225. *The Molecular Volumes and Parachors of Mercuric Halides and their Group Relationships.*

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Previous work has shown that molar volumes of liquids usually exceed the atomic volumes of their constituents under corresponding conditions, such as equal vapour pressures, the proportionate excess being different for each compound in a series such as the mercuric halides. These differences are mainly due to differences in intermolecular volumes or covolumes, which are controlled by internal pressures. These pressures, identified with van der Waals molecular attractions, a/V^2, are increased in heteropolar molecules, which have semipolar or polar bonds. The electronic systems of the molecules, through this mechanism, affect all the properties dependent upon covolume and internal pressure, including coefficients of expansion, surface tensions, and parachors. These properties have been evaluated for mercuric, cadmium, and zinc halides. In particular, the parachors of mercuric chloride and bromide have been determined by the method of maximum bubble pressure. Parachors were found to be lower than the sums of the atomic parachors in each case, but a correction for semipolar bonds brings the values into much closer agreement.

A DIMINUTION in tendency to ionise is found in the order zinc, cadmium, mercury. This is evident, not only in aqueous solutions, but also in the physical properties of the anhydrous compounds. These elements can also, by gaining six electrons, attain the configuration of an inert gas. This tendency is associated with the formation of complex ions in solution, a property which reaches its maximum at mercury; also, in the anhydrous halides, the same tendency may be shown by the formation of auto-complexes and of molecules with semipolar bonds. Evidence of this will be given below. Non-polar characteristics predominate on the whole; among these are included low boiling points, high molar volumes and coefficients of expansion, and low conductivities. Heteropolarity, including ionisation and dipole formation, affects these properties in the opposite directions.

The coefficients of decrease in density, a, from the equation $D_{t_1} = D_t[1 - a(t_1 - t)]$, are lower than those of typical all-covalent compounds. The values at the boiling point are: $ZnCl_2$ 2·3, $CdCl_2$ 2·0, $HgCl_2$ 5·1, $HgBr_2$ 5·95, HgI_2 6·55.

The product, aT_b, where T_b is the absolute boiling point, is said to be constant for many salts, the mean value being 2·7. For the mercuric halides these products are: chloride $0{\cdot}29_5$, bromide 0·41, iodide 0·41.

Electrical conductivities also are higher than those of non-polar compounds, the halides of zinc, cadmium, and mercury being classed by Biltz (*Z. anorg. Chem.*, 1924, **133**, 312; Biltz and Klemm, *ibid.*, 1926, **152**, 267) among the few transitional compounds between conductors and non-conductors. The equivalent conductivities at the melting points are:

$ZnCl_2$.	$CdCl_2$.	$HgCl_2$.	$HgBr_2$.	HgI_2.
0·02	51·4	0·0025	0·051	0·52

The existence of moderate conductivities is remarkable, since primary ionisation is low in mercuric halides, and should be lowest in the iodide. It may be attributed to the formation of auto-complexes such as $Hg^{++}(HgX_4^{--})$.

Hence, in respect of all the physical properties which have been reviewed, the halides of mercury do not behave as strictly non-polar compounds. This accounts for a considerable departure from additivity in the atomic and molecular volumes, and gives grounds for expecting a departure from additivity in parachors.

Surface Tensions.—Surface tensions of fused salts are conveniently measured by the method of maximum bubble pressure. The apparatus and methods were similar to those described by Sugden (J., 1922, **121**, 588). Constants and correction factors were found by means of pure acetone, anhydrous alcohol, benzene, carbon tetrachloride, chloroform, and water. Absolute alcohol or carbon tetrachloride was used as manometric liquid. The fused halides were contained in a tube of (blue) Jena glass. A rubber stopper carried a gas-filled thermometer and the capillary tubes (radii r_1 and r_2), which were heated before being placed in the fused compound. The tap connecting the tubes to the aspirator was then opened, and bubbles were allowed to form on the larger tube at the rate of about one per second. After the temperature had become constant, the pressures were read. A similar procedure was adopted with the smaller capillary. The mean of several readings was taken in each experiment, and several experiments were done with separate samples. The results were

	t.	*γ.*	*P.*		*t.*	*γ.*	*P.*
$HgCl_2$ ………	293°	56·1	169·7	$HgBr_2$…………	241°	64·5	197·9
				,, …………	276	59·8	200·1

Additivity of the Parachors.—Sugden's values for chlorine and bromine are 54·3 and 68—69 respectively, those of Mumford and Phillips being in good agreement with these. The values obtained from the surface tensions, etc., of the liquid halogens are: chlorine 55·7, bromine 66·0. The parachor of mercury in combination is 68·7, and that of the element is 68·8. The sums of atomic parachors under P_1 are calculated from parachors of the elements in combination, and those under P_2 from the free elements.

	P, obs.	P_1, calc.	P_2, calc.
$HgCl_2$ ……………………………	169·7	177·8	180·4
$HgBr_2$ ……………………………	199·0	205·0	201·0

Thus an approximation only to the all-covalent formula is indicated. As already shown, however, from a consideration of the electronic systems, it seems probable that these compounds each contain two semipolar bonds, by which the electronic system of mercury would be completed. According to Sugden's scheme, each of these bonds requires a deduction of 1·6 units. This brings the calculated values P_1 to 174·6 and 201·8 respectively, leaving negative deviations of 4·9 and 2·8. Apart from the presence of a small proportion of auto-complex ions, the proposed formula is $\mathrm{Cl} \longrightarrow \mathrm{Hg} \longleftarrow \mathrm{Cl}$.

