The result obtained for the atomic weight of fluorine is 18.9935.

The largest uncertainty entering into the *comparison* of the atomic weight of fluorine with the molecular weight of calcite and the atomic weight of lithium is the uncertainty in the density of lithium fluoride. This uncertainty is about one part in 26,000 or ±0.0010 in the atomic weight of fluorine. (As has been stated,[1] this uncertainty could be reduced by a factor of three to five.) The atomic weight of fluorine, if $CaCO_3 = 100.085$ and Li = 6.9390, is therefore 18.9935 ± 0.0010.

Birge has estimated the probable uncertainty in the molecular weight of calcite as ±0.005. Richards and Willard[17] state the atomic weight of lithium as 6.9390 with a probable error of less than 0.0002. The uncertainty in the computation of the absolute value of the atomic weight of fluorine is largely due to the uncertainty in the atomic weight of calcium. Using Birge's reasonably stated probable uncertainty in the molecular weight of calcite the resulting probable error for the atomic weight of fluorine is ±0.0013. The atomic weight of fluorine may therefore be stated as 18.9935 ± 0.0015.

If the atomic weight of calcium is as large as Hönigschmid and Kempter's[15] value of 40.085, the atomic weight of fluorine becomes 18.996 instead of 18.994.

The atomic weights of fluorine obtained by various physical methods are summarized in Table II.

Table II

Mass spectrographic determinations[18,20]	18.999
Gas density method, Cawood and Patterson,[21] using CF_4	18.995
Gas density method, Cawood and Patterson,[21] using CH_3F	18.997
Gas density method, Moles and Toral,[22] using SiF_4	18.995
From X-ray and density data, Hutchison and Johnston	18.994

The value calculated in this paper is seen to be in agreement with the gas density determinations on carbon tetrafluoride and silicon tetrafluoride, but not with the mass spectrographic value.

Summary

Available X-ray and density data on lithium fluoride and calcite have been used to compute the atomic weight of fluorine.

The value of the atomic weight of fluorine is found to be 18.9935 ± 0.0015, if the molecular weight of calcite is taken as 100.085 ± 0.005. The probable uncertainty stated is largely due to the uncertainty in the molecular weight of calcite.

The computed atomic weight of fluorine is in agreement with the results of gas density determinations on carbon tetrafluoride and silicon tetrafluoride, but not with mass spectrographic determinations.

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(20) This mass spectrographic value is in agreement with computations of the mass of F^{19} from nuclear reaction data, using the best available values for other masses involved (Livingston and Bethe, *Rev. Mod. Phys.*, **9**, 245 (1937)). It also agrees with theoretically computed values of the mass (Barkas, *Phys. Rev.*, **56**, 691 (1939)).

(21) Cawood and Patterson, *Trans. Roy. Soc.* (London), **A236**, 77 (1936).

(22) *Z. anorg. allgem. Chem.*, **236**, 225 (1938).

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The Heat Contents of Bivalent Sulfates in Extremely Dilute Aqueous Solutions

By A. L. Robinson and W. E. Wallace*

Young and Seligmann[1] have shown that the limiting derivative of the apparent molal heat content with respect to the square root of the concentration ($S = d\Phi L_2/dc^{1/2}$) is in striking agreement with the prediction of the Debye–Hückel limiting law for a number of salts of the 1–1 and 1–2 valence types. They also state that an incomplete study of salts of the alkaline earth metals (2–1 type) indicates similar agreement. They find, however, that existing data for salts of the 2–2 valence type, if treated by their methods, do not lead to limiting values in agreement with theory.

Recently we have applied a modification of the method of Young to new heat of dilution data for sodium sulfate at 15 and 20°.[2] The modified treatment seems to extend the usefulness of the method, particularly in the very dilute concentration region ($c^{1/2} < 0.05$), and to afford simplification of the type of equation chosen to represent

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(1) T. F. Young and P. Seligmann, This Journal, **60**, 2379 (1938).

