ISO-PIESTIC SOLUTIONS.

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It was natural that in the development of the broad general outlines of the dissociation theory by Arrhenius and others the smaller discrepancies between theory and experiment should be passed over and their consideration postponed. Now, however, that the source of these discrepancies, in the case of aqueous solutions, has in many cases been traced to the composite character of the solvent water, to the changes which take place in its constitution in the presence of a solute, and to the combinations between solvent and solute which usually occur, the study of these discrepancies promises to be fruitful.

As an example of the generalizations which can only be regarded as first approximations, one may refer to the statement of Nernst that "Iso-osmotic solutions contain the same number of molecules of dissolved substance in a given volume at a given temperature, and the number is the same as in an equal volume of a perfect gas at the same temperature and pressure."

Arrhenius and others speak of two solutions which are in osmotic equilibrium with one another as being iso-osmotic or iso-tonic, and come to the conclusion that solutions containing equivalent or equimolecular quantities per litre are iso-osmotic. Arrhenius further describes solutions which do not change their dissociation on mixing as iso-hydric, and describes iso-hydric solutions as containing the same number of gram-ions per litre.

So far as the terms iso-tonic, iso-osmotic, and iso-hydric merely express physical facts, they may be used with accuracy, but it is now recognized that the propositions involving molecular proportions per litre which they are used to connote as above are only first approximations, and they cease to be even approximate when applied to more concentrated solutions. In various papers I have endeavoured to correlate the various osmotic data with the number h of molecules of water per mol of solute, and to deduce the number n of molecules of water combined with a mol of solute.* With the object of deducing these numbers from vapour pressures, I began in 1913 a series of measurements of vapour pressures which are still incomplete, but as the completion of the work may be long delayed, it seems desirable to indicate the general character of the method and its results in this brief paper.

* See a paper of mine contributed to the recent discussion on Osmotic Pressure, *Trans. Farad. Soc.*, **13**, October 1917, and the former papers to which reference is there made.

The method of experiment was determined upon after a number of trials of very various methods and apparatus, to which it is not now necessary to refer. Briefly, the method finally adopted consisted in placing the salts or solutions to be observed in separate open vessels in a common receptacle, which was evacuated to facilitate the exchange of vapour between the solutions in an aqueous atmosphere common to them all, maintained at a uniform temperature. Under such circumstances equilibrium can only be reached by the several solutions gaining or losing water until they arrive at the same vapour pressure. Solutions under such conditions may be said to become iso-piestic. A special word is desirable to denote solutions of equal vapour pressure, since the words iso-tonic, iso-hydric, and iso-osmotic have come to connote theoretical considerations, and are sometimes used inaccurately, whilst the word iso-piestic simply expresses a *fact*, viz. the equality of vapour pressure of the solutions. Iso-piestic solutions must be, of course, strictly iso-osmotic, since it is the equality of vapour pressure which determines osmotic equilibrium.

The purpose of the main investigation was to determine the relative degrees of hydration of iso-piestic solutions of different salts. Thus, for instance, it was found that for solutions of the following salts, after their solutions had stood in the same aqueous atmosphere for several days at a temperature of 18° C. to arrive at final equilibrium, the values of h were

KCl.	NaCl.	LiCl.
$h = 12.43$	14.23	17.18

Such solutions are therefore iso-piestic at 18° C.

Some hundreds of experiments were made, covering the range from concentrated to dilute solutions, but owing to certain difficulties of manipulation the general results have not yet been completed. But from the experiments selected valuable deductions can be drawn, which will serve to indicate the capabilities of the method.

Four cylindrical glasses of about 5 cm. diameter and 4 cm. deep were arranged on a tin stand, by means of which they could be easily lifted into and out of a Hempel desiccator. Each glass was furnished with a loose ground cover and a piece of platinum for occasional stirring. The lid of the Hempel desiccator was well ground so as to make a good joint with the body, the joint being luted with vaseline. The lid was also furnished with a well-ground tap. The trough of the lid was used to contain a little water or drying substance, as required.

