AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **17**, 813 (1949); doi: 10.1063/1.1747404
View online: http://dx.doi.org/10.1063/1.1747404
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/17/9?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 17, NUMBER 9 SEPTEMBER, 1949

Magnetic Study of Some Hydrates

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(Received January 3, 1949)

Magnetic susceptibilities of a number of hydrates have been measured by the Gouy technique. In several hydrates of the same salt it has been found that the deviation in the observed molecular susceptibility from additivity, per molecule of water of crystallization, is greatest in the hydrate containing the least number of molecules of water of crystallization and tends to decrease as the number of molecules of water of hydration increases. A relation has been shown to exist between the heat of hydration per molecule of water of crystallization and the deviation in χ_m per molecule, in these hydrates. The departure from the additivity rule in hydrates has been explained on the basis of bindings between the molecules of water of crystallization and the anhydrous salt.

COMPARATIVELY few workers have studied the effect of water of crystallization on the diamagnetic susceptibility of hydrates. Duchemin[1] found that although monohydrate of $MgSO_4$ is complex, the susceptibilities of the di- and heptahydrates follow the additivity rule. Zimens and Hedvall[2] concluded from the study of the susceptibilities of $Na_2CO_3 \cdot 10H_2O$ and alum that the water of crystallization does influence the susceptibilities of the hydrates; however, in a later communication,[3] the same authors have reported that the water in these hydrates behaves in an additive fashion. Raychaudhari[4] finds that there is a loss in diamagnetism when a hydrate is formed, and therefore the susceptibility of the hydrated salt is generally less than its value calculated from the anhydrous molecule on the basis of strict additivity. Varadachari[5] considers that Raychaudhari's method of preparing the hydrates and anhydrous substances separately for magnetic measurement makes his results doubtful. He suggests that an obviously better method would be to prepare the hydrated salt and determine its magnetic susceptibility before and after dehydration; the water will be in the combined state in one case and free in the other, and hence the effect of binding alone will be recorded by the change in the magnetic susceptibility. According to this method, Varadachari studied the effect of binding of molecules of water of crystallization on the susceptibility of sodium sulphate decahydrate, by determining the changes in the susceptibility of sodium sulphate in solution below and above the temperature at which transition, from the decahydrate to the anhydrous substance, takes place. From the results obtained, Varadachari concluded that the binding of water molecules with sodium sulphate is very loose.

Varadachari's method of studying the effect of hydration is not always easy to follow. Further, according to this method, the susceptibilities of hydrates should be studied in the state of solution. Many factors other than the effect due to water of crystallization influence the susceptibilities of salts in solutions. For instance, water consists of associated molecules, and at higher concentrations these molecules tend to depolymerize, producing a slight increase in the magnetic susceptibility. Further, the effect produced by the hydration of ions on the susceptibilities of the salts in solutions is also considable. It therefore appears likely that the conclusions obtained, regarding the effect of water of crystallization on the susceptibility of a hydrate from the measurements on solutions of the hydrate below and above the transition temperature, may be erroneous in some cases. Thus, the method adopted by Raychaudhari appears to be the best approach to the problem of the effect of hydration.

Raychaudhari[4] has tried to establish a qualitative relation between the heat of hydration of a salt and the percentage deviation in susceptibility from the additivity rule, and has come to the conclusion that in cases where the heat of hydration is in the neighborhood of 20 calories, the percentage deviation is as great as 20 percent.

In the present investigation, the authors have determined the susceptibilities of a number of hydrates and their corresponding anhydrous salts in the solid state. Attempts have also been made to find how far the conclusions arrived at by Raychaudhari are correct.

The susceptibilities of a number of hydrates of the same salt, containing different number of molecules of water of crystallization, were also determined with a view to find a relation between the deviation in the susceptibility from additivity and the number of molecules of water of crystallization associated with the salt.

In order to test how far the additivity rule holds good for the hydrates in solution, susceptibilities of some hydrates and their corresponding anhydrous salts were also calculated from the measured susceptibilities of their aqueous solutions.

EXPERIMENTAL

The susceptibilities of the hydrated and anhydrous salts were measured in the solid state and in solutions

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[1] E. Duchemin, Comptes Rendus **199**, 571 (1934).