(2) W. E. Wallace and A. L. Robinson, *ibid.*, **63**, 958 (1941).

the data. When the existing data for 2–2 type salts were studied by our "short chord"[2] method, it developed that in most cases a maximum value of S at $c^{1/2} \approx 0.01$–0.05 was indicated, followed by smaller S values at lower concentrations which seem to approach S^0 values not in gross disagreement with the Debye–Hückel limiting law. Although the small number of chords and their relatively large uncertainties do not seem to justify analytical treatment at present, the qualitative results seem sufficiently interesting to warrant publication. It is intended to extend the experimental data at low concentrations in the near future and to present calculations of the limiting derivatives at that time.[3]

In most of the dilution experiments of Lange and Robinson and their co-workers a small volume (7–25 ml.) of solution of concentration c_1 was diluted with a large volume of water (usually about one liter) to a concentration c_2. With the solution of concentration c_2 remaining in the calorimeter a second dilution was performed by adding another sample of the initial solution (c_1) giving a final solution of concentration c_3. In the calculations of Young and co-workers the chords $\overline{P} = \Delta\Phi L_2/\Delta c^{1/2}$ ($\overline{P}$ is the average value of S in the concentration interval $\Delta c^{1/2}$) were computed for the dilutions between c_1 and c_2 and c_1 and c_3; these chords extend over relatively long concentration intervals. In the short chord modification $\Delta c^{1/2} = c_3^{1/2} - c_2^{1/2}$. Each pair of long dilutions thus yields a short chord in the very dilute concentration region ($c^{1/2} < 0.05$). A plot of these short chords reveals details of the trend of S, as infinite dilution is approached, which are not observed in the plot and treatment of the long chords. For sodium sulfate[2] at 25° this simpler treatment permitted derivation of an equation $S = 2418 - 13402m^{1/2}$ for the concentration range 0.0003 to 0.005m, which equation is practically indistinguishable from the equation of Young and Seligmann,[1] $S = 2432 - 14896m^{1/2} + 19533m$, for $m < 0.005$; both equations were derived from the same data.[4]

The data used for this study are shown in Table I. c_1, c_2 and c_3 are the concentrations whose significance is explained above; $\Delta c^{1/2} = c_3^{1/2} - c_2^{1/2}$. $\Delta\Phi L_2$, the heat of dilution between c_3 and c_2, is the difference between the two experimental determinations of the heat of dilution between c_1 and c_2 and c_1 and c_3; the number of experiments from which these values were obtained is indicated by the numbers in parentheses in columns two and

