XC.—*The Electrical Conductivity of Pure Salts in the Solid and Fused States. Determination of the Activity-coefficients of Ions in Solid Salts.*

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RECENT researches on *X*-ray analysis of crystal structure have proved conclusively that the atoms of a salt are arranged symmetrically in a space-lattice. Debye and Scherrer have also considered the possibility of ionisation in crystals of electrolytes (*Physikal. Zeitsch.*, 1918, **19**, 474). They assume that the diffract-

ing power of an atom depends on the number of electrons in the atom. This is equal to the Moseley number in a neutral atom. From the effective reflecting values of planes alternately wholly lithium and wholly fluorine, in a crystal of lithium fluoride, they conclude that the lithium atom has lost, and the fluorine atom has gained, an electron. Thus the internal ionisation of a solid salt is always complete.

Although ionisation is complete, the ions are not free to glide past one another, because of the great magnitude of the forces of cohesion, which prevent the displacement of an ion from its position of equilibrium in the crystal lattice. It is only at high temperatures, when the average kinetic energy of the ions has become sufficiently great for some of them to overcome this field of elastic force, that the electrical conductivity of the solid salt is observed. The number of free ions in a uni-univalent salt is given by the equation

$$2n = 2N \cdot e^{-\frac{W}{2kT}} \quad \dots \quad (1)$$

where N is Avogadro's number and W may be defined as the work that the ions of a gram-molecule must perform against the forces of elasticity before they can be free to glide past one another at the absolute temperature, T . On the assumption that Ohm's law is always valid, the specific conductivity is given by the equation

$$\mu = \frac{2n}{v} \cdot U \quad \dots \quad (2)$$

where v is the molecular volume of the salt and U the average mobility of the ions at T , or

$$\mu = \frac{U}{v} 2Ne^{-\frac{W}{2kT}} \quad \dots \quad (3)$$

Variation of W with Temperature.

The transition of ions from the bound to the free state inside the solid salt may be considered as a physico-chemical process attended with an absorption of energy, W , for each gram-molecule. In a condensed system, the variation of the energy of transition with temperature is given by the equation

$$W = W_0 + \beta T^2 \quad \dots \quad \text{Nernst theorem} \quad (4)$$

It appears plausible that equation (4) may be valid in this particular case. The nature of the forces operating in the interior of a solid salt is practically unknown, and can only be considered in a general way. Larmor has investigated the case of a fluid

composed of finite particles, and concludes that the force at an internal point, due to particles surrounding the point, is separable into two parts, one being due to the medium as a whole and the other a purely local part. The first part can be determined, as it depends on the potential due to the combined volume and surface-density distributions of Poisson. For an isotropic liquid, the second part can be easily neglected, as the particles are in a state of violent, irregular motion, and their axes are distributed quite haphazardly. In the case of a crystal, however, there is a definite geometrical configuration. The atoms, arranged in a space-lattice, immediately surrounding the point, give rise to a purely local force at that point. So long as the crystalline structure is maintained, the motion of the particles is not random, and there is no cancelling out of the forces due to each particle. The magnitude of W depends on the purely local part of the forces at an internal point, and from its very nature remains unknown. It is fairly certain, however, that it runs parallel with the forces of elastic rigidity inside a solid. It is well known that the plasticity of crystalline substances increases very rapidly with temperature, hence W diminishes with increasing temperature. β has thus a negative sign. At the melting point, where the purely local part of the forces is negligibly small, we may assume that

$$W = W_0 + \beta T_m^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where T_m is the melting point of the salt.

β can thus be easily expressed in terms of W_0 being equal to

$$- \frac{W_0}{T_m^2}.$$

Therefore at any temperature, T ,

$$W = W_0 - \frac{W_0 T^2}{T_m^2} = W_0 \left\{ 1 - \frac{T^2}{T_m^2} \right\} \quad . \quad . \quad . \quad (6)$$

Variation of the Mobility of the Ion of a Solid Salt with Temperature.

