713. *The Heat of Solution of Halides, Sulphuric Acid, Oxalic Acid, Sodium Hydroxide, and Urea in Ethyl Alcohol–Water Mixtures.*

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The heats of solution of ferric chloride (anhydrous and hydrated), of the hydrated chlorides of aluminum, copper, nickel, and cobalt, and of potassium iodide, sulphuric acid, oxalic acid (hydrated), sodium hydroxide, and urea were determined in water–ethyl alcohol mixtures. S-shaped curves were obtained when heat of solution was plotted against alcohol content, with a pronounced minimum in all cases at about 30% (wt.) of ethyl alcohol. In most cases a maximum at about 75% (wt.) is discernible.

The determination of the heat of solution was based on two measurements: (i) the change of temperature on dissolving the substance in an ethyl alcohol–water mixture; (ii) measurement of the specific heat of the resulting solution. All percentages recorded are by weight.

Table I.

Specific heat of ethyl alcohol–water mixtures at 22·5°.

C_2H_5·OH, wt. %	(0)	10	20	25	30	40
Sp. heat	(0·9986)	1·024	1·045	1·046	1·025	0·974
C_2H_5·OH, wt. %	50	60	70	80	90	93·6
Sp. heat	0·914	0·857	0·808	0·746	0·677	0·660

The recorded data for the specific heat of ethyl alcohol–water mixtures are discordant. Therefore, we made a series of measurements at a mean temperature of 22·5° (Table I). The salt solutions used were very dilute and therefore the heat of dilution was small, being only a few units % of the heat of solution. The S-shaped curves obtained with anhydrous and hydrated ferric chloride (Figs. 1 and 2) show two breaks at about 30% and 70% of ethyl alcohol. The constant difference of 26·2 kcals. between the two curves up to highest alcohol concentration is equal to the molar heat of formation of the hexahydrate at 23°. Whichever form is used initially, the same ratio of the components (hydrates or alcoholates) must exist in the final mixture, so, clearly, a quantity of heat is used for dehydration of the hexahydrate. If the hydrate is dissolved in a solvent containing 83% of ethyl alcohol, no heat effect is observed. At higher concentrations of alcohol, heat is absorbed. The maximum in the upper alcohol concentration is not always distinct (*e.g.*, with sulphuric acid), and oxalic acid and sodium hydroxide do not show it : with urea, neither the maximum nor the minimum is distinct. These indistinct maxima may be due to chemical reaction.

FIG. 1.

1, $FeCl_3$. 2, H_2SO_4. 3, $AlCl_3,6H_2O$. 4, NaOH.

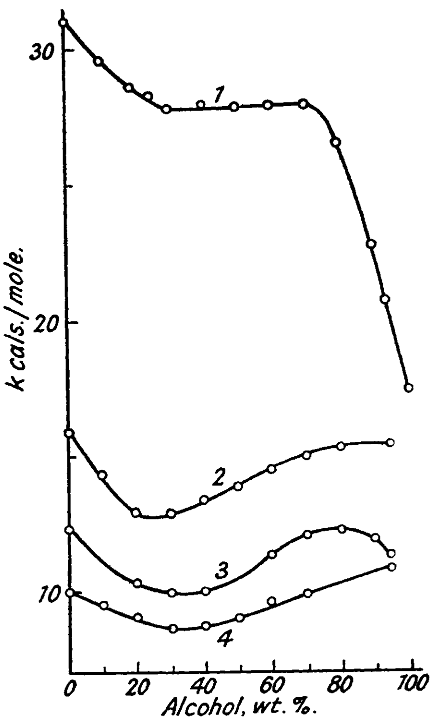
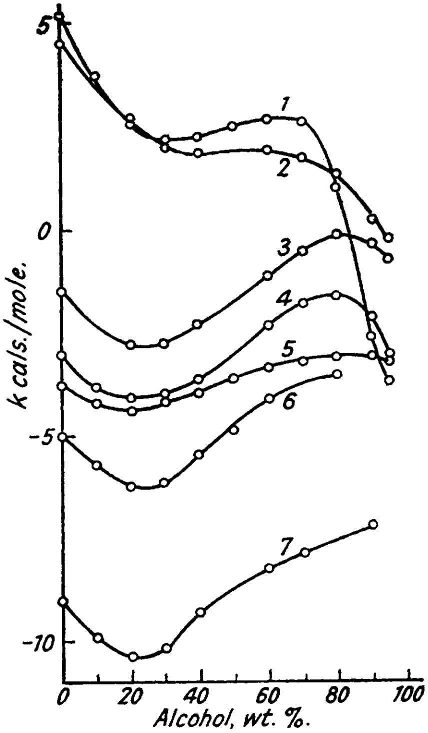


FIG. 2.

