ditions would be represented by Fig. 2, where the circle is the field of view, and PP′ and AA′ are the optical axes of the polarizer and analyzer, respectively. The areas between the lines represent areas in which elliptically polarized light would be expected. It is obvious that under such conditions the double refraction would have its smallest value and it might be so small that it could not be observed. This is in agreement with the fact,[12] which is inexplicable according to the hypothesis of a Faraday lag, that the "minima" have been observed to disappear when the analyzing Nicol is rotated from the position for which it is parallel to the polarizer.

Allison, Christensen and Waldo[7] have described some experiments with the magneto-optic apparatus in which solutions possessing zero magnetic rotation were used. According to their interpretation the results indicated the presence of a Faraday time lag, but it is obvious that they may also be explained by assuming that double refraction takes place in the Allison apparatus.

Acknowledgment.—This work was suggested by Dr. Herman Schlundt and was carried out under his direction. His intense interest in the problem and his many years of careful investigation have been a continual source of inspiration.

The members of the Physics Department of the University of Missouri, particularly Dr. H. M. Reese, have constantly contributed advice, encouragement and criticism. The extent of their aid has been so great that it may be said that this is a joint production of the Physics Department and the Chemistry Department, although the Physics Department reserves judgment as to the reality of the Allison effect.

Sincere thanks are due to Mr. Perry L. Bidstrup for making many of the observations and aiding in the performance of some of the experiments.

The author also wishes to thank Dr. T. R. Ball and R. E. Wingard of the Chemistry Department of Washington University for extending the use of their laboratory and for giving so freely of their valuable information and advice.

Summary

Definite evidence has been presented for the existence of an objective effect in the Allison apparatus. Results have been obtained which indicate that this effect is caused by the presence of a particular compound, vanishing when the concentration of the compound is reduced to a very small value. However, the latter has not been proved conclusively.

Certain experiments have been described which give some information about the properties of the magneto-optic apparatus.

A partial theoretical explanation for the Allison effect has been presented.

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[12] Bishop and Dollins, THIS JOURNAL, **54**, 4585 (1932).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MELBOURNE]

Atomic Radii from Parachor Data and from Electron Diffraction Data

BY N. S. BAYLISS

Introduction

Although the parachor[1] is the most nearly additive of all "additive" properties of liquids, it has always suffered from the lack of a clear physical interpretation. Sugden, the discoverer of the function, considers it to be a measure of molecular volume, but this interpretation has been disputed by others.[2] Attempts at a theoretical treatment[3] of the parachor have not succeeded in supplying an interpretation, and without a considerable advance in our knowledge of the theory of the liquid state, it would seem impossible to obtain one on purely theoretical grounds.

By making use of the available data on atomic and molecular dimensions, it is now possible to show that Sugden's original interpretation may be applied with marked success. It will be shown in this paper that by assuming that atomic parachor constants are a direct measure of atomic volumes, it is possible to calculate atomic radii that are in good agreement with the values obtained by the electron diffraction and X-ray methods.

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[1] (a) Sugden, "The Parachor and Valency," G. Routledge and Sons, London, 1930; (b) *J. Chem. Soc.*, **125**, 1185 (1924).

[2] (a) Ferguson, *Nature*, **125**, 597 (1930); (b) Desreux, *Bull. soc. chim. Belg.*, **44**, 249 (1935).

[3] Kleeman, *Phil. Mag.*, [6] **21**, 92 (1911); Eucken, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 340 (1933).

For the present, the discussion will be confined to molecules whose structure is simple, and that contain only quadrivalent and univalent atoms.

Atomic Parachor Constants.—From the point of view of the present problem, it is unfortunate that the literature contains several sets of atomic parachor constants,[2b,4] which differ seriously, however, only in the values assigned to carbon and hydrogen. In any derivation of atomic parachors, the fundamental constant is that of CH_2, which is found from the observed parachors of members of various homologous series. Some of the previous authors seem to have committed the error of taking the arithmetic mean of $P(CH_2)$ differences over a homologous series, a procedure that automatically cancels all the measurements except those for the lowest and highest members of the series.

