CXL.—*The Parachor and Chemical Constitution. Part XI. Arsenic and Selenium Compounds.*
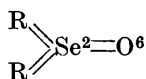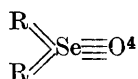
By WILLIAM JAMES REGINALD HENLEY and SAMUEL SUGDEN.

THE parachors of selenium compounds are of special interest in connexion with the question of the general validity of the octet rule. From the close chemical analogy with sulphur it would be expected that selenium in the selenoxides (I*a*) and the higher halides (II*a*), in which it exhibits valencies higher than two, would develop these
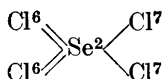
valencies by means of semipolar double bonds or singlet linkages, thus preserving a shell of eight electrons around the selenium atom. On the other hand, it has been suggested that the rule of eight
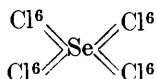
$$\begin{array}{cccc} R\diagdown & R\diagdown & Cl^6\diagdown & Cl^6\diagdown \\ \quad Se^2{=}O^6 & \quad Se{\equiv}O^4 & \quad Se^2\diagup Cl^7 & \quad Se\diagup Cl^6 \\ R\diagup & R\diagup & Cl^6\diagup \diagdown Cl^7 & Cl^6\diagup \diagdown Cl^6 \\ (Ia.) & (Ib.) & (IIa.) & (IIb.) \end{array}$$

applies only to elements of low atomic number and that heavier elements can build up a larger external electronic shell. If this were true, it would permit of the existence of non-polar double bonds in the selenoxides (Ib) and of duplet linkages with the halogen atoms as in (IIb). The recent work of Gaythwaite, Kenyon, and Phillips (J., 1928, 2280, 2287) and of Edwards, Gaythwaite, Kenyon, and Phillips (*ibid.*, p. 2293), has revealed a number of characteristic differences between the behaviour of compounds of quadrivalent selenium and sulphur. Thus, quadrivalent sulphur is readily oxidised to the sexavalent state (*e.g.*, sulphoxides to sulphones), but the corresponding selenoxides cannot be oxidised to selenones. Further, selenoxides of the type $R_1R_2Se{=}O$ have so far resisted all attempts at resolution, whereas the corresponding sulphur compounds are easily separated into their enantiomorphic forms. It seemed possible, therefore, that the octet rule might not hold for selenium, and if this were not the case the parachors of suitable compounds of this element should reveal the presence of the larger external electronic shell. It may be stated at once that the results of the investigation described below strongly support the application of the octet rule to selenium compounds and are opposed to any interpretation of the differences between sulphur and selenium compounds, which is based upon the presence of a group of more than eight electrons around the selenium atom.

Atomic Parachors of Selenium and Arsenic.—The first step in this investigation was the determination of the atomic constant for selenium. For this purpose only bivalent selenium compounds may be used, since in such substances there is no question as to the electronic structure of the linkages present in the molecule. This part of the work was facilitated by the loan of suitable substances by Dr. J. Kenyon (substances 1, 2, 3, 10, and 11) and Dr. Challenger (substances 4 and 5), to whom the authors tender their thanks. The parachors of these substances are collected in Table I, and give an atomic constant of 62·5 for selenium. Further evidence for this value is given by the parachors of selenophen (Briscoe and Peel, J., 1928, 1741), from which Se = 68·0, and of carbon sulphido-selenide (Briscoe, Peel, and Robinson, this vol., p. 58), from which Se = 58·7. This value is also supported by that of the neighbouring

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TABLE I.

Atomic Parachor of Selenium.

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No.	Substance.	Formula.	$[P]$ obs.	$\Sigma[P]$.	Se.
1	Diphenyl selenide	$SePh_2$	445·6	380·0	65·6
2	Diphenyl diselenide	SePh·SePh	506·5	380·0	63·2 × 2
3	Phenyl selenium bromide	SePhBr	321·4	258·0	63·4
4	*p*-Bromophenyl seleno-cyanate	$C_6H_4Br·SeCN$	366·1	304·6	61·5
5	*p*-Chlorophenyl seleno-cyanate	$C_6H_4Cl·SeCN$	349·3	291·1	58·2
				Mean	62·5

elements arsenic and bromine. For arsenic, measurements by Jaeger on the trichloride and tribromide were available, and to these we were able to add two chloroarsines of which specimens were kindly supplied by Dr. Johnson. The data for these compounds (Table II) give a mean parachor for arsenic of 50·3. These constants together

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TABLE II.

Atomic Parachor of Arsenic.