[2] K. E. Zimens and J. A. Hedvall, Svensk, Kem. Tid. **53**, 12 (1941).

[3] K. E. Zimens and J. A. Hedvall, Trans. Chalmers. Univ. Technd. (Gothinburg) No. 9, 3–26 (1942).

[4] D. P. Raychaudhari, Zeits. f. Physik **7**, 393 (1932).

[5] P. S. Varadachri, Proc. Ind. Acad. Sci. **2A**, 161 (1935).

by using the modified form of Gouy's balance described by Prasad, Dharmatti, and Gokhale.[6] All stable hydrates, containing the maximum number of molecules of water of crystallization, used in this investigation were extra pure compounds of either Merck or Kahlbaum. The anhydrous substances were prepared from the hydrates by heating them in an oven to constant weight at temperatures at which the transformation from the hydrate to the anhydrous substances takes place. In addition to these stable hydrates, several intermediate hydrates of some salts, containing various molecules of water of crystallization, were also prepared by heating the stable hydrates at definite temperatures at which the transition from one hydrate to the other takes place, until constant weights were obtained. As some of these intermediate hydrates are not quite stable and tend to pass into a hydrate containing a larger number of molecules of water of crystallization if kept for a long time, they were introduced in the specimen tube as soon as they were prepared, and their susceptibilities were measured immediately without allowing them to absorb moisture. As it does not generally take a long time to pack the substance in the specimen tube for susceptibility measurement, the authors' measurements for these hydrates can be taken as quite reliable. As an additional evidence to show that the substances did not absorb moisture during the susceptibility measurement, it was noted that no increase in the weight of the sample took place during the period of measurement in the solid state. The susceptibilities

TABLE I(a).

Substance	χ_a (obs.)	χ_m (obs.)	χ_a (cal.)	χ_m (cal.)	$\frac{\Delta\chi_a}{\chi_a}\times 100$	Q	$\frac{\Delta\chi_a \times 100}{\chi_a \times n}$	$\frac{Q}{n}$
$BaCl_2\cdot 2H_2O$	0.410	100.16	0.411	100.49	—	7.0	—	3.5
$BaCl_2$	0.358	74.57						
$3CdSO_4\cdot 8H_2O$	0.380	292.4	0.358	275.5	+6.1	8.1	+2.28	3.0
$3CdSO_4$	0.28	175.16						
$CdCl_2\cdot 2H_2O$	0.45	98.68	0.427	93.74	+5.38	5.6	+2.69	2.8
$CdCl_2$	0.370	67.82						
$CdBr_2\cdot 4H_2O$	0.432	148.73	0.406	139.76	+6.4	6.86	+1.6	1.71
$CdBr_2$	0.323	87.92						
$SrCl_2\cdot 6H_2O$	0.545	145.31	0.531	141.8	+2.63	18.6	+0.43	3.1
$SrCl_2$	0.404	64.05						
$SrBr_2\cdot 6H_2O$	0.462	164.27	0.501	178.16	−7.78	23.3	−1.29	3.88
$SrBr_2$	0.406	100.40						
$Ba(ClO_3)_2H_2O$	0.350	112.8	0.361	116.41	−3.0	4.8	−3.0	4.8
$Ba(ClO_3)_2$	0.340	103.45						
$K_2SO_4Al_2(SO_4)_3\cdot 24H_2O$	0.530	502.50	0.53	503.24	0.0	—	0	—
$K_2SO_4Al_2(SO_4)_3$	0.370	191.00						
$Zn_3(PO_4)_2\cdot 4H_2O$	0.360	165.0	0.383	175.34	−6.0	—	−1.5	—
$Zn_3(PO_4)_2$	0.320	123.50						
$Al_2(SO_4)_3\cdot 18H_2O$	0.485	323.20	0.489	326.33	−0.81	—	−0.04	—
$Al_2(SO_4)_3$	0.272	93.05						
$Na_2S_2O_3\cdot 5H_2O$	0.490	121.62	0.512	127.28	−4.29	13.3	−0.85	2.66
$Na_2S_2O_3$	0.395	62.48						

TABLE I(b).