The variation of the mobility of an ion in a solid with rise in temperature can be easily accounted for in a way analogous to that developed in the electron theory of metallic conduction. If X is the strength of the electric field, the force acting on an ion is Xe . If the ion were perfectly free to move, there would be a constant acceleration of $\frac{Xe}{m}$ in the direction of the field, where m is the mass of the ion. There are, however, frequent collisions

with other ions, when all the accumulated energy of the ion is lost. It may be considered as the criterion of the solid state that the whole of the velocity of the free ion, added by the electric field, is removed at each collision, and the ion starts its course again with zero velocity. Let τ be the time taken by the ion to describe the mean free path, L . The velocity of the ion at the end of the mean free path due to the electrical field is $\frac{Xe\tau}{m}$.

Therefore the average velocity added by the field in its own direction :

$$U' = \frac{1}{2} \cdot \frac{Xe\tau}{m} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If V is the speed of the ion due to the combined effect of the electrical field and thermal agitation, then $\tau = \frac{L}{V}$. Since, however, the velocity of thermal agitation is very large compared with the velocity added by the electrical field, the value of V will be almost equal to V' , the velocity due to thermal agitation alone. Therefore

$$U' = \frac{1}{2} \cdot \frac{Xe}{m} \cdot \frac{L}{V}$$

$$V' = \sqrt{\frac{3 \cdot RT}{M}}$$

so that

$$U' = \frac{1}{2} \cdot \frac{e}{m} \cdot \frac{L}{\sqrt{3 \cdot R \cdot \frac{1}{M} \cdot T}} \cdot X \quad . \quad . \quad . \quad . \quad (8)$$

Now $L = \frac{\lambda^3}{\frac{4}{3}\pi S^2}$, where λ is the mean distance of the supposedly

spherical ions and S the distance between the centres of gravity of two ions in collision. Since the coefficient of cubical expansion is negligibly small, L may always be regarded as constant.

Hence
$$U' = \frac{k'}{\sqrt{T}} \cdot X$$

or the mobility

$$U = \frac{k'}{\sqrt{T}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Variation of the Specific Conductivity of a Solid Salt with Temperature.

Substituting the values of U and W from equations (9) and (6) respectively, in equation (3) we get

$$\mu = \frac{k'}{v} \cdot \frac{1}{\sqrt{T}} \cdot 2N \cdot e^{-W_0 \left\{ 1 - \frac{T^2}{T_m^2} \right\} / 2RT} \quad \dots (10)$$

Since the change in molecular volume with temperature is negligible in the case of a solid,

$$\mu = \frac{k}{\sqrt{T}} \cdot 2N \cdot e^{-W_0 \left\{ 1 - \frac{T^2}{T_m^2} \right\} / 2RT}$$

$$\text{or} \quad \frac{W_0 \left\{ 1 - \frac{T^2}{T_m^2} \right\}}{2RT} = \log_e \frac{2N \cdot K / \mu \sqrt{T}}{e} \quad \dots (11)$$

$$\text{or} \quad \frac{W_0(T_2 - T_1)}{2R} \left\{ \frac{1}{T_1 T_2} - \frac{1}{T_m^2} \right\} = \log_e \frac{\mu_2 \sqrt{T_2}}{\mu_1 \sqrt{T_1}} \quad \dots (12)$$

Equation (12) contains only one unknown constant, W_0 , which can be easily obtained from any two values of μ . In the following tables, it will be seen how satisfactorily the above equation reproduces the observed values of μ . Column 4 of these tables contains the values of α —the activity-coefficient of the ions of a solid salt at various temperatures. They are calculated from equation (1):

$$\frac{W}{2RT} = \log_e \frac{2N}{2n} = \log_e \frac{1}{\alpha} \quad \dots (13)$$

$$\text{or} \quad \frac{W_0 \left\{ 1 - \frac{T^2}{T_m^2} \right\}}{2RT} = \log_e \frac{1}{\alpha}.$$

It will be noticed that the specific conductivity of the salts in some cases has increased almost a thousand times, but throughout this range, values of μ calculated from equation (12) agree with the observed values within 5 per cent. The observed specific conductivities in the case of sodium and potassium chlorides are taken from the work of Benrath and Wainoff (*Zeitsch. physikal. Chem.*, 1911, **77**, 257). The limits of experimental error, according to their own statement, are ± 10 per cent. The data for the haloids of silver and thallium are obtained from the work of Tubandt and Lorenz (*Zeitsch. physikal. Chem.*, 1914, **87**, 529).