TABLE I

c_1	$c_2^{1/2}$	$c_3^{1/2}$	$\Delta c^{1/2}$	$\Delta\Phi L_2$	$\overline{P}\times 10^{-2}$
		$CaSO_4$[4] 25°			
0.001258	0.01819 (4)	0.02556 (4)	0.00737	55	$74._6$
.00629	.01284 (2)	.01807 (2)	.00523	41	$78._4$
.00314	.00910 (2)	.01278 (2)	.00368	26	$70._7$
.00157	.00636 (2)	.00904 (2)	.00268	19	$70._9$
		$MgSO_4$[4] 25°			
.05	.03628 (4)	.05095 (3)	.01467	85	$57._9$
.0125	.01813 (4)	.02548 (3)	.00735	50	$68._0$
.00625	.01282 (4)	.01803 (4)	.00521	39	$74._9$
.003125	.009072 (2)	.01274 (2)	.00367	24	$65._4$
		$CdSO_4$[5] 10°			
m_1	$m_2^{1/2}$	$m_3^{1/2}$	$\Delta m^{1/2}$		
.8	.07093 (4)	.1001 (4)	.0291	100	$34._4$
.4	.05015 (6)	.07081 (4)	.02066	68	$32._9$
.2	.03547 (4)	.05009 (4)	.01462	70	$47._9$
.1	.02507 (6)	.03541 (4)	.01034	80	$77._4$
.05	.01773 (6)	.02504 (4)	.00731	49	$67._0$
.025	.01254 (6)	.01770 (8)	.00516	33	$64._0$
		$CdSO_4$[5] 15°			
.4	.05015 (4)	.07081 (4)	.02066	106	$51._8$
.2	.03547 (6)	.05009 (4)	.01462	100	$68._4$
.1	.02507 (4)	.03541 (4)	.01034	89	$86._1$
.05	.01773 (4)	.02504 (4)	.00731	74	$101._2$
.025	.01254 (4)	.01770 (4)	.00516	35	$67._8$
		$CdSO_4$[5] 20°			
.8	.07093 (6)	.1001 (6)	.0291	131	$44._9$
.4	.05015 (6)	.07081 (4)	.02066	135	$65._3$
.2	.03547 (4)	.05009 (4)	.01462	118	$80._7$
.1	.02507 (2)	.03541 (4)	.01034	105	$101._6$
.05	.01773 (4)	.02504 (6)	.00731	66	$90._3$
.025	.01254 (4)	.01770 (6)	.00516	44	$85._3$
c_1	$c_2^{1/2}$	$c_3^{1/2}$	$\Delta c^{1/2}$		
		$CdSO_4$[6] 25°			
.5	.0856 (2)	.1206 (2)	.0350	169.5	$48._4$
.25	.06051 (2)	.08526 (2)	.02475	163.2	$65._9$
.125	.04274 (2)	.06029 (2)	.01755	148.0	$84._3$
.0625	.03026 (2)	.04263 (2)	.01237	125.8	$101._7$
.03125	.02139 (2)	.03014 (2)	.00875	88.6	$101._2$
.01	.01623 (1)	.02280 (1)	.00657	75	114
		$ZnSO_4$[6] 25°			
.5	.08558 (2)	.12058 (2)	.0350	121.4	$34._7$
.2	.05412 (4)	.07626 (4)	.02214	114.7	$51._8$
.1	.03828 (2)	.05393 (2)	.01565	102.3	$65._3$
.05	.02706 (2)	.03813 (2)	.01107	83.3	$75._3$
.025	.01913 (2)	.02696 (2)	.00783	58.8	$75._1$
.0125	.01353 (2)	.01907 (2)	.00554	41.4	$75._2$
.00625	.009567 (2)	.01348 (2)	.00391	37.9	$96._9$
.003125	.006715 (2)	.009532 (2)	.002757	3.6	$13._1$
		$CuSO_4$[6] 25°			
.5	.08558 (2)	.14714 (2)	.06156	228.3	$37._1$
.5	.08558 (2)	.12058 (2)	.0350	143.3	$40._9$
.25	.06051 (2)	.08526 (2)	.02475	140.4	$56._7$
.1	.03828 (2)	.06582 (2)	.02754	209.0	$75._9$
.1	.03828 (2)	.05393 (2)	.01565	128.1	$81._9$
.05	.02706 (2)	.03813 (2)	.01107	97.0	$87._6$
.025	.01913 (4)	.02696 (4)	.00783	74.9	$95._7$
.0125	.01353 (6)	.01907 (6)	.00554	48.2	$87._0$
.00625	.009567 (4)	.01348 (4)	.00391	29.2	$74._7$
.003125	.006775 (3)	.009532 (3)	.002757	23	83

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[3] T. F. Young (*Science*, **86**, 48 (1937)) has found evidence for a maximum S, using long chords, in the data of Lange and Streeck[4] for calcium sulfate.

[4] E. Lange and H. Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

[5] T. H. Dunkelberger and A. L. Robinson, THIS JOURNAL, **60**, 1301 (1938).

[6] E. Lange, J. Monheim and A. L. Robinson, *ibid.*, **55**, 4733 (1933).

three. The last column gives the average value of S in the concentration interval $\Delta c^{1/2}$. Additional data for calcium sulfate[7] are available; they agree well with the results of Lange and Streeck but do not seem to be of equal precision.

