XIII.—*The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water.*

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ROSETTI (*Ann. Chim. Phys.*, 1867, [iv], **10**, 461; 1869, **17**, 370) has given a fairly exhaustive account of the early work carried out

on the determination of the temperature of maximum density of water and of a few salt solutions. A considerable portion of this work is due to Despretz (*Ann. Chim. Phys.*, 1839, [ii], **70**, 49; 1840, **73**, 296), and the most important result is embodied in the following law named after that investigator: "The lowering of the temperature of the point of maximum density of water caused by the addition of a solute is directly proportional to the concentration of the latter."

An attempt was made by Rosetti to connect the lowering of the temperature of maximum density brought about by the addition of a solute with the lowering of the freezing point produced by the same cause, but it was found impossible to formulate any general law, for although the ratio of the two lowerings was constant for any given solute at different concentrations, still a different ratio was obtained by the use of a second solute. In other words, whilst the lowering of the freezing point—being connected with the osmotic pressure of the solution—depends only on the concentration of the solute molecules, the lowering of the point of maximum density depends on the nature as well as on the number of dissolved molecules.

Coppet, in a series of researches (*Ann. Chim. Phys.*, 1894, [vii], **3**, 246, 268; *Compt. rend.*, 1897, **125**, 533; 1899, **128**, 1559; 1900, **131**, 178; 1901, **132**, 1218; 1902, **134**, 1208), has determined the molecular lowering of the temperature of maximum density for a number of salts of the alkalis, that is, the lowering produced by a gram-molecule of salt per litre, and the following table contains the more important of his results:

TABLE I.

	Chloride.	Bromide.	Iodide.
Rubidium	11.7	13.2	15.6
Potassium.....	11.6	12.8	15.4
Sodium	13.2	14.5	17.0
Lithium	6.0	7.0	8.3
Ammonium	7.2	8.7	11.1

From an examination of these figures, Coppet points out that of the three acid radicles, the iodide has the greatest and the chloride the least effect, and as a general conclusion states that: "Le rapport entre les abaissements produit par le chlorure et le bromure (ou le bromure et le iodure) du même métal est sensiblement le même pour tous les métaux du groupe." The ratio varies between the values 0.78 and 0.91.

From the results of the present investigation, carried out with

monobasic inorganic acids and their salts with univalent metals, it will be shown that the lowering produced by any given salt conforms to a simple general rule, and can, in fact, be calculated from the known lowerings produced by other salts. The results of the measurements are given in table II, which contains the figures obtained for solutions varying in strength between semi- and one-sixteenth-molecular, the normal, or molecular lowerings, being calculated from those of lower concentration.

TABLE II.

Lowering of the Temperature of Maximum Density of Salt Solutions.

	<i>M</i> /16.	<i>M</i> /8.	<i>M</i> /4.	<i>M</i> /2.	Molecular lowering.
HCl	—	0.7	1.3	2.6	5.2
LiCl	—	—	1.4	2.8	5.6
NaCl	—	1.6	3.1	6.2	12.4
KCl	—	1.4	2.8	5.5	11.0
NH ₄ Cl	—	1.0	1.8	3.6	7.2
HBr	—	0.9	1.8	3.7	7.4
LiBr	—	—	1.9	3.8	7.6
NaBr	—	1.8	3.7	7.4	14.8
KBr	—	1.6	3.2	6.5	13.0
NH ₄ Br	—	1.2	2.3	4.7	9.4
HI	—	1.2	2.2	—	8.8
LiI	—	1.2	2.3	—	9.2
NaI	1.0	2.0	4.0	—	16.4
KI	0.9	1.8	3.7	—	14.8
NH ₄ I	0.7	1.4	2.7	—	10.8
HNO ₃	0.8	1.6	3.1	—	12.4
LiNO ₃	—	1.6	3.1	—	12.4
NaNO ₃	1.3	2.5	5.0	—	20.0
KNO ₃	1.1	2.2	4.5	—	18.0
NH ₄ NO ₃	0.9	1.8	3.6	—	14.4

It will be seen at once that the results agree with the law of Despretz, the semi-molecular solutions giving twice the depression of the corresponding fourth-molecular. Further, it is obvious that the lowering is not connected with the osmotic pressure, as the values shown for the molecular lowerings of different solutes vary greatly; nor is a consideration of the difference in the degree of ionisation sufficient to account for this abnormality, since the various solutions of any given concentration are practically ionised to the same extent.

The regularity running through all the measurements can readily be seen if the difference between the lowering shown by any acid and, say, its sodium salt is considered. This difference for the four

acids tabulated has the values 7.2, 7.4, 7.6, and 7.6; thus the replacement of the hydrogen ion by sodium causes a practically constant increase in the molecular lowering. A similar increase is found when potassium is used instead of sodium, the average value being 5.75, whilst for ammonium the value is 2.0. Further, the same effect is observed in the case of the acid radicle; thus, the replacement of chlorine by bromine increases the molecular lowering by 2.1, whilst the substitution of iodine for chlorine causes an increase of 3.7.