Four pure salts were taken, viz. KCl, NaCl, LiCl, and KNO₃ (in weights of 2 to 3 grams), dried and placed hot in the glasses, with stirrers and covers previously weighed, cooled in the evacuated desiccator and weighed. The first three had been melted into beads on platinum. The glasses were then arranged on the stand and placed in the desiccator, the covers removed, the desiccator closed, with a little water in the trough, and evacuated by means of a good filter pump, capable of reducing the pressure to about that of the water vapour. The external tube of the tap was then closed by means of a rubber tube and stopper and the desiccator immersed in a large water-bath kept at a regulated temperature of about 18° and constantly stirred. After an interval of one to three days, the desiccator was taken out of the bath and opened, the covers replaced on the glasses, and each glass weighed to ascertain the amount of water taken up by the salt. A little more water was now placed in the trough and the process repeated.

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The results of the earlier stages of an experiment are given in Table I.

TABLE I.

Successive Values of h at 18° C.

	KCl.	NaCl.	LiCl.	KNO ₃ .
1913				
Nov. 12	0	0	8.02	0
15	0	0	8.55	0
17	0	0	9.34	0
19	0	0	9.82	0
21	0	0	10.33	0
23	0	0	10.79	0
25	0	0.005	11.24	0
28	0	0.297	11.45	0
Dec. 1	0	1.10	11.59	0
5	0	1.86	11.40	0
7	0	2.09	11.37	0
12	0	5.37	11.34	0
16	0	7.68	11.41	0
20	0	8.21	11.39	0
25	0	8.86	11.42	0
26	0	8.98	11.41	0
28	0	9.08	11.41	0
		all dissolved		
30	0	9.08	11.40	0

The vapour pressures at each stage can be ascertained from those of the LiCl solutions, which furnish a convenient scale of pressures. It will be observed that up to November 23rd the vapour pressure is being continually increased by drops of water added, sometimes in the trough and sometimes to the LiCl solution, but none of the other salts takes up any water from the aqueous vapour in the desiccator.

On November 25th the attack of the water on the NaCl has begun, and after this date it proceeds rapidly, the vapour pressure from November 28th to December 30th remaining practically constant and equal to that of a saturated solution of NaCl. The concentration of the LiCl varies between $h=11.59$ and 11.37 , but this is due to equilibrium conditions not being always established at the time of weighing. On December 28th all the NaCl crystals were dissolved, and we therefore have $h=9.08$ for a saturated solution of NaCl corresponding to a vapour pressure given by the $h=11.40$ LiCl solution.

Strictly speaking, the observation of November 25th leaves open the possibility of there being a solid hydrate of NaCl with a lower vapour pressure corresponding to $h=11.24$ for LiCl. But $\frac{1}{2}$ per cent. of water with NaCl corresponds to a hydrate composed of 60 mols NaCl to 1 mol of water, and the existence of such a hydrate is unlikely. The existence of a trace of hygroscopic impurity is the more probable explanation.

Another series of experiments gave the critical point at which NaCl begins to take up water as the vapour pressure corresponding to

NaCl.	LiCl.
$h=9.18$	11.49

This was in March 1914, when the thermo-regulator was probably running at a slightly higher temperature than in December 1913.

Table II takes up the same series from the point reached on December 28th, when the NaCl had just all dissolved and formed a solution saturated at 18°.

TABLE II.

Successive Values of h at 18° (continued).