Substance	χ_a (obs.)	χ_m (obs.)	χ_a (cal.)	χ_m (cal.)	$\frac{\Delta\chi_a \times 100}{\chi_a}$	Q	$\frac{\Delta\chi_m}{n}$	$\frac{\Delta\chi_a \times 100}{\chi_a \times n}$	$\frac{Q}{n}$
$CaSO_4\cdot 2H_2O$	0.424	73.02	0.432	74.36	−1.9	4.74	−0.67	−0.95	2.37
$CaSO_4\cdot \frac{1}{2}H_2O$	0.365	52.97	0.378	54.94	−3.43	—	−4.34	−6.86	—
$CaSO_4$	0.356	48.44							
$ZnSO_4\cdot 7H_2O$	0.480	137.97	0.506	145.6	−5.1	22.69	−1.09	−0.73	3.24
$ZnSO_4\cdot H_2O$	0.353	63.34	0.378	67.86	−6.6	8.48	−4.52	−6.60	8.48
$ZnSO_4$	0.340	54.88							
$MgSO_4\cdot 7H_2O$	0.550	135.5	0.578	142.40	−4.8	24.08	−0.99	−0.69	3.44
$MgSO_4\cdot 5H_2O$	0.517	108.7	0.554	116.56	−6.7	18.0	−1.57	−1.34	3.60
$MgSO_4H_2O$	0.440	60.78	0.467	64.72	−5.8	6.98	−3.94	−5.80	6.98
$MgSO_4$	0.430	51.76							
$BaBr_2\cdot 2H_2O$	0.385	128.3	0.400	132.90	−3.46	9.11	−2.30	−1.73	4.56
$BaBr_2H_2O$	0.370	116.6	0.380	119.95	−2.6	—	−3.35	−2.60	—
$BaBr_2$	0.360	107.0							
$Na_2B_4O_7\cdot 10H_2O$	0.592	225.7	0.551	210.10	7.4	36.1	1.56	0.74	3.61
$Na_2B_4O_7\cdot 2H_2O$	0.486	115.3	0.448	106.42	8.5	—	4.45	4.25	—
$Na_2B_4O_7H_2O$	0.450	98.68	0.426	93.46	5.6	—	5.22	5.60	—
$Na_2B_4O_7$	0.400	80.5							

χ_a = specific susceptibility; χ_m = molecular susceptibility; $\Delta\chi_a$ = difference between the calculated and observed specific susceptibility; $\Delta\chi_m$ = difference between calculated and observed molecular susceptibility; n = number of molecules of water of crystallization; Q = heat of hydration in kcals.

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[6] Prasad, Dharmatti, and Gokhale, Proc. Ind. Acad. Sci. **20**, 224 (1940).

of the anhydrous substances were also measured in the solid state after taking the same precautions against the absorption of moisture.

Results obtained from the measurement of the hydrated and the anhydrous salts in the solid state are given in Tables I(a) and I(b) and are a mean of six independent readings. Throughout this paper, the susceptibility values have been expressed in terms of -1×10^{-6} c.g.s. units.

For the measurement of the susceptibilities in solutions, about five solutions of different concentrations were prepared by dissolving a known weight of the anhydrous or the hydrated salt in a known weight of conductivity water. Throughout the investigation, the concentration (C_s) of a solution has been expressed as the weight of the solute divided by the weight of the solution. The susceptibility of pure conductivity water has also determined and was found to be -0.72×10^{-6}. It was not possible to determine the susceptibilities of solutions of more than 4 or 5 concentrations because of the following experimental difficulties:

(1) The solubilities of some of the compounds are quite low and, therefore, it was not possible to prepare their solutions of concentrations beyond a certain range.

(2) It was necessary to use solutions of widely different concentrations since the differences in the susceptibilities of solutions of concentrations very near to each other were very small.

(3) Concentrated solutions were not used as there is a possibility that mixture law may not hold at high concentrations.

(4) Solutions of concentrations lower than about 5 percent were also not employed because, in such solutions, the quantity of the solute is so small that the differences between the specific susceptibilities of water and these solutions will be quite small, and the experimental error involved in the measurement of susceptibility will appreciably vitiate the correctness of the values of the susceptibility of the solid deduced from such solutions.