It was therefore thought advisable to recalculate the fundamental constants, and it will be seen that the resulting set agrees best with the set proposed by Mumford and Phillips.[4] The linear expression $P(C_nH_{2n+2}) = nP(CH_2) + 2P(H)$ was fitted by least squares to the data on the *n*-paraffins,[5] with the result that $P(CH_2) = 39.92 \pm 0.04$, $P(H) = 15.4 \pm 0.1$, $P(C) = 9.1 \pm 0.2$. The other fundamental parachors that were necessary for the purpose of this paper were those of the halogens, which were calculated from the data on the *n*-alkyl halides[6] by the relation $P(X) = P(C_nH_{2n+1}X) - nP(CH_2) - P(H)$. The recalculated atomic constants are compared with previously recorded values in Table I, where it is seen that the only significant differences are in the values for carbon and hydrogen.

TABLE I

ATOMIC PARACHORS

Atom	Sugden	M. & P.	Vogel	Desreux	This paper
CH_2	39.0	40.0	40.3	39.9	39.92
C	4.8	9.2	11.5	8.3	9.1
H	17.1	15.4	14.4	15.8	15.4
F	25.7	25.5	..	26.1	26.4
Cl	54.3	55	..	55.0	54.6
Br	68.0	69	..	68.5	68.5
I	91.0	90	..	90.0	90.3

Atomic Dimensions of Quadrivalent Atoms.—The closeness of approach of two atoms is governed by their bond radii (denoted hereafter by *r*) if they are chemically bound, and by the vaguer "packing" radii (*r*′) if they are not. The comparison of atomic parachors with atomic volumes will begin with the case of quadrivalent atoms that occupy the central position in a tetrahedral molecule. Such atoms touch only those atoms to which they are chemically bound, and since the space that they occupy is determined by their bond radii only, it will be assumed that their volume is that of a sphere whose radius is *r*. Adopting the well established value of $r = 0.77$ Å. for the carbon atom,[7] and assuming that the atomic parachor of carbon is a measure of its atomic volume, one obtains the relation that *one parachor unit* = 0.210 Å.[3] This relation may then be used to calculate the bond radii of other quadrivalent atoms whose atomic parachors are known, the result being shown in Table II, which includes the Pauling and Huggins[7] bond radii for comparison. The atomic parachors of the elements in question have been recalculated to conform with Table I; but the differences from the Sugden values are insignificant, except in the case of carbon.

TABLE II

	Atomic parachor		Bond radius, Å.	
Atom	Sugden	This paper	Calcd.	Pauling and Huggins
C	4.8	9.1	(0.77)	0.77
Si	25.0	26.2	1.10	1.17
Ti	45.3	44.1	1.30	1.22[c]
Ge	37.4[a]	36.0	1.22	1.22
Sn	57.9	55.4	1.41	1.40
Pb	76.2	75.6	1.56	1.46
Te	..	56.7[b]	1.42	1.32[d] 1.37[e]

[a] Sidgwick and Laubengayer, THIS JOURNAL, **54**, 948 (1932). [b] Singh and Krishen, *J. Ind. Chem. Soc.*, **12**, 711 (1935). [c] Calculated from Wierl, *Ann. Physik*, **8**, 521 (1931), assuming that *r* for Cl = 0.99 Å. [d] Tetrahedral radius. [e] Covalent bond radius.

The agreement between the two sets of bond radii is good, but becomes better when some individual cases are considered in detail. It has been shown recently that in the chlorides and fluorides of certain quadrivalent atoms, the observed bond distances are less than those calculated from the Pauling and Huggins bond radii,[8] whereas the corresponding tetraalkyl compounds have been found to behave normally.[9] This behavior is reflected in the parachors, since the atomic parachors of silicon, germanium and tin are lower in their tetra-

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(4) Sugden, ref. 1a, p. 181; Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929); Vogel, *ibid.*, 333 (1934).

(5) Brit. Assoc. Advancement Sci. Report, 1932, p. 264. Unless indicated otherwise, all parachor data quoted in this paper will be taken from this report.

(6) For data on *n*-alkyl fluorides, see ref. 2b.

(7) Pauling and Huggins, *Z. Krist.*, **87**, 205 (1934).

(8) Brockway and Wall, THIS JOURNAL, **56**, 2373 (1934); Brockway, *ibid.*, **57**, 958 (1935).

(9) Brockway and Jenkins, *ibid.*, **58**, 2036 (1936).

halides than in their tetraethyls. Bond radii calculated for these elements from the parachors of their tetrachlorides and their tetraethyls are given in Table III, and are compared with the bond radii obtained from similar compounds by the electron diffraction method.[8,9] A simplification has been made in making the central atom of the tetrahedral molecule wholly responsible for the changes in both the parachor and the bond distance. The case of lead has also been included in Table III, since the bond radius calculated from the parachor is in better agreement with the value observed in lead tetramethyl[9] than with the Pauling and Huggins radius.

