



XXXVIII. The nature of solution.—Part II. Boiling-points of salt-solutions

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to establish the relation between the force of molecular attraction and "the repulsive force of heat," on which our whole argument has been based. This relation is, as we have seen, the expression of a relation between observed quantities, and is one which we must suppose to hold good even in the limit where the observed quantities are vanishingly small. Laplace, by confining his attention to this limiting case, overlooked the relation, and accordingly failed to perceive the reality of the surface-tension; and his theory is in consequence absolutely inapplicable to the explanation of any of those phenomena of horizontal motion on a liquid surface which are due solely to variations of the surface-tension, and are not necessarily accompanied by an elevation or depression of the liquid.

XXXVIII. *The Nature of Solution.*—Part II. *Boiling-Points of Salt-Solutions.* By W. W. J. NICOL, M.A., B.Sc., F.R.S.E., F.C.S., &c., Lecturer on Chemistry, Mason College, Birmingham*.

VERY little indeed is known of the temperatures at which salt-solutions of definite composition boil. Almost the whole of our knowledge is confined to the boiling-points of saturated solutions; and these have been determined in very many cases with but little pretence to accuracy. With the exception of the experiments made by Légrand †, nothing has been done to determine the effect on the boiling-point of water produced by the presence of various quantities of salts dissolved in it. The vapour-pressure of water from salt-solutions of various strengths has also received but little attention; the results of Wüllner ‡, Babo, and one or two others comprising all that is known on this subject.

From the time when I began first to work at the subject of solution, it appeared to me that it was in this direction that most knowledge of the nature of solution was to be gained; but it is only recently that I have been able to turn my attention to this point. The following pages contain an account of my experiments on the pressures under which saturated salt-solutions boil at different temperatures. These experiments are merely preliminary to a more extended and more accurate series of determinations of the pressure of aqueous vapour from such solutions. Still the results of these first attempts

* Communicated by the Author.

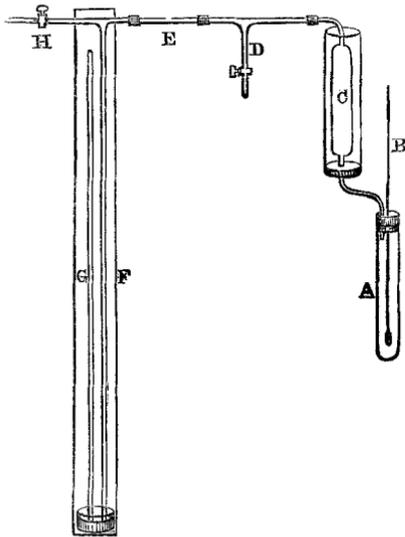
† *Ann. Chim. et Phys.* lix. p. 423.

‡ *Pogg. Ann.* ci., cv., cx.

are so striking and so totally at variance with all received ideas on this subject, while they agree so completely with the theory of solution put forward by me in the paper of which this is the continuation*, that I feel they possess sufficient interest, and are of sufficient importance, to warrant their publication.

My method of experiment is as follows :—

A wide test-tube A, 200 millim. by 30 millim., is fitted with an india-rubber cork through the centre of which passes a thermometer B. By a hole at the side of the thermometer is attached the upright condenser C: this is made of thin-walled wide glass tube, and is surrounded with a cylinder through which cold water flows; the upper end of the condenser communicates with the T-piece D, one arm of which has a stopcock, and the other is connected with a piece of capillary tubing E, 100 millim. long and about .3 millim. in internal diameter; this in its turn is joined to the gauge E, and has a stopcock H by means of which the whole may be placed in communication with the atmosphere. The gauge stands side by side, in a trough of mercury, with a barometer-tube G in front of a mirror-scale divided into millimetres, the pressure of the vapour in A being given by the difference in height of the mercury in G and F. In making an experiment, a quantity of salt along with a piece of granulated zinc



or tin is introduced into A, and water sufficient to rather more than cover the bulb of the thermometer is then added. The quantity of salt is so great that some of it remains undissolved at the highest temperature reached during the experiment. The tube is then placed in position and surrounded by a bath of water, the temperature of which is governed by a thermostat. The temperature of the water is then raised to

* Phil. Mag. February 1883.