The susceptibilities of the solutes were calculated from the observed susceptibilities of the solutions by a graphical method. The values of the susceptibilities of solutions (χ_{sol}) were plotted against their concentrations (C_s) and the plotted points were found to lie on straight lines. According to the mixture law, $\chi_{\text{sol}}=C_s\chi_a+(1-C_s)\chi_\omega$, which evidently holds in these cases, the intercepts of these straight lines on the susceptibility axis give the value of the specific susceptibility of water, and the slopes are the values of $(\chi_\omega-\chi_a)$ where χ_a is the specific susceptibility of the solute. It was found that the value of the intercepts in all cases was -0.72×10^{-6}, which is the standard value of the susceptibility of water. The values of χ_a, calculated from the slopes, are given in the 4th column of Table II, and the values of the molecular susceptibility χ_m in the 5th column.

DISCUSSION OF RESULTS

The specific or molecular susceptibilities of the compounds, studied in this investigation by the authors either in the solid state or in solutions, were compared, wherever available, with the values obtained by other workers (cf. Table III). It will be seen from the table that the authors' values for the solids do not agree with those reported by Raychaudhari for many compounds, but the agreement between their values and those reported by other workers is quite good. The authors' values deduced from solutions of anhydrous $BaCl_2$ and $SrCl_2$ agree well with those obtained by Flordal and Frivold[7] but the values of χ_m obtained for the anhydrous $BaBr_2$ and $SrBr_2$ are slightly higher than those of other workers. Whenever the difference between the authors' values and those reported by other workers was quite large, the experiments were carefully repeated with different samples and the reliability of the authors' values has been established.

(a) Susceptibilities of Hydrates in the Solid State

If Pascal's additivity rule holds good in the case of hydrates, the molecular susceptibility of a hydrate

TABLE II.

Substance	C_s %	χ_{sol}	χ_a	χ_m
$BaCl_2\cdot2H_2O$	25	0.6413	0.42	102.8
	16.66	0.6728		
	12	0.6861		
	6	0.7025		
$BaCl_2$	19.37	0.654	0.37	78.05
	14.4	0.6703		
	10.8	0.6861		
	6	0.700		
$BaBr_2\cdot2H_2O$	42	0.583	0.40	132.11
	40	0.598		
	30	0.624		
	13	0.6803		
	7	0.6969		
$BaBr_2$	40	0.5828	0.37	110.00
	32	0.6062		
	25	0.6413		
	20	0.6546		
	10	0.685		
$SrCl_2\cdot6H_2O$	25	0.6839	0.55	147.00
	12	0.6998		
	6	0.7108		
$SrCl_2$	20	0.6624	0.425	67.38
	13	0.684		
	10	0.6922		
	8	0.6982		
$SrBr_2\cdot6H_2O$	47.4	0.6087	0.48	170.6
	32	0.6428		
	24	0.6631		
	20	0.6711		
	8	0.7003		
$SrBr_2$	40	0.6033	0.42	103.9
	32	0.6229		
	20	0.6591		
	10	0.6933		
	5	0.7046		
$Na_2S_2O_3\cdot5H_2O$	48	0.6159	0.50	125.1
	24	0.6764		
	12	0.6946		
	8	0.7023		
$Na_2S_2O_3$	45	0.5764	0.42	66.91
	40	0.608		
	24	0.646		
	20	0.664		
	6	0.7031		

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[7] M. Flordal and O. E. Frivold, Ann. d. Physik **23**, 425 (1935).

TABLE III.