From a consideration of these results, it is evident that each acidic or basic radicle has its own effect on the lowering of the point of maximum density, and that the effect produced by a salt is equal to the sum of the lowerings caused by the metallic and acidic radicles. Hence, if we take the molecular lowering of hydrochloric acid—which gave the smallest effect of all the substances examined—as standard, we can obtain the molecular lowering of any salt or acid by the addition of two numbers, one corresponding with the acidic and the other with the basic radicle of the salt. It will at once be seen that there is a close resemblance between the above conclusion and Valson's law of moduli, which states that the density of a normal salt solution is the sum of an acidic and a basic effect, and can, in fact, be calculated by adding to the density of a normal solution of a standard substance—ammonium chloride—two figures or moduli, one characteristic of the acidic and the other of the basic radicle of the salt.

The moduli for the lowering of the point of maximum density are given in table III, and the molecular lowering of any salt can be found by adding to the molecular lowering of hydrochloric acid (5.2) the two moduli corresponding with the given salt. For example, the calculated lowering for potassium nitrate would be $5.2(\text{hydrochloric acid}) + 5.75(\text{potassium}) + 7.2(\text{nitrate}) = 18.15$, the actual value found being 18.0. Several values for each modulus calculated from different salts are shown in the table, together with the mean value derived from them.

TABLE III.

	Cl.	Br.	I.	NO ₃ .	Average.	
Li	0.6	0.2	0.4	0.0	0.3	
Na	7.2	7.4	7.6	7.6	7.45	
K	5.8	5.6	6.0	5.6	5.75	
NH ₄	2.0	2.0	2.0	2.0	2.0	
	H.	Li.	Na.	K.	NH ₄ .	Average.
Br	2.2	2.0	2.4	2.0	2.2	2.2
I	3.6	3.6	4.0	3.8	3.6	3.7
NO ₃	7.2	6.8	7.6	7.0	7.2	7.2

It should be noted that a similar set of moduli could be calculated from the molecular lowerings given by Coppet, although as a rule his values would not be identical with those tabulated; the results, however, approximate to one another fairly closely considering the difference in the experimental methods employed.

We may next consider the results obtained with the weak monobasic organic acids in comparison with their highly ionised salts. Formic, acetic, and propionic acids, together with their sodium and ammonium salts, have been examined.

TABLE IV.

	<i>N</i> /8.	<i>N</i> /4.	<i>N</i> /2.	<i>N</i> .
Formic acid	—	1.7	3.6	7.2
Na salt	1.6	3.2	—	12.8
NH ₄ salt	—	1.7	3.6	7.2
Acetic acid	—	1.8	3.7	7.4
Na salt	1.5	3.0	—	12.0
NH ₄ salt	—	1.6	3.1	6.2
Propionic acid	—	2.0	4.0	8.0
Na salt	1.5	3.0	—	12.0
NH ₄ salt	—	1.7	3.4	6.8

The results do not show the normal change, 7.6, which was obtained with strong acids when the hydrogen atom was replaced by sodium, but the difference between the values for the sodium and ammonium salts is constant in all three cases and is identical with that obtained in the case of the inorganic acids. In other words, the highly ionised salts of organic acids behave in the normal manner, whilst the feebly ionised acids themselves are abnormal.

The dibasic acids, with their acid and neutral salts, are also of interest.

TABLE V.

	<i>M</i> /16.	<i>M</i> /8.	<i>M</i> /4.	<i>M</i> .
Sulphuric acid	—	3.0	6.1	24.4
NaH salt.....	2.0	4.0	—	32.0
Na ₂ salt	2.0	4.0	—	32.0
Oxalic acid	—	1.5	3.0	12.0
NaH salt.....	—	2.4	—	19.2
Na ₂ salt	2.0	4.0	—	32.0
Succinic acid	—	1.7	3.4	13.6
NaH salt.....	—	2.5	—	20.0
Na ₂ salt	1.5	2.9	—	23.2

It will be seen that the replacement of one hydrogen atom by

sodium in the two stronger acids gives values approximating to the normal, whilst succinic acid gives a slightly lower value, thus resembling the weak monobasic acetic and propionic acids. In all cases, the replacement of the second hydrogen atom is quite abnormal and differs widely in the three cases. From the normal behaviour of the acid salt, it may be concluded that the ions of sodium hydrogen sulphate consist mainly of Na^+ and HSO_4^- , and not H^+ and NaSO_4^- . It should be noticed that as the greatest concentration examined in these acids was $M/4$, the results are not so accurate as with the monobasic acids.

