THE TRANSITION TEMPERATURE AND SOLUBILITY OF SODIUM SULPHATE IN PRESENCE OF SODIUM CHLORIDE OR SODIUM BROMIDE.*

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[Contribution from the Department of Chemistry, Yale University.]

In connection with the work described in the preceding paper it was necessary to determine the concentration of sodium chloride at which the transition temperature of sodium sulphate is just 25.0°; accordingly series of determinations were made of the concentration of sodium chloride (and also of sodium bromide) and of the sulphate corresponding to a measured transition temperature.

The experimental method was as follows. About 60 grams decahydrate (S_{10}), partly melted, and 10 grams crystallized anhydrous sodium sulphate (S_0) were put into a thermos flask provided with a cork through which passed a calibrated thermometer. The flask was shaken, and the purity of the salts assured by the constancy of transition temperature. To this mixture was then added some of the third component—e.g. pure sodium chloride—and the flask shaken again continuously; the system soon came to equilibrium, the temperature remaining within 0.02° for an hour, whereupon a sample of the solution was withdrawn for analysis. More chloride was now added and the procedure repeated. The sample was withdrawn by the usual method of suction through glass tubes provided with plugs of glass wool, into a weighing tube; when the temperature of the room was below that of the solution, the sampling tube was warmed so as to prevent crystallization during the process of transfer. The weighed solution was diluted and aliquot parts taken for analysis. Halide was determined by titration with silver nitrate in neutral solution, with sodium chromate as indicator, the purity of the halides used being also checked by this method. Another portion of the diluted solution was evaporated to dryness, heated at 120° for half an hour, the residue weighed, and the sodium sulphate determined by difference. The experimental results, expressed in terms of molalities, are presented in Table I. In

[*] From the dissertation presented by Francis J. Norton in June, 1924, to the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy.

the literature there are analogous data for these and a few other solutes; they[1] are brought together in Table II.

TABLE I. Measured concentration (mols per 1,000 g. water) of Na_2SO_4 and (a) NaCl (b) NaBr in equilibrium with the pair of solid phases $Na_2SO_4.10\ H_2O$ and Na_2SO_4 at a series of temperatures.

	(a) Molality mols per 1,000 g H_2O			(b) Molality mols per 1,000 g H_2O	
t	NaCl	Na_2SO_4	*t*	NaBr	Na_2SO_4
32.38	0	3.56	32.38	0	3.56
30.00	1.41	2.57	31.97	0.242	3.30
29.02	1.80	2.38	30.77	0.930	2.75
27.38	2.55	1.94	29.86	1.43	2.40
25.90	3.09	1.63	28.80	1.90	2.06
25.50	3.30	1.56	26.70	2.83	1.51
25.00	3.42	1.47	25.56	3.24	1.34
23.96	3.79	1.33	24.02	3.75	1.09
23.48	3.93	1.31	22.26	4.29	0.912
22.56	4.24	1.23	20.78	4.68	0.764
21.68	4.46	1.11	18.10	5.32	0.623
21.00	4.72	1.00	16.39	5.71	0.575
18.41	5.38	0.816			
17.98	5.51	0.788			

In discussing these results, let us first consider the relation between transition temperature S_{10}—S_0 and concentration of added solute, as illustrated by Fig. 1 which includes all of the data of Tables I and II. The figure brings out the rather unexpected fact that a single curve suffices to cover all of the points for sodium chloride, bromide (except at the two highest concentrations), iodide and glucose, within the accuracy of the data.[2] Moreover, if we bear in mind that to add 1 mol. H_2SO_4 is in this case equivalent to adding 2 mols. $NaHSO_4$, we see that the point so interpreted falls very close to the curve. The only points off the curve are those for addition of alcohol and sodium phthalate, and the single point for sodium hydroxide and for sodium nitrate.

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[1] Excepting the cases in which the solution was not analyzed, the authors being interested in sodium sulphate solution as a cryoscopic solvent, the solutions being dilute with respect to the added component. Löwenherz, Z. physik. Chem., **18**, 70, 1895; Boutaric and Léonhardt, Compt. rend., **155**, 825, 1912; D'Armois and Périn, Compt. rend., **177**, 762, 1923; Turner and Patterson, Trans. Faraday Soc., **20**, 345, 1924.

[2] A repetition and extension of the determinations with NaOH, NaI, and some other solutes, has now been begun.