Substance	Authors' values χ_a and χ_m	Values of other workers χ_a or χ_m	
		Values obtained from solids	
$BaCl_2\cdot 2H_2O$	0.41	0.41	*International Critical Tables*
	100.16	0.39	Raychaudhari[a]
		0.407	Prasad, Dharmatti, and Kanekar[b]
$BaCl_2$	0.358	0.36	*International Critical Tables*
	74.57	0.33	Raychaudhari[a]
$3CdSO_4\cdot 8H_2O$	0.380	0.27	Raychaudhari[a]
	292.4	0.374	Hollens and Spencer[c]
$3CdSO_4$	0.28	0.22	Raychaudhari[a]
	175.16	0.281	Kido[d]
		0.284	Hollens and Spencer[c]
$CdCl_2$	0.370	0.368	Kido[d]
	67.82	0.378	Hollens and Spencer[c]
$CdBr_2$	0.323	0.32	Kido[d]
	87.92	0.343	Hollens and Spencer[c]
$SrCl_2$	0.404	61.3	Kido[d]
	64.05	69.6	Hollens and Spencer[c]
		0.402	Prasad, Dharmatti, and coworkers[e]
$SrBr_2$	0.406	0.39	*International Critical Tables*
	100.4	96.28	(Meyer) *International Critical Tables*
$Ba(ClO_3)_2\cdot H_2O$	0.350	0.358	Prasad, Dharmatti, and Kanekar[b]
	112.8		
$CaSO_4\cdot 2H_2O$	0.424	0.433	Prasad, Dharmatti, and Gokhale[e]
	73.02		
$CaSO_4$	0.356	0.38	Raychaudhari[a]
	48.44	0.364	Pascal
$BaBr_2\cdot 2H_2O$	0.385	0.39	Prasad, Dharmatti, and Kanekar[b]
	128.28		
$BaBr_2$	0.36	0.39	*International Critical Tables*
	106.99	0.32	Kido[d]
	0.395	0.391	*International Critical Tables*
$Na_2S_2O_3$	62.48		
$MgSO_4\cdot 7H_2O$	0.550	0.43	Raychaudhari[a]
	135.5	0.557	Pascal
		0.546	Prasad, Dharmatti, and Amin[f]
$MgSO_4$	0.430	54.18	*International Critical Tables*
	51.76	0.37	Raychaudhari[a]
		45.08	Pascal
		47.2	Ishiwara[g]

TABLE III—(*Continued*).

Substance	Authors' values χ_a and χ_m	Values of other workers χ_a or χ_m	
		Values obtained from solids	
$ZnSO_4\cdot 7H_2O$	0.480	0.45	Raychaudhari[a]
	137.97	0.496	Prasad, Dharmatti, and Amin[f]
		0.48	*International Critical Tables*
$ZnSO_4$	0.340	61.88	*International Critical Tables*
	54.88	0.32	Raychaudhari[a]
		52.08	Prasad, Dharmatti, and Amin[f]
K_2SO_4, $Al_2(SO_4)_3$	0.530	0.53	Raychaudhari[a]
$\cdot 24H_2O$	502.50	493.00	Trew[h]
		510.00	B. N. Ghosh
$K_2SO_4\cdot Al_2(SO_4)_3$	0.370	0.37	Raychaudhari[a]
	191.00	197.00	B. N. Ghosh
$Na_2B_4O_7\cdot 10H_2O$	0.592	0.59	*International Critical Tables*
	225.7		
$Al_2(SO_4)_3\cdot 18H_2O$	0.485	0.46	Raychaudhari[a]
	323.2		
$Al_2(SO_4)_3$	0.272	0.48	*International Critical Tables*
	93.05		
		Values obtained from solution data	
$BaCl_2$	78.05	74.0	Ikenmeyer[i]
		76.3	Flordal and Frivold[j]
		72.6	Hocart[k]
$BaBr_2$	110.00	100.7	Veiel[l]
		103.6	Ikenmeyer[i]
$SrCl_2$	67.38	64.2	Veiel[l]
		61.6	Ikenmeyer[i]
		65.3	Flordal and Frivold[j]
		63.0	Hocart[k]
$SrBr_2$	103.9	87.9	Veiel[l]
		85.3	Ikenmeyer[i]
		87.9	Flordal and Frivold[j]

should be equal to the sum of the molecular susceptibilities of the anhydrous salt and the molecules of water of crystallization ($\chi_m = -12.96\times 10^{-6}$). Values calculated for the molecular susceptibilities of different hydrates on the additivity basis, using authors' values for the molecular susceptibilities of anhydrous salts, are given in column 5 of the Tables I(a) and I(b). From these values the specific susceptibilities have been calculated and are given in column 4 of the tables. It will be seen that the calculated values of χ_a (column 4) depart from the observed ones (column 2). These departures may be due to factors such as the strength of the binding of water molecules (tighter the binding, the greater the departure) and distribution of charge in the molecule of the hydrate.