	KCl.	NaCl.	LiCl.	KNO ₃ .
1913				
Dec. 30	0	9.08	11.40	0
31	0	10.71	13.05	0
1914				
Jan. 2	0	12.18	14.67	0
3	traces	13.54	16.12	0
5	0.38	14.52	17.17	0
6	3.21	14.41	17.36	0
7	5.20	14.29	17.26	0
8	7.66	14.25	17.20	0
10	9.61	14.17	17.08	0
11	10.02	14.14	16.97	0
12	10.22	13.99	16.82	0
13	10.54	14.07	16.89	0
14	10.90	14.21	16.92	0
16	11.27	14.15	16.98	0
17	11.51	14.15	17.07	0
18	11.73	14.14	17.05	0
20	11.96	14.10	17.00	0
25	12.02	14.06	16.94	0
26	12.16	14.07	16.95	0
28	12.26	14.05	16.92	0
31	12.43	14.11	16.98	0
Feb. 2	12.40	14.11	16.99	0
4	12.39	14.11	16.98	0

It will be observed that the KCl and KNO₃ remained substantially unattacked by water until January 5, 1914, from which point, until February 4th, the vapour pressure remains substantially constant at the pressure of saturated KCl, which is probably slightly lower than that which corresponds to the last stage. Here, again, the first attack of the water on the KCl on January 3rd is at a pressure slightly lower than the vapour pressure of saturated KCl, possibly owing to traces of a hygroscopic impurity.

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Another series which arrived at equilibrium with saturated KCl in April 1914 gave the following final values:

KCl.	NaCl.	LiCl.
$h = 12.43$	14.22	17.16

Hitherto there has been no attack on the KNO_3 . Table III takes up the same series from the point where the KCl has dissolved in saturated solution on February 4th.

TABLE III.

Successive Values of h at 18° (continued).

	KCl.	NaCl.	LiCl.	KNO_3 .
1914				
Feb. 4	12.39	14.11	16.98	0
6	12.46	14.18	17.04	0
8	12.47	14.19	17.07	0
10	12.48	14.20	17.08	0
13	12.76	14.47	17.34	0
15	13.36	15.02	17.84	0
17	13.57	15.29	18.19	0
18	14.11	15.86	18.91	0
20	14.75	16.47	19.46	0
21	15.68	17.35	20.37	0
22	16.57	18.20	21.22	0
24	17.18	18.89	22.06	trace

Unfortunately, the series came to an end on February 24th, owing to the accidental spilling of a drop of solution. The figures of that date may, however, be taken approximately as giving the point at which dry KNO_3 begins to be attacked, for the following reason. The series

TABLE IV.

Successive Values of h at 18° C.

	KCl.	NaCl.	LiCl.	KNO_3 .
1913				
Nov. 4	13.18	16.09	17.46	7.26
5	14.63	17.23	18.87	3.76
7	15.66	18.06	20.13	0.93

of figures given in Table IV was obtained by the reverse process. The weighed salts were first allowed to absorb water and then to come to equilibrium among themselves. The KNO_3 solution was a saturated solution containing undissolved crystals.

These figures do not represent accurate equilibrium figures, as the process of vapour transfer has not come to an end. But they are interesting as showing the reverse process of the drying of the KNO_3 in the presence of the other solutions.

One important result of the whole series is to show that in each case there is a critical hydration pressure below which no attack is made by the water upon a salt.

The vapour pressure of solid salts which crystallize with water of crystallization has been studied by Andreae, Frowein, Pareau, and others, and the principles relating thereto have been shortly formulated by van't Hoff.* The vapour pressures of the three solid hydrates of copper sulphate furnish one of the most familiar examples. These principles do not appear to have been developed or generally recognized in relation to the solution and drying of anhydrous solid salts. For example, one finds the statement that "pure NaCl is very slightly hygroscopic, taking up about $\frac{1}{2}$ per cent. of water from moist air."

The deduction to be drawn from the observations above described is that—

For a pure salt (such as NaCl), without water of crystallization, there is, at a given temperature, a certain vapour pressure of water, below which the dry salt surrounded by aqueous vapour will not take up water, and will, if it is not dry, become dried. This pressure may be called the critical hydration pressure of the salt at the given temperature.

If the salt forms a series of solid hydrates, like CuSO_4 , the critical hydration pressure would be the vapour pressure of the first solid hydrate. If the salt forms no solid hydrates under the given conditions, the critical hydration pressure is the vapour pressure of the saturated solution of the salt. The vapour pressure of the saturated solution is, of course, the equilibrium vapour pressure reached when part of the salt is dry and part in solution.