1, $FeCl_3,6HO$. 2, $CuCl_2,2HO$. 3, $NiCl_2,6H_2O$. 4, $CoCl_2,6HO_2$. 5, Urea. 6, KI. 7, $H_2C_2O_4,2H_2O$.



a shows the number of g. of substance dissolved in 200 *g. of solvent.*
b ,, ,, mols. of water per mol. of substance for the solution in pure water.

	a.	*b.*	*Notes.*
$FeCl_3$	3	600	
$FeCl_3,6H_2O$	7	429	
$AlCl_3,6H_2O$	5	536	*Curves similar to those for* $FeCl_3$.
$CuCl_2,2H_2O$	5	307	*Breaks at* ca. 30% *and* 70% *of* EtOH.
$NiCl_2,6H_2O$	10	264	*Heat of solution negative ; min. at* 25%, *max. at* 80% EtOH.
$CoCl_2,6H_2O$	10	264	*Curve similar to preceding ; heats more negative.*
KI	10	185	*Heat of solution negative ; min. at* 25% *; above* 80%, *rate of solution too slow for exact measurement.*
H_2SO_4	3·65 *	299	*Minimum at* 25% EtOH.
$H_2C_2O_4,2H_2O$	5	280	,, ,, ,,
NaOH	2	222	,, 30% ,,
Urea	4·67	143	*Indistinct maximum and minimum.*

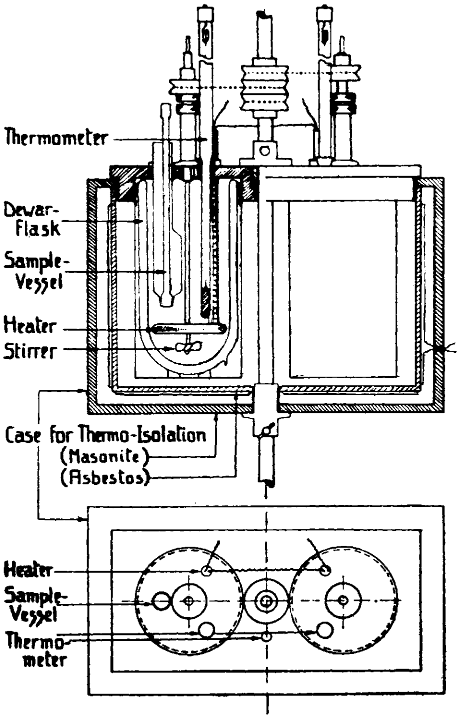
* 95% *Acid.*

The results conform well with the general picture developed in the following paper.

EXPERIMENTAL.

Apparatus.—Electrically heated twin calorimeters of special design were used : one served for the measurement of the heat of solution, and the other contained only water and served as a control. The calorimeters themselves (Fig. 3) were two Dewar 500-c.c. flasks in metal sockets. The necessary fittings such as salt-container, stirrers, electric heaters, and Beckmann thermometers were mounted on an ebonite plate. The Dewar flasks could be screwed in or removed from the same ebonite plate at will. The salt-container (sample-vessel) was made entirely of glass with a ground stopper at the bottom which could be opened from above and held open by a clamp. The stirrers were made of glass and were driven by a motor, so that both were rotated at the same rate. The temperature in each of the Dewar flasks was recorded on a Beckmann thermometer divided into 0·01°, which could be read to 0·001° by means of a lens. The water equivalent of the calorimeter was found to be 1·122 by dissolving 10 g. of potassium chloride in 200 g. of water at a mean temperature of 25°, Wüst and Lange's data (Landolt–Börnstein "Tabellen," 1927, p. 842) being used as reference values. The difference between the water equivalent of the two Dewar flasks, and that between the two Beckmann thermometers, were determined and a curve was drawn from which the necessary corrections (which did not exceed 2%) were directly obtained.

FIG. 3.



Procedure.—The quantity of the sample (2—15 g.) was calculated to give a temperature change of 1—2°. The powdered and weighed substance was introduced into the sample vessel. In order to prevent the absorption of moisture, this was closed at the top by a bored rubber stopper. The Dewar flasks containing the exactly weighed solvent were screwed into the ebonite plate. One of the flasks contained 200 or 300 g. of ethyl alcohol–water mixture, and the other an amount of water calculated to be of approximately the same heat content.

