

TABLE I
CONDUCTANCES OF SILVER CHLORATE SOLUTIONS

C	C ^{1/2}	Λ
0.0010256	0.03202	123.43
.0013694	.03700	122.94
.0029782	.05457	121.14
.0032500	.05701	120.95
.006693	.08181	118.57
.007223	.08499	118.29
.011165	.10567	116.38
.020409	.14286	113.05
.025945	.16110	111.52
.029471	.17167	110.70
.030005	.17322	110.57
.045927	.21421	107.33
.061064	.24711	104.82
.085240	.29196	101.58
.092665	.30441	100.80
.13630	.36920	96.50
.19945	.4466	91.90
.28488	.5336	87.15

The limiting conductance of silver chlorate was found by two methods. A large-scale plot of Λ vs. $C^{1/2}$ gave a limiting value of $\Lambda_0 = 126.62$ with a slope of 99.96. A plot of the Shedlovsky function⁴ $\Lambda'_0 = (\Lambda + \beta C^{1/2}) / (1 - \alpha C^{1/2})$ vs. C , gave a value of 126.53. The Shedlovsky plot showed the typical low slope and deviation from a linear relationship found previously in many silver, potassium and thallium salts. The slope was lower (31.7) and the deviation larger than for potassium salts. An average value of $\Lambda_0 = 126.57$, together with the known ionic conductance of the silver ion (61.92) will yield a value of 64.65 for the ionic conductance of the chlorate ion. Up to 0.08 m , with two exceptions, the experimental points are within 0.02% of the smoothed curve through the points for the Shedlovsky function plot. The accuracy in the evaluation of Λ_0 should be greater than 0.1%. The data of Loeb and Nernst, although not consistent, would extrapolate (Λ vs. $C^{1/2}$) to approximately the same value as reported here but their slope was only 67 and hence the individual measurements vary more and more as concentration increases. The only other value found for the ionic conductance of the chlorate ion is that of 63.13, computed from the conductance at 18° and the temperature coefficient listed in the "International Critical Tables."⁵

(4) T. Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932).

(5) "International Critical Tables," Vol. VI, p. 23.

THE CHEMICAL LABORATORY
INDIANA UNIVERSITY
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Isotonic Solutions: Activity Coefficients of Potassium Bromate at 25°

By JAMES HOMER JONES

Measurements have been completed in this Laboratory on the concentrations of solutions of

potassium bromate and sodium chloride that are isotonic. The apparatus and procedure have been previously described.¹ The potassium bromate was purified by crystallization from redistilled water, dried at 180° in platinum, and stored in a vacuum desiccator over anhydrous. The purification of sodium chloride has been previously described.¹ All solutions were prepared directly from weighed amounts of salt and water. The data are collected in Table I.

TABLE I
CONCENTRATIONS OF ISOTONIC SOLUTIONS

m_{KBrO_3}	Ratio	m_{NaCl}	ϕ_{KBrO_3}
0.2077	0.1977	0.9520	0.8802
.2188	.2081	.9510	.8789
.2204	.2090	.9483	.8764
.2246	.2128	.9474	.8755
.2840	.2657	.9355	.8616
.3198	.2965	.9271	.8543
.4117	.3740	.9084	.8363
.4266	.3865	.9060	.8337
.4274	.3876	.9064	.8345
.4744	.4267	.8894	.8280

From these data and the published values for sodium chloride,² the osmotic coefficients, ϕ , for potassium bromate were computed. Using the computed values of the osmotic coefficients in the equation

$$-\ln \gamma_{\pm} = 1 - \phi + 2 \int_0^m \frac{1 - \phi}{m^{1/2}} dm^{1/2}$$

the activity coefficients of potassium bromate were calculated. The integral was evaluated graphically from a large scale plot of $(1 - \phi)/m^{1/2}$ vs. $m^{1/2}$. The values of the d parameter (distance of closest approach of the ions) varied almost linearly with concentration, having a value of 1.96 Å. at 0.2 m and 1.49 Å. at 0.45 m . The extrapolation of the above plot to infinite dilution was made by finding a value of d (2.6 Å.) which made the deviations between the observed and calculated values of the function $(1 - \phi)/m^{1/2}$ proportional to the concentration for the experimental points. This same proportional variation was assumed to hold to infinite dilution. The osmotic and activity coefficients at rounded concentrations are tabulated in Table II.

TABLE II
ACTIVITY AND OSMOTIC COEFFICIENTS OF POTASSIUM BROMATE

m	ϕ	γ_{\pm} (KBrO ₃)	γ_{\pm} (KClO ₃)
0.15	0.8944	0.702	
.20	.8813	.671	0.678
.25	.8693	.644	
.30	.8590	.622	.632
.35	.8488	.602	
.40	.8393	.584	.596
.45	.8310	.568	
.50	.8225	.553	.566

(1) James Homer Jones, *THIS JOURNAL*, **65**, 1353 (1943).

(2) Stokes and Levien, *ibid.*, **68**, 337 (1946).

The writer has found no previous determinations for comparison. The activity coefficients for potassium chlorate determined in this Laboratory³ are entered in Table II for comparison.

(3) Jones and Froning, *THIS JOURNAL*, **66**, 1672 (1944).

