possible on foods and food additives, toxicology of modern drugs, forensic chemistry, water treatment, industrial hygiene and atmospheric pollution. He expects to return at the end of August. During his absence Mr. D. F. Nelson will be acting in his stead.

Mr. G. J. E. Hunter, Travis Research Fellow, has been appointed Senior Lecturer in the Biochemistry Dept. of the Otago University Medical School. Mr. Hunter worked at the Dairy Research Institute, Massey Agricultural College, prior to his appointment five years ago to the Travis Tuberculosis Research Laboratory where he has been working on the metabolism of *Mycobacteria.*

BOOK REVIEWS

Biochemical Preparations, Vol. III. Edited by E. E. Snell, 128 pp., John Wiley and Sons, New York, Nov. 1953. $3.50. In this third volume of a series that is becoming increasingly well known and valuable for its well authenticated methods for the preparation of substances of interest to biochemists there are details for the preparation of a further 24 products. The descriptive details given appear very full and are well referenced. Each method has been checked by an independent group of workers whose comments where applicable have been included. A cumulative index for the three volumes so far published is given. Binding and printing are typically good—G.M.W.

General Chemistry (2nd Edition), by Linus Pauling. 722 pp., W. H. Freeman and Co., San Francisco, September, 1953. $6. Four years ago we reviewed the first edition of this book, J.N.Z.I.C., 1950, XIV., 144. Pauling has revised the first edition "in such a way as to make it especially suited to use by first-year college students who plan to major in chemistry and by other well prepared students with a special interest in the subject." On reading this second edition one is amazed at the excellent coverage Pauling has given of the many facets of modern chemistry. One is, however, left with the impression that in some things, particularly descriptive chemistry, the book is weak but, in defence of this, Pauling in his preface states "in particular, a smaller amount of time can now be devoted to learning the facts of descriptive chemistry, because many of these facts have been correlated and systematised by new principles." The coverage of the modern theory of chemistry is excellent for the degree of instruction intended. The book is extremely ably illustrated by Roger Hayward with a resultant clarity in the text. The application of the theoretical and descriptive chemistry to industrial uses has been amply illustrated, this is of great assistance in maintaining a high level of interest by the student. This well produced book could be highly recommended for post-matriculation students and as supplementary reading for Stage I. students. The binding and printing are an improvement on the first edition.—G.M.W.

Introduction to Chemistry, by R. T. Sanderson. 542 pp., John Wiley and Sons, New York, January, 1954. $5.50. In the preface the author states, "This book is long on explanations and short on purely descriptive chemistry. There are several excellent textbooks on the market which contain almost everything related to chemistry, but this is not one of them. . . . true learning is composed both of memorisation and understanding, the former being greatly aided by the latter. What I have tried to do in this book is to give only the most essential information, and explain it as thoroughly and simply as possible." This text book has been written for the equivalent of our matriculation students and in many respects the facts are well presented with a logical build-up but the author, both in style and in the information given, has at times underestimated the intelligence of his readers whilst on other occasions he has included information which, although relevant to the matter being discussed, belongs more correctly to physics than to chemistry. The reviewer feels that the author has attempted too much in covering the amount of chemical theory that he has, resulting in restrictions in the amount of descriptive amplification he could give to the more advanced theoretical chemistry. It would appear that a concise summary of the chemistry that students learned in their Junior High School classes would be sufficient to revive this background thus leaving the author most of the first 80 pages free for more valuable information. Some of the descriptive chemistry includes too little useful information to be of value for any purpose and could have been left out without loss. The practice of inserting odd chapters of descriptive chemistry as a sandwich between theoretical considerations for which the descriptive chemistry was of no special value for amplification proved disconcerting and spoiled the continuity of the book. The book has some excellent chapters, particularly on valence and periodicity but the price for a college text-book is too high.—G.M.W.