From the known fact that $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ has a definite vapour pressure of 4.4 mm. (at 50°), and that the vapour pressure is zero for dry CuSO_4 , one might infer the critical hydration pressure of 4.4 mm. It is well, however, to place the principle on a broader foundation and to formulate it definitely, as it has an obvious practical application in reference to the drying of salts and the consolidation of the crystals into a compact mass under atmospheric influences.

In order to translate the figures above obtained into vapour pressure expressed in mm. of mercury, we require a scale of vapour pressures. If this can be established for one of the salts, it gives the vapour pressure for the iso-piestic solutions. A means of doing this is given by the osmotic and ionization relations established in a former paper.† It was there shown ‡ that the relation

$$n = 38\alpha - 14$$

held approximately for the relation between the ionization α and the number n of combined water molecules in the case of LiCl solutions at 18° . A closer working out of the figures gives the relation as

$$n = 36.3\alpha - 13.22.$$

* *Lectures on Theoretical and Physical Chemistry* English ed., Part I, p. 56.

† Bousfield, *Trans. Chem. Soc.*, 106, 1809, 1914.

‡ Loc. cit., p. 1820.

It was also shown that the dilution law

$$\frac{\alpha^2}{1-\alpha} = K(h-n)^{\frac{1}{2}}$$

was an accurate law, where K could with considerable accuracy be taken as a constant, although the mass action law theoretically demanded a small amount of variability of K with the variation of the composition of the free water of the solution. Neglecting this small variation, we can, from the expressions

$$n = h - \frac{\alpha^4}{K^2(1-\alpha)^2},$$

$$n = 36.3a - 13.22,$$

by taking various values for α , make a table of corresponding values of h and n , from which the scale of vapour pressures of LiCl solutions at 18° may be obtained by means of the relation *

$$\frac{\partial p}{p} = \frac{1+\alpha}{h-n},$$

where p is the vapour pressure of water at 18° and ∂p is the vapour pressure lowering.

TABLE V.

Values of $\partial p/p$ for LiCl Solutions at 18° .

α .	n .	h .	$\partial p/p$.	Difference for $\Delta h = 1$.
0.44	2.75	7.00	0.3388	
0.45	3.12	7.95	0.3002	0.0406
0.46	3.48	8.95	0.2669	0.0333
0.47	3.84	10.02	0.2379	0.0271
0.48	4.20	11.19	0.2117	0.0224
0.49	4.57	12.46	0.1888	0.0180
0.50	4.93	13.83	0.1685	0.0148
0.51	5.29	15.32	0.1505	0.0121
0.52	5.66	16.95	0.1346	0.00975
0.53	6.02	18.74	0.1203	0.00799
0.54	6.38	20.68	0.1077	0.00649
0.55	6.75	22.83	0.09639	0.00526
0.56	7.11	25.19	0.08628	0.00428
0.57	7.47	27.79	0.07726	0.00347
0.58	7.83	30.67	0.06918	0.00281
0.59	8.20	33.86	0.06196	0.00226
0.60	8.56	37.39	0.05550	0.00183

The validity of this table rests on Tammann's experimental values † for ∂p for LiCl solutions of four strengths at temperatures between 40°

* Loc. cit., p. 1818.

† Landolt Bernstein Tables.

and 100°. From these the figures at 18° are diagrammatically extrapolated.* These extrapolated values are given in Table VI, together with the values calculated directly from Table V. It will be seen that Table V gives values completely in accord with Tammann's experimental results. The difficulty of obtaining accurate vapour pressures at the low temperature of 18° by direct measurement is very great. Tammann's pressures at higher temperatures, which give a range of 25 values between 40° and 100° for each concentration, furnish a basis for extrapolation

TABLE VI.

LiCl Solutions at 18°.