TABLE II. Measured concentrations (mols. per 1,000 g. water) of various solutes and of Na_2SO_4 in equilibrium with the pair of solid phases S_{10} and S_0

t	Molality		Reference
	NaCl	Na_2SO_4	
29.0	1.79	2.32	a
28.9	1.83	2.30	
26.7	2.76	1.78	
24.7	3.48	1.44	
	NaBr		
29.3	1.70	2.22	a
27.9	2.34	1.82	
26.3	2.94	1.48	
	NaI		
29.8	1.58	2.06	a
28.6	2.19	1.64	
27.2	2.78	1.24	
25.5	3.36	0.95	
	glucose	Na_2SO_4	
31.2	0.70	3.42	a
30.2	1.24	3.40	
	C_2H_5OH		
31.1	1.65	2.20	a
30.9	4.99	1.21	
	NaOH		
25.0	3.90	1.20	b
	H_2SO_4		
25.0	1.84	4.92	c
	Na phthalate		
25.0	2.89	0.76	d
23.0	3.34	0.63	
	$NaNO_3$		
25.0	4.76	1.76	e

a Biron and Malchevski, J. Russ. Phys-Chem. Soc., **40**, 1619, 1908. They also used Na_2CrO_4 which however forms mix-crystals with Na_2SO_4. The data are not referred to in the abstracts and we did not know of them until our experimental work had been completed.
b D'Ans and Schreiner, Z. anorg. Chem., **67**, 437, 1910.
c Foote, J. Ind. Eng. Chem., **11**, 629, 1919.
d Foote and Smith, J. Am. Chem. Soc., **46**, 84, 1924.
e Foote, this Journal, **9**, 441, 1925.

The equal lowering of transition temperatures by sodium chloride (for instance) and by glucose is presumably to be interpreted on the basis that sodium sulphate under such conditions is practically completely ionized and therefore that addition of NaCl is in effect merely addition of one new ionic species, namely Cl^-. The case is similar to that of the lowering of freezing temperature of sodium chlorate by added sodium salts, investigated by Foote and Levy;[3] and to that of lead chloride by lead bromide.[4]

The curve as drawn becomes steeper with increase of concentration of the solute, in accordance with the effect of a similar solute upon the freezing temperature of water. For

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[3] Foote and Levy, Am. Chem. J., **37**, 494, 1907.

[4] Goodwin and Kalmus, Physic. Rev, **28**, 1, 1909; see also Lewis and Randall "Thermodynamics" (McGraw-Hill) p. 219.

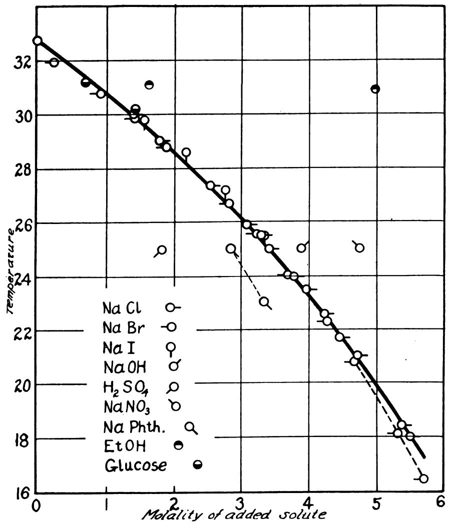

Fig. 1. Depression of transition temperature of sodium sulphate (decahydrate-anhydrous) by an added solute.

example, if we derive by interpolation, for even molalities of sodium chloride, corresponding values of transition temperature, from our own data, and of freezing temperature, from the data by Rodebush,[5] we obtain the following result:

Molality of NaCl mols/1,000 g H_2O	Total lowering of transition temp. $-\Delta t_s$	diff.	freezing temp. $-\Delta t_f$	diff.
1	1.70		3.32	
		2.10		3.58
2	3.80		6.90	
		2.43		3.90
3	6.23		10.80	
		2.86		4.40
4	9.09		15.20	
		3.35		4.90
5	12.44		20.10	

The graph of Δt_s against Δt_f is very nearly a straight line, the change in Δt_f being about 50% greater than in Δt_s.

The transition temperature of sodium sulphate is, as we have seen, lowered by the same amount by a specified concentration of sodium chloride, bromide, or iodide; but the con-

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[5] Rodebush, J. Am. Chem. Soc., 40, 1204, 1918.