The results obtained for the salts of the bivalent metals show great irregularities, probably on account of the complex ions which are present. For example, the molecular lowering obtained for barium chloride was 24.6 and for barium nitrate 32.8, from which the two values 14.2 and 8.0 are obtained for the modulus of barium. Similar varying results can be obtained from the figures given by Coppet and Müller (*Compt. rend.*, 1902, **34**, 1208) for the lowerings shown by the halogen salts of barium and calcium.

TABLE VI.

	Molecular lowering.		Modulus.
Barium bromide	25.14	26.28	10.9
Barium iodide	29.24	29.42	11.7
Calcium chloride	18.0	18.3	7.8
Calcium bromide	20.12	20.93	5.7
Calcium iodide.....	26.09	26.63	8.7

It will be seen at once that there is no regularity comparable with the case of the univalent metals.

EXPERIMENTAL.

The apparatus employed is shown in the diagram; it consists of a dilatometer with a capacity of about 50 c.c. and fitted with a stem 25 cm. long and of 0.5 mm. bore. To compensate for the change in volume with temperature, a portion of the bulb is filled with mercury; the fraction of the total dilatometer volume thus filled is equal to the ratio between the coefficients of cubical expansion of glass and mercury, so that, on a change of temperature, the expansion or contraction of the metal exactly compensates the expansion or contraction of the bulb, the volume of the latter unoccupied by the mercury thus remaining constant.

The dilatometer is filled by means of a tap funnel and a vacuum

pump. The stem of the dilatometer passes through a rubber cork fitted into the opening of the tap funnel which contains the liquid to be introduced into the dilatometer. The funnel and the attached dilatometer is now inverted and connexion made between it and a filter pump. As the pressure is lowered, the air in the dilatometer bulb bubbles through the liquid in the funnel, and on detaching from the pump, the liquid is forced into the dilatometer by the action of the atmospheric pressure. A second and a third exhaustion are usually necessary, and the last trace of air in the bulb is removed by heating. The dilatometer, with the funnel still attached, is now placed in a vacuum-jacketed vessel filled with brine at about 5° , and allowed to cool. When the apparatus has attained the temperature of the surrounding liquid, it is disconnected from the tap funnel and a few shavings of ice are added to the liquid in the vacuum flask; air is then driven through the cooling mixture, so as to stir it until the ice has melted. The apparatus is now left for a quarter of an hour to allow the dilatometer to assume the temperature of the bath; this temperature is then noted, and the level of the liquid in the dilatometer tube measured; the apparatus is again left, and readings are taken at five-minute intervals until the liquid in the dilatometer ceases to contract; this precaution is necessary in order to ensure that the whole apparatus is in a state of thermal equilibrium. A further small quantity of ice is now added so as to lower the temperature a fraction of a degree, and the process repeated. After several additions of ice, the liquid in the dilatometer reaches its point of maximum density, and on further cooling it expands. As this point is approached, the coefficient of expansion of the liquid diminishes, so that it is difficult to determine the exact temperature of maximum density, and the readings given are only accurate to within about 0.2° .

After a measurement, the instrument is warmed so as to expel a little of the contents, and is then inverted so that the mercury runs out. This mercury is dried and reserved for the next determination, whilst the rest of the contents of the dilatometer are removed by means of the filter pump. The instrument is then rinsed with the next liquid to be investigated, and, after the re-

introduction of the mercury, it is filled with the solution and the measurement made as before.

A few other points may be noted. The coefficient of expansion of the glass was calculated between the ordinary temperature and 100° by filling the instrument with mercury and weighing the quantity expelled when heated in a steam-jacket, whilst the volume of the bulb was measured by filling with water and weighing at a known temperature. The stem of the instrument was not graduated, but the level of the liquid below the upper end was determined by means of a depth gauge fitted with a vernier; by this means, a change of level of 0.1 mm. could be detected, and, moreover, the labour of regraduation of the stem after an accident was avoided.

Conclusions.

(1) The lowering of the temperature of the maximum density of water produced by the addition of a solute is directly proportional to the concentration of the latter (law of Despretz).

(2) The lowering produced by a highly ionised binary electrolyte is composed of two separate, independent effects, one due to the acid radicle and the other due to the basic radicle of the electrolyte.

(3) The lowering produced by a highly ionised binary electrolyte of molecular concentration can therefore be calculated by the addition of two moduli to the lowering produced by a molecular solution of a chosen standard substance. The chosen standard was *N*-hydrochloric acid, which gives a lowering of 5.2.

(4) The acid salts of the dibasic acids behave normally, but the neutral salts of such acids and the salts of the bivalent metals do not follow any simple rule in their effect on the temperature of the maximum density.

(5) Feebly ionised organic acids show abnormal effects, but the highly ionised salts derived from them behave in the normal manner.

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