<i>h.</i>	$\partial p/p$ from Tammann.	$\partial p/p$ from Table V.	Difference.
7.275	0.326	0.327	1
10.40	0.229	0.229	±
16.25	0.140	0.141	1
29.19	0.073	0.073	±

which probably leads to more accurate results for 18° than could be obtained by direct measurement. The more accurate and authoritative determination of such a scale for LiCl, by the collaboration of various observers, is greatly to be desired. It would render the determination of the vapour pressure of any solution by comparison with the LiCl standard by the method above described a simple matter.

With the help of Table V it is now possible to express the critical hydration pressures for KCl and NaCl at 18° in terms of mm. of mercury with some accuracy. The values of *h* for LiCl solutions corresponding to the critical pressures for the other salts are—

	KCl.	NaCl.	KNO ₃ .
for LiCl	$h = 14.50$	10.80	22.00

the value for KNO₃ being only an approximate figure. The values of $\partial p/p$ calculated from Table V are

KCl.	NaCl.	KNO ₃ .
$\partial p/p = 0.160$	0.220	0.101

and the corresponding critical vapour pressures at 18° in mm. of mercury are therefore

12.92	12.00	13.83
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the vapour pressure of water at 18° being taken as 15.38.

We may give a further example of the kind of information which iso-piestic solutions will give us when the basic data for a standard substance are accurately determined. To follow the *modus operandi*

* Loc. cit. p. 1812.

in detail it is necessary for the reader to have before him the former paper.*

Our two sets of values for solutions iso-piestic with a saturated solution of KCl at 18° are

KCl.	NaCl.	LiCl.
12.43	14.22	17.16
12.39	14.11	16.98

The mean values are

12.41	14.16	17.07
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From the standard table for LiCl values we get the value of $\delta p/p$ when $h=17.07$ as

$$\delta p/p = 0.1336.$$

For the values of the constant K we have

KCl.	NaCl.	LiCl.
$1/K=5.370$	5.821	5.966

whence we get

$$\log \frac{K^2}{\delta p/p} = \bar{1}.41425 \quad \bar{1}.34459 \quad \bar{1}.32283.$$

Thence for the values of α we get from the table †

$$\alpha = 0.5395 \quad 0.5251 \quad 0.5207.$$

It would thus appear that the ionization of a saturated KCl solution is greater than that of the iso-piestic solutions of NaCl and LiCl, which is probably connected with the fact that there is more free water in a saturated solution of KCl than there is in the more dilute solutions of the other salts. Since

$$(h-n)\delta p/p = 1 + \alpha$$

we can calculate the free water $h-n$, and we obtain

KCl.	NaCl.	LiCl.
$h-n=11.52$	11.41	11.38

from which we get for the combined water

$$n = 0.89 \quad 2.75 \quad 5.69$$

for these iso-piestic solutions.

It thus appears that for these iso-piestic solutions the amounts of free water are nearly the same, the balance of the water being made up by the differing amounts of combined water, which are roughly one, three, and six molecules respectively for the different salts, when the free water for all is about eleven and a half molecules.

* "Ionization and the Law of Mass Action, Part III," *Trans. Chem. Soc.*, 106, 1811, 1914.

† Loc. cit., p. 1828.

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It is of interest to compare the results for saturated solutions of the three salts at 18°, which are given in the following table, those for LiCl being taken from the former paper,* and those for NaCl being calculated from the iso-piestic data in the mode above described for KCl.

TABLE VII.

Comparative Data for Saturated Solutions at 18° C.

	<i>h.</i>	$\frac{dp}{p}$	<i>a.</i>	<i>h-n.</i>	<i>n.</i>
KCl	12.43	0.1336	0.540	11.54	0.89
NaCl	9.13	0.2072	0.486	7.18	1.95
LiCl	3.00	0.875	0.400	1.60	1.40

The above examples will serve to illustrate the kind of results which may be obtained by the study of iso-piestic solutions. The method appears to admit of a *relative* accuracy in the determination of vapour pressures of a high order. The accurate determination of the absolute values of vapour pressures of one substance, such as LiCl, would enable the absolute values of other substances to be readily determined with equal accuracy by the iso-piestic method.