The percentage deviations of the observed χ_a values from the calculated ones are given in column 6 of the tables. Data for the heats of hydration (Q) of the hydrates studied in this investigation have been collected, wherever available, from the literature and are given in column 7 of the tables. It will be seen from the values given in columns 6 and 7 that the percentage deviation from additivity does not bear any relation to the heat of hydration as pointed out by Raychaudhari.[4]

Since the substances investigated have different number of molecules of water of crystallization, a comparison between the percentage deviation and the total heat of hydration will not be quite correct. Values were, therefore, calculated for the percentage deviation in χ_a from additivity per molecule of water of crystallization, and were plotted against the values for the heat of hydration per molecule of water of crystallization. The curve obtained is shown in Fig. 1; the plotted points lie slightly scattered about a mean curve. The curve shows that on an average the percentage deviation tends to decrease, approaches to zero, and then tends to become more and more negative as the heat of hydration per molecule increases. These conclusions are

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[a] See reference 4.

[b] N. Prasad, S. S. Dharmatti, and C. R. Kanekar, Proc. Ind. Acad. Sci. **15**, 307 (1942).

[c] W. R. A. Hollens and J. F. Speneer, J. Chem. Soc. **147**, 495 (1935).

[d] K. Kido, Sci. Rep. Tohoku Imp. Univ. **21**, 149, 289 (1932); **22**, 835 (1935).

[e] Prasad, Dharmatti, and Gokhale, Proc. Ind. Acad. Sci. **20**, 224 (1940).

[f] Prasad, Dharmatti, and Amin, Proc. Ind. Acad. Sci. **26**, 312 (1947).

[g] J. T. Ishiwara, Sci. Rep. Tohoku Imp. Univ. Series 1, **3**, 303 (1914); **5**, 53 (1916); **9**, 232 (1920).

[h] V. C. J. Trew, Trans. Faraday Soc. **32**, 1658 (1936).

[i] K. Ikenmeyer, Ann. d. Physik **1**, 169 (1929).

[j] See reference 7.

[k] See reference 8.

[l] Veiel, Ann. d. Physik **24**, 697 (1935).

general as they have been drawn from the consideration of the different hydrates of several substances.

Interesting observations are made when the values for $(\Delta\chi_m/n)$ (Cf. column 8, Table I(b)), in the case of several hydrates of the same salt, are considered. It will be seen that in all cases these values numerically increase as the number (n) of molecules of water of crystallization decreases. It is worth mentioning here that, in some cases, the deviations $(\Delta\chi_m/n)$ are negative, that is, the observed values are greater than the calculated ones, while in others, the reverse is the case. However, in both cases the values of $(\Delta\chi_m/n)$ tend towards zero as n increases. As stated previously, the deviations from additivity rule are caused as a result of the variability of the binding strength between the ions of the anhydrous salt and the molecules of the water of crystallization. If the binding between the two is tight, it will appreciably affect the distance between them and will bring about a strain because of the overlapping of the electronic orbits in the anhydrous salt and the molecules of the water of crystallization, and, hence, cause a deformation of the whole molecule of the hydrate which will give rise to a large deviation in the value of χ_m from additivity. However, if the binding is weak these deviations will be comparatively small. The observations stated in the previous paragraph, therefore, show that in the case of a hydrate containing the smallest number of molecules of water of crystallization [largest values of $(\Delta\chi_m/n)$] the binding of the molecules of water with the anhydrous salt is quite tight. The decrease in the value of $(\Delta\chi_m/n)$, when n increases, that is, more molecules of water of crystallization are added on, shows that the binding is considerably weakened, probably because the ions are now further apart and hence do not cause as much deformation as when the number of molecules of the water of crystallization is smaller. The behavior observed for the several hydrates of the same salt appears to be a general phenomenon (true for the hydrates of any substance) as shown in Fig. 2 by plotting the numerical values irrespective of signs of $(\Delta\chi_m/n)$ for all the hydrates, against the ratio of the weight of molecules of water of crystallization to the weight of the anhydrous salt, which is the factor of association of water of crystallization with the salt. The graph is a smooth curve drawn through the plotted points.