TABLE III

Atom	Compound	Parachor	Bond radius, Å. from Parachor	Bond radius, Å. from Electron diff.
Si	Tetraethyl	31.0	1.16	1.16[a]
	Tetrachloride	23.8	1.06	1.03
Ge	Tetraethyl	38.5	1.25	1.21[a]
	Tetrachloride	34.8	1.20	1.11
Sn	Tetraethyl	60.1	1.45	1.41[a]
	Tetrachloride	54.4	1.40	1.30
Pb	Tetraethyl	75.6	1.56	1.52[a]

[a] Values obtained from tetramethyls.

Atomic Dimensions of Univalent Atoms.—The volume of a univalent atom is determined largely by its packing radius, which is less easily defined than its bond radius. This case may be treated by adopting the rather naïve atomic model of a segment of a sphere (see Fig. 1) of radius r', and with the plane surface at a distance r from the center. Values of r and r' cannot both be derived from parachor data alone; but by using the relation *one parachor unit* = 0.210 Å.,[3] and by assuming the Pauling and Huggins values of r, it is possible to determine values of the packing radii of hydrogen and the halogens from their atomic parachors, as shown in Table IV. The value 1.03 Å. for hydrogen is in good agreement with those of 1.1 and 1.0 Å. quoted by Stuart,[10] and with that of 1.07 Å. observed by Pauling and Carpenter.[11] The values of the packing radii calculated for fluorine and chlorine may be compared with the following experimental values obtained by the electron diffraction method:[12] $^1/_2$(F–F) in carbon tetrafluoride = 1.12 Å., $^1/_2$(Cl–Cl) in carbon tetrachloride = 1.44 Å. and in chloroform = 1.47 Å. The results of Dornte[13] give values rather greater than the calculated packing radii of bromine and iodine, the experimental results being: $^1/_2$(Br–Br) in bromoform = 1.73 Å. and in methylene dibromide = 1.81 Å., $^1/_2$(I–I) in methylene diiodide = 2.03 Å. There is some evidence, however, that the values of Dornte are high, since Brockway and Jenkins[9] find the bond distance C–Br = 1.91 Å., which, assuming the tetrahedral angle, gives $^1/_2$(Br–Br) = 1.56 Å., and the Pauling and Huggins radii predict that C–I = 2.10 Å., which gives $^1/_2$(I–I) = 1.71 Å., in good agreement with the values in Table IV.

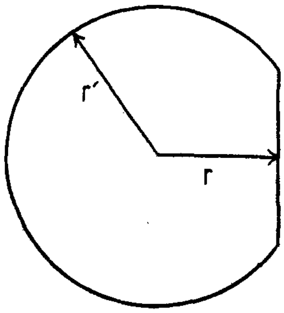

Fig. 1.—Atomic radii from parachor data and from electron diffraction data.

TABLE IV

Atom	H	F	Cl	Br	I
Packing radius, Å.	1.03	1.16	1.44	1.54	1.67

Conclusion

Although the approach to the subject has been empirical, the examples quoted above provide strong evidence that atomic parachors must be interpreted as atomic volumes. Divalent and trivalent atoms have not been included in the discussion, because of the lack of packing radius data with which to compare the atomic parachors. It is probable that many of the anomalies encountered in the study of the parachor could be explained on the basis of the above interpretation; Parachor anomalies *must* be expected in cases where there is a tendency to ionic binding or resonance, since both phenomena are accompanied by changes in molecular dimensions. It is in just such cases, unfortunately, that attempts have been made to use the parachor to determine the structure. Parachor increments due to such features as double and triple bonds find at least a qualitative explanation in the suggestion of Noyes and Singh[14] that the shorter distance between such atoms is more than compensated by their greater packing radius.

Summary

1. Revised atomic parachor constants have been calculated from existing parachor data.

2. On the assumption that atomic parachors

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(10) Stuart, "Molekülstruktur," Verlag J. Springer, Berlin, 1934, pp. 47, 48.

(11) Pauling and Carpenter, THIS JOURNAL, **58**, 1274 (1936).

(12) Pauling and Brockway, *ibid.*, **57**, 2684 (1935).

(13) Dornte, *J. Chem. Phys.*, **1**, 630 (1933).

(14) Noyes and Singh, THIS JOURNAL, **58**, 802 (1936).

are a measure of atomic volume, and that the volume of the carbon atom is that of a sphere of radius 0.77 Å., it is found that *one parachor unit* = 0.210 Å.[3]

3. By adopting simple atomic models, this relation is then used to calculate bond radii for quadrivalent atoms and packing radii for univalent atoms that are in good agreement with existing data.