Dictionary of Organic Compounds, Sir Ian Heilbron and H. M. Bunbury, Editors-in-Chief; A. H. Cook and E. R. H. Jones, Editors. New and Revised Edition, 1933. 654, 845, 838, 694 pages. London: Eyre and Spottiswoode. £7 per volume (U.K.). This is in effect the first complete revision of this well-known work since it was first issued in the years 1934-37. In 1943 a new edition of Volume I. was issued, but owing to war conditions, the other two volumes could only be reprinted with brief supplements. The high esteem in which the original work has been held will assure a welcome for this new edition. The inclusion of 2500 new compounds and a corresponding number of derivatives has led the publishers to issue this edition in four volumes for convenience in handling. An increase in page size to 10 x 7¼ inches has also assisted in this direction. The Dictionary is so familiar that it is hardly necessary to describe its original form which has been maintained by giving the following information about each compound:—Structural and empirical formula, molecular weight, physical properties, some characteristic reactions, and some leading references. The number of details given about each compound vary with its importance. Apart from the inclusion of new compounds, the literature has been searched for more recent information on the original entries. The selection of new information seems reasonable though there is a definite leaning towards compounds of biochemical interest. No compounds containing deuterium have been included and there are signs that the revision of data on compounds of less biological interest has not been so thorough, e.g., boiling point of 110-120° for 3-methyl heptane. On the other hand errors are very few indeed which is an achievement in view of the vast amount of checking and counter-checking required. The issue of the whole of the new edition at one time, is also commendable. The printing and binding are such that the volumes are very pleasant to use with a clear type-face of reasonable size and good quality paper. The price is not unreasonable though beyond the reach of individual chemists. The widely advertised offer of these volumes in New Zealand at a surcharge of £9/10/- per set seems hard to justify.—S.G.B.

Lehrbuch der Organischen Chemie, by Paul Karrer. 12th Edition, 949 pages. Stuttgart: George Theime Verlag. D.M.59.70. The most obvious change in the new edition is the use of a larger page size and rather thinner paper which makes the volume much more pleasant to handle. The whole volume has therefore been reset, but only a few changes occur in the actual text. It is regretted therefore that this edition is in some ways less up-to-date than the latest English edition (which is also cheaper). The translators evidently picked up some points missed by the author, which raises the question:—Can so eminent a chemist as Prof. Karrer by his own unaided efforts keep a large textbook of organic chemistry up-to-date through twelve editions?—G.S.

Structure and Mechanism in Organic Chemistry, by Professor C. K. Ingold, of University College, London. 828 pages. G. Bell and Sons Ltd. (London), 1953. Price £3/17/6. As a book on the more academic aspects of structure and mechanism in Organic Chemistry, this book cannot be surpassed both in its completeness of subject matter and the exceedingly lucid method of presentation. Its title makes it sufficiently clear that it is not a book on general Organic Chemistry. After some introductory chapters on basic theory of valence, molecular structure and interactions both between and within molecules, Ingold goes on to discuss the physical properties of molecules. As we have been recently favoured by a visit from the author, many members of the Institute will be acquainted with the general method of presentation followed in the book. Surprisingly, very little use is made of molecular orbitals in the discussion of mechanism of organic reactions—mostly the more familiar concept of electron displacement is used. This has the effect of making the book intelligible to the non-mathematician; hence will be almost universally favoured among Chemists. The chapters on Classification of Reagents and Reactions, Electrophilic Aromatic Substitution and Nucleophilic Aliphatic Substitution form the real foundations for the book. Here the concepts of the mesomeric and inductive effects are discussed and the directional nature of aromatic and aliphatic substitution developed. Then follow chapters which discuss Olefin-forming Eliminations, Saturated Rearrangements, Additions and their Retrogression, Acids and Bases, Carboxyl Reactions and Nucleophilic Aromatic Substitution. The large extent to which this book is a record of the contributions of Ingold and co-workers to the mechanisms of Organic reactions, can be judged from the frequency with which the author's name appears in its references to original literature. In its references the book is very up-to-date and it also includes the results of much research which had not appeared in the Chemical literature at its date of publication. The book is very well set out and printed. To sum up it is a book which should strongly appeal to all Chemists who are interested in the mechanism of Organic reactions.—H.B.