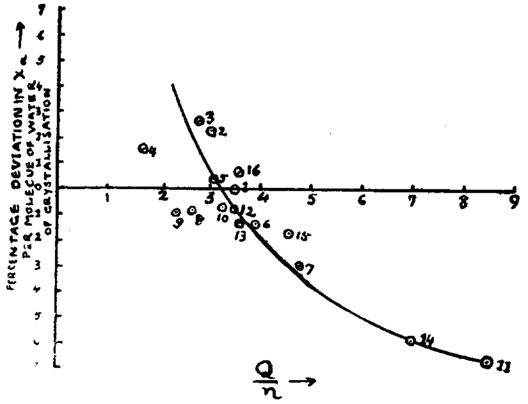

FIG. 1. 1—$BaCl_2$, $2H_2O$; 2—$3CdSO_4$, $8H_2O$; 3—$CdCl_2$, $2H_2O$; 4—$CdBr_2$, $4H_2O$; 5—$SrCl_2$, $6H_2O$; 6—$SrBr_2$, $6H_2O$; 7—$Ba(ClO_3)_2$, H_2O; 8—$Na_2S_2O_3$, $5H_2O$; 9—$CaSO_4$, $2H_2O$; 10—$ZnSO_4$, $7H_2O$; 11—$ZnSO_4$, H_2O; 12—$MgSO_4$, $7H_2O$; 13—$MgSO_4$, $5H_2O$; 14—$MgSO_4$, H_2O; 15—$BaBr_2$, $2H_2O$; 16—$Na_2B_4O_7$, $10H_2O$.

Table I(b) also shows that the values of (Q/n), wherever available (given in column 9 of the table), increase with an increase in the numerical values of $(\Delta\chi_m/n)$ for the several hydrates of the same salt, that is, they increase as n decreases. Thus, there appears to be a direct relation between the two quantities. It has not been possible to determine the exact nature of this relation for want of sufficient data.* The heat of hydration of any substance is a measure of the energy of the association of water molecules with the ions of the anhydrous salt in the hydrate. It follows, therefore, from the observation made above that the energy per molecule of water of crystallization decreases as the number of molecules of water of crystallization increases. Thus, the amount of energy required to drive out a molecule of water of crystallization from a hydrate salt containing a large number of molecules of water of crystallization will be small, and this amount will increase for the same salt containing less water of crystallization. This conclusion is supported by the fact that a hydrate containing several molecules of water of crystallization will dehydrate easily and form a hydrate of smaller content of water of crystallization at comparatively low temperatures, but the latter hydrate requires a higher temperature for further dehydration; this discussion, there-

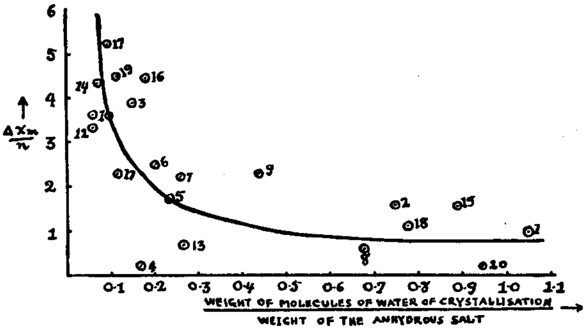

FIG. 2. 1—$MgSO_4$, $7H_2O$; 2—$MgSO_4$, $5H_2O$; 3—$MgSO_4$, H_2O; 4—$BaCl_2$, $2H_2O$; 5—$8CdSO_4$, $3H_2O$; 6—$CdCl_2$, $2H_2O$; 7—$CdBr_2$, $4H_2O$; 8—$SrCl_2$, $6H_2O$; 9—$SrBr_2$, $6H_2O$; 10—$Ba(ClO_3)_2$, H_2O; 11—$BaBr_2$, $2H_2O$; 12—$BaBr_2$, H_2O; 13—$CaSO_4$, $2H_2O$; 14—$CaSO_4$, $\frac{1}{2}H_2O$; 15—$Na_2B_4O_7$, $10H_2O$; 16—$Na_2B_4O_7$, $2H_2O$; 17—$Na_2B_4O_7$, H_2O; 18—$ZnSO_4$, $7H_2O$; 19—$ZnSO_4$, H_2O; 20—$Al_2(SO_4)_3$, $18H_2O$.