It has been stated that the parachor of a liquid bears a constant ratio to its volume at the absolute zero, which may be calculated by one of the methods referred to in the table below. This ratio, $P/V_0 = 2{\cdot}9 \pm 0{\cdot}5$, is approximately constant only for liquids whose surface tensions at low temperatures fall within a certain range. Mercuric chloride and bromide have a different ratio, *viz.*, 3·54 and 3·28, respectively. Since molar parachors

Various functions of the properties of mercuric chloride and bromide, referred to g.-mols. or g.-atoms.

	$HgCl_2$.	$HgBr_2$.	Ratio $f(HgBr_2)/f(HgCl_2)$.
(1) Vol. at b. p. ………………………………………………	62·44	74·47	1·19
(2) Sum of atomic vols. at b. p.'s …………………………	61·68	68·35	1·11
(3) Vol. of solid …………………………………………	50·0	59·1	1·18
(4) Vol. at 0° K. from extrapolation of density ……………	48·2	52·7	1·10
(5) Vol. at 0° K. from formula with coefficient of expansion	48·0	61·0	1·27
(6) Sum of atomic zero volumes …………………………	52·3	57·9	1·10
(7) Sum of vols. occupied by atoms, from atomic radii …	13·2	15·9	1·20
(8) Parachor ………………………………………………	169·7	199·0	1·17
(9) Sum of atomic parachors (calc. from compounds) ……	177·8	205·0	1·15
(10) Sum of atomic parachors (free elements) ………………	180·4	201·0	1·12
(11) Parachor from revised equation (p. 1205) ………………	186·0	218·5	1·175

(1) J., 1910, **97**, 1032. (2) From Hg = 16·16, Cl_2 = 45·32, Br_2 = 52·19. (4) Calculated by the mean-density method. (5) Calculated from $D_l - D_v = D_0(1 - T_r)^{0\cdot 3}$, in which T_r is the reduced temperature, T_c for $HgCl_2$ being 703°, and for $HgBr_2$ 1011°. (7) The radii are those of the uncharged elements: Hg = 1·50, Cl = 0·97, Br = 1·13 A. From these, the volumes are calculated as those of atomic spheres, multiplied by the Avogadro number.

are approximately equal to the sums of the atomic values, the ratios $\Sigma P_\phi/\Sigma V_0$ should be similar: they are 3·4 and 3·56 respectively.

The preceding table contains all available data relating to the volumes of the compounds and of their constituent elements under various corresponding conditions.

Discussion of the Table.—The ratios of the volumes under various corresponding conditions of the bromide and the chloride fall into two classes, having values of about 1·20 and 1·10 severally. To the first class, with the exception of (4), belong the volumes of the compounds; to the second, except (9), belong the sums of the atomic volumes. Hence, expansion on combination, under corresponding conditions, is greater for the bromide than for the chloride. An explanation in terms of internal pressures is given below.

A connexion between internal pressure and surface tension has been demonstrated by Eucken (*Nachr. Ges. Wiss. Göttingen, Math.-phys. Klasse, Heft* 3). The internal pressure Π, identified with the van der Waals forces of intermolecular attraction a/V^2, in condensed isotropic substances varies as a high power of the radii r of atoms or molecules. Also the work A required to form a new surface in such substances is equal to $a/3r^8$. By combining these two relations it was shown that $\Pi = 12A/\sqrt{2}r$, in which A should be identified with the specific surface enthalpy, $i_\sigma = -T(\mathrm{d}\sigma/\mathrm{d}T)_p$. From the constancy of the product of surface enthalpy and molecular surface, values of i_σ can be calculated. Also at $T = 0°$, $i_\sigma = \sigma$. From all these relations it was deduced that, under pressures which are low compared with the internal pressures, $V^{3\frac{1}{3}}\sigma = \text{constant}$. Revised parachors have been calculated by this equation [see (11)].

Although in the above deductions, internal pressures have been eliminated from the final result, it seems that the introduction of surface tension into the parachor really depends on some relation between internal pressures and intermolecular volumes. Internal pressures can be calculated by the equations:

$$a/V^2 = R(1/\alpha - 2\mathrm{T})/V \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$a/V^2 = L/V \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

α being defined as a on p. 1203, and L being the latent heat of vaporisation. These equations yield results which are not identical but usually follow the same order. In the case of homopolar molecules, it should be possible to define internal pressures which will determine such intermolecular volumes as will give additive volume relations. In the case of heteropolar molecules, however, the attractive forces are higher under conditions which are " corresponding " as judged by other physical properties.

The following internal pressures, p (in dynes per sq. cm. × 10^{-9}), have been calculated by equations (1) and (2):

	Cl_2.	Br_2.	I_2.	$HgCl_2$.	$HgBr_2$.	HgI_2.
p, from (1)	1·764	2·42	2·52	4·15	2·94	2·50
p, from (2)	4·076	$5{\cdot}64_5$	—	9·32	7·98	6·66

These are in the expected order of heteropolar character. The tendency to separation of charges is greatest for chlorides; therefore internal pressures should diminish in the order found. On the other hand, the dipoles of the halogens are: Cl_2 0·13, Br_2 0·6, I_2 1·2, so the intermolecular attractions should increase with rise of atomic weight.

Thus, considering the combination with mercury under corresponding conditions, halogens of *higher* atomic weight having *higher* internal pressures and therefore *lower* intermolecular volumes combine to form halides having *lower* internal pressures and therefore *higher* volumes. This explains the result (Prideaux, J., 1910, **97**, 2043) that when the elements under corresponding conditions form the compounds also under corresponding conditions, expansion on combination is greater for the bromide than for the chloride [see table; (1), (2)]. Under parachor conditions, contraction on combination is greater for the chloride than for the bromide [see table; (8), (9), (10)].

In a projected extension of the present investigation, attempts will be made to obtain the molar surface enthalpies of the bromide and iodide, and to define further the relations between surface tension, internal pressure, and intermolecular volume of such liquids as show some heteropolar characters.

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