The solution with the suspended sample vessel was heated by the internal heater to the required temperature while being constantly stirred. At the same time the space inside the outer case was heated to the same temperature. Thermal equilibrium in the calorimeter was reached after 10—15 minutes. The course of the temperature changes was then uniform. The temperature was read at intervals of 30 secs., and the preheating (or cooling) curve—the equilibrium drift—noted. Then the sample vessel was raised out of the solvent and the salt dropped into the Dewar flask by opening the bottom stopper. The last was held in a raised position by a clamp, while the sample vessel was again lowered to its former position, so that any residue adhering to the walls of the vessel or to the stopper was dissolved. Dissolution took a few minutes, after which the equilibrium drift was immediately measured. The exact temperature difference was obtained graphically.

The specific heat of the salt solution was determined by electrically heating both liquids to a fixed equal temperature. The equilibrium drift was measured, followed by heating for about 1°. Then the post-heating curve was measured, and the temperature difference determined graphically as above. By comparing the temperature difference and the weights of the liquids, the specific heat of the solution was obtained. This value was extrapolated for the mean temperature of the dissolution. In order to evaluate the temperature coefficient of the specific heat of these dilute salt solutions, special experiments were carried out. As there was only a small difference (about 1°) between the mean temperature of the dissolution and the temperature at which the specific heat was determined, the corrections were very small.

TABLE II.

Heat of solution.

Substance :	$FeCl_3$.	$FeCl_3,6H_2O$.	$AlCl_3,6H_2O$.	$CuCl_2,2H_2O$.	$NiCl_2,6H_2O$.	$CoCl_2,6H_2O$
Mean temp. :	24°	22°	23°	22·5°	22·5°	22·5°
$C_2H_5{\cdot}OH$, wt. %.			Kcals. per mole.			
0	31·3	5·12	12·43	4·50	−1·45	−2·95
10	29·8	3·68	—	—	—	−3·70
20	28·8	2·44	10·21	2·54	−2·68	−4·09
30	27·9	2·04	9·92	1·93	−2·66	−4·00
40	28·0	2·08	9·99	1·79	−2·22	−3·52
50	27·9	2·41	—	—	—	—
60	27·9	2·55	11·32	1·99	−1·10	−2·35
70	28·0	2·46	12·00	1·70	−0·55	−1·87
80	26·5	+0·97	12·21	1·26	−0·14	−1·60
90	22·7	−2·61	11·85	+0·23	−0·41	−2·14
93·8	20·5	−3·65	11·19	−0·26	−0·61	−3·06
100	17·4	—	—	—	—	—

Substance :	KI.	H_2SO_4.	$H_2C_2O_4$.	NaOH.	Urea.
Mean temp. :	24·5°	23·5° .	24·5°	23°	25°
$C_2H_5{\cdot}OH$, wt. %.			Kcals. per mole.		
0	5·05	15·84	− 9·01	10·00	−3·71
10	5·70	14·39	− 9·83	9·60	−4·13
20	6·28	13·00	−10·35	9·09	−4·35
30	6·20	12·96	−10·16	8·65	−4·14
40	5·48	13·35	− 9·29	8·74	−3·88
50	4·92	13·80	—	9·01	−3·56
60	4·11	14·45	− 8·24	− 9·52	−3·36
70	—	14·99	− 7·86	9·73	−3·17
80	3·41	15·28	—	—	−3·08
90	—	—	—	—	−3·15
93·8	—	15·31	− 7·20	10·74	−3·23
100	—	—.	—	—	—

The salt solutions used were very dilute and therefore the heat of dilution was small and amounted only to a few units % of the heat of solution (*e.g.*, for anhydrous ferric chloride and pure water in the molar ratio 1 : 600, +31·3 kcals.; in the molar ratio 1 : 360, +30·4 kcals).

Results.—Determination of the heat of solution of various substances in ethyl alcohol–water mixtures. The heat of solution H of 1 g.-mol. of salt was calculated by the formula $H = wWsM \,.\, \Delta T/1000$ g., where H = heat of solution (in kcals.), w = water equivalent of the apparatus, W = weight of solution, s = specific heat of the solution, M = molecular weight of salt, g = weight of salt (in g.), and ΔT = temperature difference. The results are given in Table II and Figs. 1 and 2.

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