Elementary Quantitative Analysis, by Ralph L. Van Peursem and Homer C. Innes. pp. 383, 1953. McGraw Hill Book Co. Inc. 34/-. This is an excellent book. It is primarily a text book dealing with both theoretical and practical aspects of quantitative analysis but it could justify its existence on the shelves as a first reference book. The content is based on a national survey of first year quantitative analysis courses in the U.S.A. As all topics, whether of theoretical or laboratory application, which are treated in at least 25 per cent. of such courses have been included the text book has a very wide scope. Not only is there a good coverage but the individual sections are treated very thoroughly. The book is in four sections: I. Principles, II. Calculations, III. Laboratory experiments, IV. Techniques. The section on Principles includes such topics as preparation of samples, measurements of quantity, chemical equilibria, precipitation phenomena, quantitative separations, determination of the desired constituent, neutralisation, electrodeposition and oxidation and reduction. All the sections begin at first principles and generally end at a reasonably advanced level. The section on laboratory exercises includes a wide variety of analyses which are mostly typical of a number of common determinations. The last section contains advice on many techniques which every trainee should know but which are frequently left for him to discover by chance. There are adequate references throughout to more standard texts and, where necessary, to the journals. Many questions and problems are also included. The index is adequate but could probably be improved. All in all this is a book which can be strongly recommended. It should find its place in every teaching laboratory and laboratories where laboratory assistants are trained.—H.S.M.

Experiments, Theory and Problems in General Chemistry, by H. W. Stone and J. D. McCullough, pp. 352, 1953, McGraw Hill Book Co., Inc. 45/-. This book covers the first half year's laboratory work in chemistry at the University of California. The teaching of chemistry is approached through the laboratory work with less emphasis on formal teaching. The reviewer feels that this is a dangerous approach as it tends to develop a habit of generalising far beyond the data available, but this may, however, be a personal matter. The experiments in the course are elementary and detachable data and report forms are provided. These are interesting as a teaching device in the handling of large numbers of students but seem to spoon-feed the students too much. It is claimed that such a method creates an orderly habit in recording experimental results but it could be argued that the student will have little idea of what to do when printed forms are not available. A feature of the course is the number of experiments dealing with 'unknown' samples. Probably as a result of the 'practical' method of teaching the theoretical sections are fairly sketchy. There is, however, a large number of problems which cover a wide range of difficulty. —H.S.M.

Laboratory Experiments in General Chemistry and Semi-Micro Qualitative Analysis, by George W. Watt and L. O. Morgan, pp. 228, 1953, McGraw Hill Book Co. Inc. 26/6. This is a laboratory course in general chemistry and semi-micro qualitative analysis designed to cover a year's work. It is presumably the course used at the University of Texas as the co-authors are respectively Professor and Associate Professor of Chemistry at that University. The experiments which are generally supplemented by labelled diagrams of the assembled apparatus are quite worthwhile and in some cases quite novel. Many of the experiments are interesting in using very simple apparatus and this may help to dispel a common belief that American colleges and universities are unable to do anything without elaborate ground glass apparatus. The section on analysis is well introduced by experiments dealing with the reactions of cations generally before proceeding to the group separations. The book is interesting as an example of a teaching method in that report sheets are included for all experiments. These sheets, which are printed with blanks left for the insertion of the student's results, are perforated for easy removal and punched for subsequent ring binding. While this type of result sheet might save the teacher a considerable amount of work it will probably leave the student at a loss in later work where such forms are not available. On the whole this book could prove a useful guide to teachers of elementary chemistry.—H.S.M.