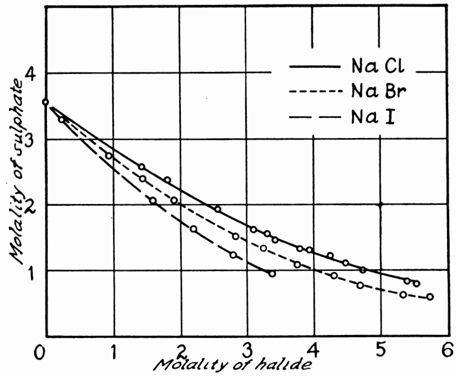

Fig. 2. The solubility (mols per 1000 g water) of sodium sulphate at its transition temperature in presence of sodium halide.

centration of sodium sulphate in the equilibrium solution differs in the three cases. This is apparent from Fig. 2, in which the molality of sulphate at the respective transition temperature is plotted against that of halide; there are three separate curves, that for iodide being lowest, for chloride highest. This is in line with the effect of these three salts upon freezing of water, and with the idea that the iodide is the most highly hydrated.

Now at a given temperature the vapor pressure of the system S_{10}—S_0—L'—V is fixed and independent of what the added solute (or solutes) may be; but as we have seen, the three halides are equally effective in lowering the transition temperature (at which alone both S_{10} and S_0 can exist). Thus the same lowering of vapor pressure of water (for example at 26.15°) is caused by 3 NaCl + 1.69 Na_2SO_4, by 3 NaBr + 1.45 Na_2SO_4 and by 3 NaI + 1.14 Na_2SO_4, each pair dissolved in 1,000 grams water; and the difference in effectiveness, at this concentration, between bromide and chloride is equal to 0.24 Na_2SO_4, and between bromide and iodide likewise 0.31 Na_2SO_4. We may look upon this phenomenon as a sort of competition for water as between the sulphate and the halide; for, since we fix the halide concentration, adjustment to identical vapor pressure can take place only through the ejection from the solution of more or less of the sulphate. On this basis, sodium iodide is a stronger competitor for water than bromide, which in turn is stronger than chloride. This is illustrated by the following interpolated table which shows for several rounded molalities of halide, the molality of Na_2SO_4 in contact with both S_{10} and S_0.

		Molality of sulphate in presence of S_{10}, S_0 and					
		Chloride		Bromide		Iodide	
Molality of halide	temp.	S_1	$-\Delta S_1$	S_2	$-\Delta S_2$	S_3	$-\Delta S_3$
0	32.38	3.56		3.56		3.56	
1.5	29.68	2.53	1.03	2.35	1.21	2.15	1.41
2.0	28.58	2.23	1.33	2.02	1.54	1.76	1.80
2.5	27.38	1.94	1.62	1.72	1.84	1.41	2.15
3.0	26.15	1.69	1.87	1.45	2.11	1.14	2.42

The graph of the lowering of solubility ($-\Delta S_1$) by chloride against that by bromide or iodide ($-\Delta S_2$ or $-\Delta S_3$) is in each case a straight line, which however must curve slightly at low halide concentrations to pass through the origin. Nevertheless we may state, as a close approximation for any given halide concentration, that if the lowering of concentration of Na_2SO_4 by chloride be x, that by bromide will be about 1.15 x and that by iodide about 1.55 x; yet in all three solutions the activity of the water is the same. According to this criterion, glucose is a very much weaker competitor than sodium chloride.

The curve of transition temperature may be regarded as the locus of intersection of the solubility curves of S_{10} and S_0, the effect of an added solute depending upon its effect upon the solubility of both S_{10} and S_0. If the lowering of the two curves is nearly equal (as by alcohol[6]) the transition temperature is changed very little; in the more usual case that the solubility curve for S_0 is lowered much more than that of S_{10} (as by NaCl[7]) the transition temperature is lowered. There may even be a lowering of the solubility of S_0 with an increase in that of S_{10}, as is the case upon addition of urea.[8] Still in all cases the concentration of sulphate in the solution at the transition temperature adjusts itself so that the vapor pressure of water in equilibrium with the system S_{10}—S_0—L'—V has the fixed value characteristic of that temperature.

[6] de Bruyn, Z. physik. Chem., 32, 98, 1900.

[7] Seidell, Am. Chem. J., 27, 52, 1902.

[8] Löwenherz, Z. physik. Chem., 18, 70, 1895.

SUMMARY.

Measurements are presented of the lowering of transition temperature of sodium sulphate decahydrate by sodium chloride and bromide, and of the concentration of halide and of sulphate in the solution in equilibrium with the pair of solid phases $Na_2SO_4 . 10\ H_2O$ and Na_2SO_4 at these temperatures. A discussion of the results brings out the fact that sodium chloride, bromide and iodide, and glucose are all practically equally effective in lowering the transition temperature, although they differ markedly in repressive effect upon the concentration of sulphate in the solutions.

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