5° above the point at which the vapour-pressure is to be determined. The temperatures at which determinations were made were 65°, 75°, 85°, 95°, as indicated by the thermometer B. The temperatures of the bath were therefore respectively 70°, 80°, 90°, and 100°. The temperature of the bath having become constant, the stopcock H is closed and D is opened, communication with a water-pump being thus established. As soon as ebullition has commenced, D is closed and opened occasionally till the reading of B is one degree or so lower than the temperature of experiment. After steady boiling for some time, H is momentarily opened; the temperature, as indicated by B, rises immediately a tenth or so: in this way the temperature of ebullition is slowly raised till the desired point is reached. The heights of F and G are then read, and one observation is completed. D is again opened and closed and the whole operation repeated; and the mean of the two differences in height of the mercury in F and G is entered as the pressure of water-vapour at t° from the salt-solution saturated at t° . Two observations are also made with another quantity of the same salt. Thus the results entered in the following tables are based on four determinations. The use of the capillary E is to deaden the oscillation of the mercury in F, which would otherwise be produced by the brisk ebullition in A. Thus the reading of F gives the mean of the momentary pressures in A, as the thermometer shows the mean of the momentary temperatures. The piece of granulated zinc or tin is added to obviate bumping; and it is practically unattacked, as only a trace of dissolved metal could be detected after even four hours' boiling.

As these experiments were merely tentative, no attempt was made to correct the temperature-readings nor the readings of the barometer; and necessity for this was to a great extent removed by making a series of observations with pure water and comparing the results with the figures calculated from Regnault's experiments.

Table I. contains the figures I obtained from two sets of double determinations. As is seen from it, my results are uniformly lower than Regnault's by $7.25 \pm .5$; but as no attempt was made to read closer than .5 millim., the concordance is satisfactory; and it is only necessary to apply as corrections the numbers in the difference-column to the pressures of water-vapour of salt-solutions afterwards given, to obtain the true pressures at the true temperatures.

In Table II. are given the results I obtained corrected as above, and the temperatures to which these pressures of

TABLE I.

t° .	p_1 and p_2 .	Mean p .	p' (Regnault).	Difference.
65 ^o	180	180	186.9	-6.9
"	180			
75	281.5	281	288.5	-7.5
"	280.5			
85	426	426.3	433	-6.7
"	426.5			
90	626	626	633.8	-7.8
"	626			

TABLE II

Salt.	t .	p .	p cor.	t' .	$t-t'$.
NaNO ₃	65 ^o	114.0	120.9	55.6 ^o	9.4 ^o
	75	172.0	179.5	64.1	10.9
	85	249.7	256.4	72.2	12.8
	95	355.0	362.8	80.5	14.5
KNO ₃	65
	75	213.5	221.0	68.8	6.2
	85	308.0	314.7	77.1	7.9
	95	419.3	427.1	84.6	10.4
Na ₂ CO ₃	65	148.0	154.9	60.9	4.1
	75	232.0	239.5	70.6	4.4
	85	357.7	364.4	80.6	4.4
	95	529.0	536.8	90.5	4.5
K ₂ CO ₃	65
	75	116.0	123.5	56.0	19.0
	85	166.0	172.7	63.2	21.8
	95	237.0	244.8	71.1	23.9
MnSO ₄	65	160.3	167.2	62.5	2.5
	75	249.0	256.5	72.1	2.9
	85	388.0	394.7	82.6	2.4
	95	584.0	591.8	93.1	1.9
FeSO ₄	65	158.8	165.7	62.3	2.7
	75	251.8	259.3	72.4	2.6
	85	386.0	392.7	82.5	2.5
	95	580.0	587.8	93.0	2.0
KNO ₃ Same strength.	65	146.0	152.9	60.6	4.6
	75	224.0	231.5	69.8	5.2
	85	335.0	341.7	79.1	5.9
	95	491.5	499.3	88.7	6.3
FeSO ₄ Same strength.	65	163.0	169.9	62.9	2.1
	75	256.0	263.5	72.8	2.2
	85	388.0	394.7	82.7	2.3
	95*	580.0	587.8	93.0	2.0

* Saturation took place at 90°.

aqueous vapour correspond. This is the usual method of expressing the action of a salt on the vapour-pressure of water—that is, it raises the boiling-point so many degrees.