TABLE I.

Sodium Chloride. $W_0 = 51.2$ kg. cal. $T_m = 1083$ absolute.

T (absolute).	μ calc. $\times 10^6$.	μ obs. $\times 10^6$.	α calc.
903	—	12.6	0.0127
923	21.2	21.2	0.0216
943	35.4	35.0	0.0363
983	91.0	95.0	0.0988
1023	240.0	240.0	0.2551
1073	729.0	729.0	0.8034

TABLE II.

Potassium Chloride. $W_0 = 50.9$ kg. cal. $T_m = 1063$.

T .	μ calc. $\times 10^6$.	μ obs. $\times 10^6$.	α calc.
923	—	6.5	0.0324
933	8.4	8.4	0.0423
983	29.2	28.8	0.1469
1013	59.6	59.6	0.3095
1043	120.0	133.0	0.6295

TABLE III.

Silver Chloride. $W_0 = 25.6$ kg. cal. $T_m = 726$.

T .	μ calc.	μ obs.	α calc.
523	—	0.0003	0.0026
573	0.0016	0.0015	0.0142
623	0.0068	0.0065	0.0645
673	0.0260	0.0260	0.2587
723	0.0980	0.1100	0.9292

TABLE IV.

Silver Bromide. $W_0 = 24.8$ kg. cal. $T_m = 690$.

T .	μ calc.	μ obs.	α calc.
473	—	0.00052	0.00089
513	0.00238	0.00230	0.00427
553	0.01000	0.00910	0.01734
623	0.08000	0.08000	0.15600
673	0.36600	0.38000	0.63720

TABLE V.

Thallous Chloride. $W_0 = 23.75$ kg. cal. $T_m = 700$.

T .	μ calc.	μ obs.	α calc.
523	—	0.00005	0.00625
573	0.00024	0.00024	0.03162
623	0.00098	0.00090	0.23310
673	0.00360	0.00370	0.50870
694	0.00600	0.00610	0.86140

TABLE VI.

Thallous Bromide. $W_0 = 21.67$ kg. cal. $T_m = 730$.

T .	μ calc.	μ obs.	α calc.
523	—	0.00004	0.00612
623	0.00055	0.00055	0.09204
673	0.00170	0.00160	0.29510
720	0.00440	0.00470	0.81280

TABLE VII.

Thallous Iodide. $W_0 = 18.7$ kg. cal. $T_m = 710$.

T .	μ calc.	μ obs.	α calc.
523	—	0.0001	0.0160
623	0.0010	0.0010	0.1747
673	0.0027	0.0027	0.4898
702	0.0046	0.0048	0.8567

Electrical Conductivity of Fused Salts.

It follows from equation (6) that at the melting point all the ions are free to glide past one another, since W is zero at this temperature. Indeed, the belief is held generally that the activity-coefficient of fused salts is always unity. Thus, on considerations based on the molecular kinetic theory of Einstein, Lorenz draws the conclusion that fused salts are completely split up into free-moving ions ("Nernst Festschrift," p. 226. Halle, 1912). In the case of univalent molten salts, Arndt (*Zeitsch. Elektrochem.*, 1907, **13**, 510, 809) drew the same conclusion on the basis of investigations relating the viscosity with the molecular conductivity of the fused salt. Thus the specific conductivity of fused salts does not vary with temperature in a logarithmic way. This is to be expected, as all the ions present contribute to the conduction of electricity. As a general rule, the equation

$$\mu_2 = \mu_1 \{1 - a(t_2 - t_1)\} \quad . \quad . \quad . \quad . \quad (14)$$

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is found to express satisfactorily the variation of conductivity with temperature, indicating that it is a simple case of variation of the mobility of the ion.

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