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Tetrahedral Interactions and Diamagnetic Susceptibilities

BY JOHN R. LACHER

Recently French and Trew¹ have summarized the molar susceptibilities of the polyhalogen derivatives of methane. These compounds are anomalous in the sense that they deviate seriously from Pascal's additivity rule. It is desired here to show that the data can be interpreted empirically by assuming that the molar susceptibility is the sum of the atomic susceptibilities and six interaction terms directed along the edges of a tetrahedron. The geometry of a tetrahedron is useful in the interpretation of diamagnetic susceptibilities as well as the heats of disproportionation reactions.² The compounds under consideration together with the experimental molar susceptibilities¹ are given in Table I columns one and two. The susceptibilities calculated by summing Pascal's atomic susceptibilities are in column three. The necessary data are from the "International Critical Tables"³ and the constitutive correction factor for a single halogen bonded to carbon was not used. These calculated values are all higher than the experimental ones and the deviations increase with increasing number of halogens on the same carbon. In case of tetrahalogen compounds, the difference is close to 30%.

TABLE I

EXPERIMENTAL AND CALCULATED DIAMAGNETIC SUSCEPTIBILITIES

Compound	χ_M exp $\times 10^6$	χ_A Pascal $\times 10^6$	χ_M calcd. $\times 10^6$
CH ₄	16	17.7	17.7
CH ₃ Cl	32.0	34.9	33.3
CH ₂ Cl ₂	46.6	51.2	46.3
CHCl ₃	58.6	69.2	56.6
CCl ₄	66.8	86.4	64.8
CH ₃ Br	42.8	45.4	44.3
CH ₂ Br ₂	65.9	73.1	65.8
CHBr ₃	82.2	100.7	82.1
CBr ₄	93.7	128.4	93.4
CH ₃ I	57.2	59.4	58.5
CH ₂ I ₂	93.5	101.1	91.7
CHI ₃	117.3	142.7	117.2
CI ₄	135.6	184.4	135.2

The molar susceptibilities listed in the last column of the table were calculated on the assumption

(1) French and Trew, *Trans. Faraday Soc.*, **41**, 439 (1945).

(2) J. R. Lacher, *THIS JOURNAL*, **68**, 526 (1946).

(3) "International Critical Tables," Vol. VI, p. 349.

that they could be represented as the sum of atomic susceptibilities plus six appropriate interaction terms. The equations used are

$$\text{CH}_4: \chi_M = \chi_C + 4\chi_H$$

$$\text{CH}_3\text{X}: \chi_M = \chi_C + 3\chi_H + (\chi_X + 3\text{H}\cdot\text{X})$$

$$\text{CH}_2\text{X}_2: \chi_M = \chi_C + 2\chi_H + 2(\chi_X + 3\text{H}\cdot\text{X}) - (2\text{H}\cdot\text{X} - \text{X}\cdot\text{X})$$

$$\text{CHX}_3: \chi_M = \chi_C + \chi_H + 3(\chi_X + 3\text{H}\cdot\text{X} - 3(2\text{H}\cdot\text{X} - \text{X}\cdot\text{X}))$$

$$\text{CX}_4: \chi_M = \chi_C + 4(\chi_X + 3\text{H}\cdot\text{X}) - 6(2\text{H}\cdot\text{X} - \text{X}\cdot\text{X})$$

The atomic susceptibilities for carbon and hydrogen, χ_C and χ_H , are from Pascal.³ The constitutive correction due to a hydrogen-hydrogen interaction, H·H, was arbitrarily placed equal to zero. The susceptibility due to a halogen and three hydrogen-halogen interactions, $\chi_X + 3\text{H}\cdot\text{X}$, was calculated to give the best fit for the data of French and Trew.¹ The difference between two hydrogen-halogen and a halogen-halogen interaction, $2\text{H}\cdot\text{X} - \text{X}\cdot\text{X}$, was also calculated from the experimental data. The numerical values of all these quantities are summarized in Table II. The susceptibilities due to $\text{X} + 3\text{H}\cdot\text{X}$ are close to the values of Pascal's constants for chlorine, bromine and iodine. The latter are 20.1, 30.6 and 44.6, respectively.

TABLE II

ATOMIC AND CONSTITUTIVE SUSCEPTIBILITIES			
Element or interaction	$\chi \times 10^{16}$	Element or interaction	$\chi \times 10^{16}$
C	6.0	Br + 3H·Br	29.5
H	2.93	I + 3H·I	43.7
H·H	0.0	2H·Cl-Cl·Cl	2.6
Cl + 3H·Cl	18.5	2H·Br-Br·Br	5.1
		2H·I-I·I	7.6

The molar susceptibilities calculated from the above equations and the data in Table II are given in the fourth column of Table I. The agreement between the experimental ones and those calculated in this way is quite satisfactory. Experimental studies on mixed halogen derivatives of methane would be interesting.

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Halogenated Sulfonanilides

BY A. MOORADIAN AND G. W. LEUBNER

In a previous contribution¹ from these laboratories, there was described a series of N¹-phenyl sulfanilamides in which the N¹-phenyl group was variously substituted with chlorine and bromine atoms. Since substituents in the 3,5-positions were found most effective as far as antibacterial activity is concerned, more compounds of this general type have now been prepared for study. Not only have chlorinated and brominated compounds been prepared and studied further, but also the iodinated and trifluoromethylated deriva-

(1) Kaplan and Leubner, *THIS JOURNAL*, **67**, 1076 (1945).