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* The heat of hydration of a salt is not an exact measure of the interaction of the ions with the solvated water molecules, since the crystal structure of the anhydrous salt is usually different from that of the hydrate. However, it would appear that the difference in the crystal energy of the two structures, which constitutes part of the energy of hydration, is not the predominant term since there is a definite correlation between the overall energy of hydration of water molecules and $\Delta\chi/n$.

TABLE IV.

Substance	χ_m(obs.)	χ_m(cal.)	$\Delta\chi_m$
$BaCl_2\cdot 2H_2O$	102.8	103.97	−1.17
$BaBr_2\cdot 2H_2O$	132.1	135.92	−3.82
$SrCl_2\cdot 6H_2O$	147.0	145.14	1.86
$SrBr_2\cdot 6H_2O$	170.6	181.60	−11.00
$Na_2S_2O_3\cdot 5H_2O$	125.10	131.70	−6.60

fore, establishes that in the lower hydrate of the same salt, the binding of the water molecules with the anhydrous salt must be stronger than the binding in the case of a higher hydrate.

(b) Susceptibilities of Hydrates in Solutions

It is apparent that by applying the mixture law, one can calculate a formal value of χ_a and hence χ_m for either an anhydrous salt or its hydrate from the susceptibility of the respective solution.

A comparison of the values of the molecular susceptibilities given in column 3 of tables I(a) and I(b) and those in column 5 of Table II indicates that the values of the molecular susceptibilities obtained for substances from solutions are in all cases higher than those obtained for the same salts from the measurements in the solid state. This observation confirms the findings of Flordal and Frivold[7] and Hocart.[8] The differences between the two sets of values are, however, small, but since they are observed in all cases they may be quite significant. These differences are possibly due to the fact that the forces which keep the ions of a salt together and thus exert a strain on these ions in the solid state are weakened when the salt is dissolved in water. The effect would probably be much greater if it were not for the fact that the interaction of ions with the salt is almost as pronounced as the interaction of the ions with each other in the anhydrous crystal.

The molecular susceptibilities of the hydrates have been calculated on the additivity basis using the observed values of the susceptibilities of the anhydrous substances obtained from solutions. These calculated values are given in column 3 of Table IV with the observed χ_m values for the hydrates obtained from solutions (column 2). It will be seen from the table that the calculated values of χ_m are definitely higher than the observed ones in all cases excepting $SrCl_2\cdot 6H_2O$. These differences are shown in column 4 of the table. The significance of these differences cannot be definitely understood at this stage.

SUMMARY

Magnetic susceptibilities of a number of hydrates have been measured by modified form of Guoy's balance along with the susceptibilities of their corresponding anhydrous salts, in the solid state. The values obtained have been compared with those calculated for the hydrates on the strict additivity basis. The results indicate that the percentage deviation from additivity of the observed values, for specific susceptibilities of the hydrates from the calculated ones, bears no generalized relation of any nature with the total heat of hydration. The percentage deviation in specific susceptibility per molecule of water of crystallization has, however, been found to decrease as the heat of hydration per molecule of water of crystallization increases in the case of several hydrates.

In the case of several hydrates of the same salt, it has been found that the deviation in the observed molecular susceptibility from additivity, per molecule of water of crystallization, is greatest in the hydrate containing the least number of molecules of water of crystallization and tends to decrease as the number of molecules of water of hydration increases. There appears to be some relation between the heat of hydration per molecule of water of crystallization and the deviation in χ_m per molecule, in the case of these salts.

The departure from the additivity rule in hydrates has been explained on the basis of bindings between the molecules of water of crystallization and the anhydrous salt. Susceptibilities of some hydrates have also been calculated, with their corresponding anhydrous salts, from the susceptibilities of their aqueous solutions. The values obtained in solution are in all cases higher than those obtained for the same salts from the measurement in the solid state. The molecular susceptibilities of the hydrates, calculated on the additivity basis using the observed values of the susceptibilities of the anhydrous salts obtained from solutions, are higher in most cases than the observed values of hydrates measured from solutions.

The authors are indebted to Dr. W. K. Wilmarth of the University of Southern California for valuable discussion and suggestions.

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[8] R. Hocart, Comptes Rendus 188, 1151 (1929).