Inspection of the last column of Table I shows a maximum value for S for calcium sulfate, magnesium sulfate and copper sulfate at 25° and cadmium sulfate at 10, 15 and 20°. The evidence for the maximum value of S is weaker for zinc sulfate and cadmium sulfate at 25°. However the most dilute chord for cadmium sulfate at 25° is based on two unchecked longer dilutions and the two adjacent chords, derived from duplicate experiments, do give some support to the suggestion of a maximum here also. In the case of zinc sulfate the three chords between $c^{1/2} = 0.014$ and $c^{1/2} = 0.038$ show a constant slope of about 7500; the two most dilute chords seem to be inconsistent with the others and suggest the influence of errors. It might also be noted that the most dilute chord for copper sulfate, although derived from the average of three experiments, is of questionable weight since the original data[6] indicate that the ΦL_2 values used to derive it have by far the largest probable error of all the copper sulfate measurements. In no case therefore is there complete absence of evidence for the presence of a maximum value of S between $10^{-4}m$ and $10^{-3}m$.

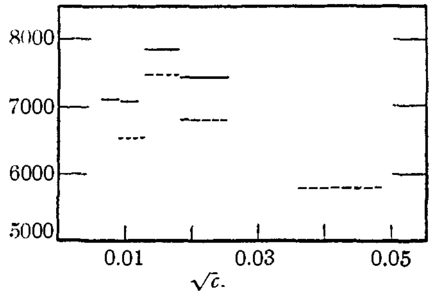

Fig. 1.—Experimental chords for $CaSO_4$, ———, and $MgSO_4$, - - - -, at 25°; $S = d(\phi L_2)/dc^{1/2}$.

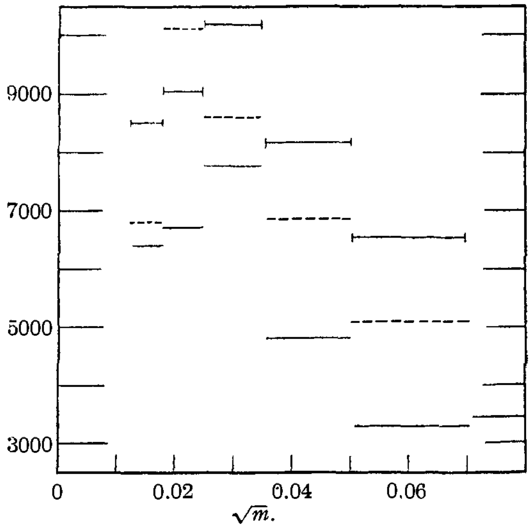

Fig. 2.—Experimental chords for $CdSO_4$: ———, 10°; - - - -, 15°; |———|, 20°; $S = d(\phi L_2)/dm^{1/2}$.

A plot of the chords for calcium sulfate and magnesium sulfate at 25° and cadmium sulfate at 10, 15 and 20° is shown in Figs. 1 and 2. Without attempting to fit smooth curves to these chords by some graphical or analytical method, it seems evident that, if the maxima indicated are real, an extrapolation to the theoretical limits S^0 might well be justified. In any case the values of S^0 previously reported for the salts, using extrapolations based on the assumption that S is constant between $c = 0$ and 0.01, must be considerably in error. The theoretical values of S^0, computed from the dielectric constant measurements of Wyman,[8] are 2840, 3144, 3472 and 3816 at 10, 15, 20 and 25°. Previous values reported for cadmium sulfate at 10,[4] 15,[4] 20[4] and 25°[5] are higher than the theoretical values by factors of 2.23, 2.64, 2.54 and 2.83, respectively.

Summary

A modification of the method of Young and coworkers has been applied to the heats of dilution of bivalent sulfates. Evidence is found for the existence of a maximum value of S between $c^{1/2} = 0.02$ and 0.03. No attempt has been made to obtain values for the limiting derivative S^0 but there is strong indication that better agreement with the Debye–Hückel limiting law exists than previously reported.

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7) E. Lange and J. Monheim, *Z. physik. Chem.*, **150A**, 349 (1931).

(8) J. Wyman, *Phys. Rev.*, **35**, 623 (1930).