MELBOURNE, AUSTRALIA RECEIVED DECEMBER 30, 1936

[CONTRIBUTION FROM THE NORTHWESTERN UNIVERSITY CHEMICAL LABORATORY]

The Specific Heats of Aqueous Sucrose Solutions at 20 and 25° and the Apparent Molal Heat Capacity of Non-electrolytes[1]

BY FRANK T. GUCKER, JR., AND FRED D. AYRES

Introduction

The specific heats of aqueous solutions of electrolytes have been studied recently by a number of investigators. The behavior of such solutions is summarized conveniently in terms of the apparent molal heat capacity. Randall and Rossini[2] first showed that over a wide range the apparent molal heat capacity is a linear function of the square root of the concentration and that the slopes of the curves increase with the valence type of the electrolyte, in qualitative agreement with the Debye–Hückel limiting law. The extrapolated value of the apparent molal heat capacity at infinite dilution is usually negative for strong electrolytes, and increasingly more negative for electrolytes of higher valence type.[3]

The apparent molal heat capacity of non-electrolytes is usually assumed to be a constant independent of concentration and nearly equal to the heat capacity of the pure solute in the liquid state. The present investigation is the beginning of a systematic study of the thermochemistry of non-electrolytic aqueous solutions, undertaken to find out how ideal these solutions are and what light they may throw on the general properties of solutions. Sucrose was chosen as the first solute because it could be obtained pure and because other thermodynamic properties of its solutions already had been investigated carefully.

Preparation of the Sucrose Solutions.—The sucrose used in these experiments was the best material obtainable, purified by the Bureau of Standards as a standard for polarimetry[4] and supplied to us through the courtesy of Dr. F. D. Rossini and Dr. F. J. Bates. Following the procedure recommended by the Bureau of Standards, the sucrose was pulverized in an agate mortar and dried for four hours at 65–70° in a vacuum of about 0.01 mm. This procedure is found to reduce the moisture content to less than 0.01%. The solutions were made up determinate, with distilled water freshly boiled to remove air. In the concentrated solutions, the sucrose and water were weighed successively into the same flask in which the solution was made up. In the dilute solutions, the smaller amounts of sucrose were determined with sufficient accuracy by weighing from a weighing bottle. All weights were reduced to the vacuum basis. In order to conserve material, the most concentrated solution (Expt. 4, Table I) was diluted quantitatively in two successive steps (Expts. $4a_1$, $4a_2$) while solution 3 was divided into two portions, each of which was diluted quantitatively to form solutions 3a and 3b.

Experimental Results.—The specific heats were determined by means of the differential twin calorimeter apparatus previously described.[5] Each value represents the average of at least two experiments with heating ratios on either side of the exact balancing ratio. The dilute sucrose solutions were handled as easily as the salt solutions, and their specific heats are probably accurate to ±0.01% as in our previous work. The great viscosity of the concentrated solutions introduced two complications which seem unavoidable in any calorimetric apparatus. First, the heat of stirring was increased enormously (amounting to about 0.001° per minute in the 5.8 *m* solution). This large temperature trend increased the uncertainty in determining the balancing resistance ratio to about 0.02% error in the specific heat. A second effect of the high viscosity of the solution was a lag in the distribution of heat from the coil in the working calorimeter. Heat may be lost from the working calorimeter by increased conduction up the heater lead wires, if the temperature of the heater in this calorimeter is greater than that in the tare. On the other hand, heat may be gained by the working calorimeter, because the temperature of the rest of its surface is lower than that of the tare. Fortunately these errors tend to

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[1] Parts of this paper were presented at the Midwest Sectional Meeting of the American Chemical Society at Louisville, November, 1935, and at the Group Symposium on "The Electrochemistry of Solutions" at the Kansas City Meeting of the American Chemical Society, April, 1936.

[2] Randall and Rossini, THIS JOURNAL, **51**, 323 (1929).

[3] For a discussion of this and related thermodynamic properties of electrolytes see (a) Gucker, *Chem. Rev.*, **13**, 111 (1933). For a discussion of the limiting slope, see (b) Young and Machin, THIS JOURNAL, **58**, 2254 (1936).

[4] Standard Sample No. 17. For the method of purification and specifications see "Polarimetry," Circular No. 44 of the Bureau of Standards.

[5] Gucker, Ayres and Rubin, THIS JOURNAL, **58**, 2118 (1936).