It will be seen that the number of degrees that the boiling-point of water is raised is a quantity that increases with the temperature in all cases where the solubility also increases, but diminishes in a more or less marked manner when the solubility decreases with the rise of temperature. All this can be readily explained. It is only to be expected that the larger number of molecules of salt present should have a greater influence on the water-molecules; but this explanation fails when the case of KNO_3 of the same strength is examined. Here the quantity of salt remained the same, and yet the increase of rise of boiling-point is very well marked. That the strength of the solution was the same at the end as at the beginning of the experiment was proved by weighing the tube before and after: the loss of water and salt adhering to the thermometer did not amount to .08 per cent. In this case, then, it appears that the restraining effect of the salt on the water increases with the rise of temperature.

Before attempting to explain this, I wish to draw attention to a much more convenient mode of expressing the action of salt on water with regard to its vapour-pressure. If at a temperature t the vapour-pressure of water is p_t , and at the same temperature the pressure of water-vapour from a salt-solution is p'_t , then the pressure of pure water is diminished by the salt $p_t - p'_t$ millim. Now as the value of p increases faster than the temperature, in order to compare $p_t - p'_t$ with $p_v - p'_v$ we must divide by p_t and p'_t respectively, giving us

$$1 - \frac{P'_t}{P_t} \text{ and } 1 - \frac{P'_v}{P_v}, \text{ \&c.},$$

numbers expressing the effect of the salt at those temperatures. If the salt-solution have the strength n molecules of salt to the

100 molecules of water, then $\frac{1 - \frac{P'}{P}}{n}$ expresses the effect of each molecule of salt at that particular temperature.

In Table III. are given the values of $\left(1 - \frac{P'}{P}\right) \times 10,000$ and the solubilities at the corresponding temperatures, with the

values of $\frac{1 - \frac{P'}{P}}{n}$ also multiplied by 10,000. It is evident that the effect of rise of temperature on the attraction of salt for

water is to diminish it, as was to be expected, in the case of all the salts when in a saturated solution. But in the case of the

TABLE III.

Salt.	65°.	75°.	85°.	95°.	
NaNO ₃	3667	3879	4142	4329	$\left(1 - \frac{P_1}{P_2}\right) \times 10,000.$
KNO ₃	2402	2402	2775	3302	
Na ₂ CO ₃	1778	1744	1609	1549	
K ₂ CO ₃	5872	6106	6214	
MnSO ₄	1094	1139	898	692	
FeSO ₄	1178	1039	945	735	
KNO ₃	1839	2028	2142	2149	
FeSO ₄	944	890	899	735	
NaNO ₃	27.1	29.86	32.82	36.21	
"	135.3	129.9	126.2	119.6	
KNO ₃	22.08	27.59	33.65	40.24	mol.
"	87.1	82.5	82.1	
Na ₂ CO ₃	15.69	15.69	15.59	15.49	mol.
"	113.3	111.1	103.3	100.0	
K ₂ CO ₃	35.68	37.51	39.33	mol.
"	164.5	162.8	158.0	
MnSO ₄	14.76	14.76	14.71	13.89	mol.
"	74.1	77.2	61.0	49.8	
FeSO ₄	15.43	15.16	14.16	12.08	mol.
"	76.3	68.6	66.7	60.9	

Solubility taken from Mulder (*Bijdragen tot de Geschiedenis van het scheikundig gebonden Water* (Rotterdam, 1864).

solutions of constant composition the attraction of salt for water is increased with KNO₃, and diminished with FeSO₄; and this is also found with MnSO₄ at the temperatures 65° and 75°—so long as the solubility remains constant the value of $1 - \frac{P'}{P}$ increases. Now KNO₃ has its solubility largely increased by rise of temperature, while that of FeSO₄ is diminished; and we have seen above that when $n = \text{constant}$, $1 - \frac{P'}{P}$ increases in the case of KNO₃ and diminishes in the case of FeSO₄. The explanation of this apparently anomalous behaviour must lie in a change in the molecular relations in the solution. I have stated in previous papers that, from other experiments, I have come to the conclusion that the solubility of a salt is dependent on the attraction of salt for water and of salt for salt: if the former increases faster than the latter with the rise of temperature, then the salt is more soluble at a high temperature than at a lower, and *vice versa*. Now in

a strong solution the molecular volume of each salt-molecule is greater than it is in a weak solution, owing to the attraction of salt for salt having to a certain extent overcome the attraction of salt for water. If, however, the solubility of the salt increases with rise of temperature, then the effect of heat will be to weaken to a great extent the attraction of salt for salt, and to a small extent that of salt for water; but the diminution in the attraction of salt for salt may be so great as to be practically equal to an *increase* of the attraction of salt for water; and such is the case with the solution of KNO_3 given above. On the other hand, when solubility decreases with rise of temperature, then the attraction of salt for water diminishes faster than that of salt for salt; and this is to be seen in the case of FeSO_4 above.

Some experiments I have made on the coefficient of expansion of concentrated solutions will make this even more clear. I experimented with NaCl , KCl , NaNO_3 , and KNO_3 in nearly saturated solutions at 20° , and determined their density at 20° , 40° , and 98°C . The results and approximate strengths of the solutions are given in Table IV.; and the volumes at

TABLE IV.

Salt.	$\delta 20^\circ$.	$\delta 40^\circ$.	$\delta 98^\circ$.	<i>n</i> .
NaCl	1.19987	1.19614	1.19939	10.5 (c)
KCl	1.1827	1.18073	1.18602	8.5 „
NaNO_3	1.14573	1.14107	1.13763	5.5 „
KNO_3	1.17311	1.16906	1.16668	5+
Water at 20° , 40° , and 98° taken as unity.				
Density referred to Water at 20° and Volumes.				
Salt.	t° .	δ_{20} .	Volume.	Volume— vol. of water.
NaCl	20°	1.19987	100,000	
	40	1.18911	100,905	+312
	98	1.15349	104,021	+ 42
KCl	20	1.1827	100,000	
	40	1.17374	100,763	+ 170
	98	1.14063	103,688	- 291
NaNO_3 ...	20	1.14573	100,000	
	40	1.13435	101,004	+411
	98	1.0941	104,720	+741
KNO_3	20	1.17311	100,000	
	40	1.16217	100,941	+348
	98	1.12203	104,552	+573

these temperatures (volume at 20° = 100,000) are compared with the volume of water at the same temperature, that of water being taken as follows:—

At 20°	=	100,000,
„ 40°	=	100,593,
„ 98°	=	103,979.

Thus it is seen that, comparing the expansion between 20° and 40°, or 20° with that between 40° and 98° or 58 degrees, that of water is about as 1 : 6, while in all the salt-solutions it is less than 1 : 1 ; and in the case of KCl the volume at 98° is very considerably less than that of water, contraction having taken place between 40° and 98°. This has also been observed by Kremers, as I have shown in a previous paper*, and the table of molecular volumes at 20° and 40° that I have already published † also fully bears this out ; so that it is clear that, in a strong solution, the effect of rise of temperature is to cause an expansion which, as the temperature rises, becomes more and more similar to that of water alone, and after that actually is considerably less than it; so that at a high temperature the volume may be even less than that of water.

Thus the experiments on the vapour-pressures of salt-solutions of constant strength, and on the coefficient of expansion of such solutions, show most plainly that, by rise of temperature, the attraction of salt for salt is so greatly diminished that it is equivalent to an increase in attraction of salt for water. That this is not the case with constantly saturated solutions is due to the attractions of salt for water and of salt for salt being in such solutions in equilibrium. Thus the effect of heat is, as usual, to diminish the attraction of salt for water,

as is shown by the diminution of the value $\frac{1 - \frac{P'}{P}}{n}$.

It is by a comparison of the values of $\frac{1 - \frac{P'}{P}}{n}$ for various salts at the same temperature that I hope to be able to arrive at the comparative value of the attraction of water for salt, the second factor in solution, while the ratios of the fraction $\frac{P'}{P}$ ‡ give the comparative values of the attraction of salt for salt.

* Phil. Mag. February 1883.

† Ibid. August 1883.

‡ "Saturation of Salt-Solutions," Phil. Mag. June (Supplement) 1884.