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No.	Substance.	Formula.	$[P]$ obs.	$\Sigma[P]$.	As.
6	Arsenic trichloride	$AsCl_3$	212·0	162·9	49·1
7	Arsenic tribromide	$AsBr_3$	253·5	204·0	49·5
8	Phenyldichloroarsine	$C_6H_5·AsCl_2$	348·3	298·6	49·7
9	Diphenylchloroarsine	$(C_6H_5)_2AsCl$	487·1	434·3	52·8
				Mean	50·3

with those determined in earlier papers of this series show a regular variation of atomic parachor with atomic number. The vertical and the horizontal differences between the constants for adjacent atoms show a regular distribution and indicate that the constant for tellurium should be in the neighbourhood of 86 units.

Higher Valencies in Selenium Compounds.—The higher-valent compounds of selenium are conveniently divided into two classes for the purpose of discussing the type of valency linkage which they contain. The first group includes substances in which the valency is raised above the normal value of 2 by combination with a bivalent element, *e.g.*, oxygen in the selenoxides. If the octet rule

applies to selenium, then compounds of this group will contain a semipolar double bond (Formula Ia). In the second group the additional valencies are used to hold univalent atoms, $e.g.$, chlorine in selenium tetrachloride, and here the octet rule requires the use of singlet linkages (Formula IIb).

TABLE III.

Semipolar Double Bonds in Selenium Compounds.

No.	Substance.	Formula.	[P] obs.	Semi-polar.	Non-polar.
10	Diphenyl selenoxide	$Ph_2Se{=}O$	461·6	460·9	485·7
11	Phenylseleninic acid ...	$\begin{smallmatrix}Ph\\HO\end{smallmatrix}{>}Se{=}O$	299·5	308·0	332·8
12	Selenium oxychloride ...	$Cl_2Se{=}O$	181·1	189·5	214·3

Data for three compounds of the first group are in Table III. The parachors found for these substances indicate clearly that the double bond is semipolar. For diphenyl selenoxide the observed and the calculated parachors are in good agreement, but the other two substances give parachors even lower than that predicted for a semipolar double bond. In both cases this appears to be due to association.

The typical associated liquids, $viz.$, the lower alcohols and fatty acids, give parachors 4—8 units lower than the calculated (Sugden, J., 1924, **125**, 1189; Jones, J., 1928, 1196; Hunter and Maass, *J. Amer. Chem. Soc.*, 1929, **51**, 161). Since phenylseleninic acid contains a hydroxyl group, it should behave similarly, and the low value of its parachor can thus be accounted for.

The anomaly with selenium oxychloride requires a closer scrutiny, for the corresponding sulphur compound, thionyl chloride, gives a normal parachor ([P] obs. 174·5, [P] calc. 175·2 ; Sugden, Reed, and Wilkins, J., 1925, **127**, 1526). Two specimens of selenium oxychloride were examined, one, a commercial product purified by repeated distillation and fractional freezing and melting at 8°, and the second, a larger specimen, prepared from elementary selenium and repeatedly frozen until of constant melting point, 10° (corr.). Both gave the same value for the parachor; hence the anomaly found cannot be due to the presence of impurities.

The molecular weight of this substance in benzene was then investigated.* Over a range of concentration of 2—20 g. per 100 g. of benzene, the values found ranged from 166·5 to 195·7 ($SeOCl_2 = 166·1$). There is clearly a marked tendency for this substance to associate in benzene solution, and a still higher degree of association may be expected in the pure liquid. Further evidence for classify-

* Thionyl chloride gives a low molecular weight (109 instead of 119) by the cryoscopic method in benzene (Oddo and Sena, *Gazzetta*, 1899, **29**, ii, 318).

ing selenium oxychloride as an associated liquid is furnished by its low Ramsay–Shields coefficient $d\gamma(Mv)^{\frac{2}{3}}/dt = -1\cdot33$, its high dielectric constant ($46\cdot2$ at $20°$; Wildish, *J. Amer. Chem. Soc.*, 1920, **42**, 2607), and its remarkable solvent power.

The monohydrate of selenium oxychloride has also been examined. This substance, described by Lenher (*J. Amer. Chem. Soc.*, 1920, **42**, 2498), may be prepared either by adding water to the oxychloride or by the action of hydrogen chloride on selenium dioxide. The latter reaction has recently been studied by Robinson and Parker (J., 1928, 2853), who found that the compound could be distilled, but with some decomposition. From these methods of formation it probably has the structure $Se(OH)_2Cl_2$, and hence, if the octet rule holds, it should contain two singlet linkages (compare IIa). The parachor found agrees with this hypothesis : $[P]$ obs. $= 222\cdot8$, $[P]$ calc. (singlet formula) $= 222\cdot1$. It is not possible without further evidence to determine whether the hydroxyl groups or the chlorine atoms are held by singlet links ; since in phosphorus and antimony pentachlorides chlorine atoms linked by singlets appear to be moderately stable (Sugden, *loc. cit.*), the latter hypothesis seems the more probable.

EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, **121**, 158; 1924, **125**, 27), and densities by means of the U-shaped pyknometer described in J., 1924, **125**, 1171. The tables below are set out in the same manner as in earlier papers of this series; the parachors are calculated by the formula $[P] = M\gamma^{\frac{1}{4}}/(D{-}d)$ where M = molecular weight, γ = surface tension (dynes/cm.), and D and d are the densities of liquid and vapour, respectively, d being neglected for the substances studied.

Arsenic trichloride and tribromide. The following data are due to Jaeger (*Z. anorg. Chem.*, 1917, **101**, 1) :

Arsenic trichloride ($M = 181\cdot3$).				Arsenic tribromide ($M = 314\cdot7$).			
$t.$	$\gamma.$	$D.$	$[P].$	$t.$	$\gamma.$	$D.$	$[P].$
—$21\cdot0°$	$43\cdot8$	$2\cdot245$	$207\cdot7$	$49\cdot6°$	$49\cdot6$	$3\cdot328$	$251\cdot0$
$0\cdot0$	$41\cdot4$	$2\cdot205$	$208\cdot5$	$74\cdot5$	$46\cdot6$	$3\cdot261$	$252\cdot2$
$20\cdot8$	$39\cdot4$	$2\cdot165$	$209\cdot8$	$90\cdot0$	$44\cdot8$	$3\cdot234$	$251\cdot7$
$35\cdot3$	$38\cdot0$	$2\cdot136$	$210\cdot7$	$105\cdot5$	$43\cdot0$	$3\cdot184$	$253\cdot1$
$50\cdot2$	$36\cdot6$	$2\cdot105$	$211\cdot9$	$121\cdot0$	$41\cdot0$	$3\cdot143$	$253\cdot4$
$64\cdot8$	$35\cdot1$	$2\cdot073$	$212\cdot9$	$135\cdot0$	$39\cdot6$	$3\cdot111$	$253\cdot8$
$75\cdot7$	$34\cdot2$	$2\cdot051$	$213\cdot7$	$149\cdot6$	$38\cdot2$	$3\cdot076$	$254\cdot4$
$90\cdot0$	$32\cdot8$	$2\cdot016$	$215\cdot2$	$165\cdot0$	$37\cdot0$	$3\cdot041$	$255\cdot2$
$110\cdot0$	$31\cdot0$	$1\cdot968$	$217\cdot8$	$179\cdot7$	$36\cdot1$	$3\cdot008$	$256\cdot5$
		Mean	$212\cdot0$			Mean	$253\cdot5$

Phenyldichloroarsine, $C_6H_5{\cdot}AsCl_2$, $M = 223\cdot0$, b. p. $118°/9$ mm. Densities determined : $D_4^{17\cdot5°}\ 1\cdot655$; $D_4^{39\cdot5°}\ 1\cdot628$; $D_4^{60\cdot5°}\ 1\cdot601$; $D_4^{79\cdot5°}\ 1\cdot578$; whence $D_4^{\circ} = 1\cdot677 - 0\cdot00125t.$

t	18·5°	42·0°	62·6°	79·0°
γ	44·64	41·51	38·72	37·33
D	1·654	1·624	1·600	1·578
$[P]$	348·3	348·3	347·5	349·1

Mean 348·3

Diphenylchloroarsine, $(C_6H_5)_2AsCl$, $M = 264·5$, b. p. $172°/7$ mm. Densities determined : $D_4^{16·0°}$ 1·482 ; $D_4^{42·0°}$ 1·387 ; $D_4^{62·5°}$ 1·368 ; $D_4^{80·5°}$ 1·350 ; whence $D_4^{t°} = 1·427 - 0·000955t$.

t	17·9°	42·5°	61·0°	80·5°
γ	45·30	42·65	40·37	38·32
D	1·411	1·386	1·369	1·350
$[P]$	486·3	487·6	487·0	487·5

Mean 487·1

Diphenyl selenide, $(C_6H_5)_2Se$, $M = 233·3$, b. p. $168—170°/17$ mm. Densities determined : $D_4^{15·5°}$ 1·359 ; $D_4^{43·5°}$ 1·332 ; $D_4^{59·5°}$ 1·316 ; $D_4^{77·5°}$ 1·298 ; whence $D_4^{t°} = 1·374 - 0·00098t$.

t	16·5°	39·5°	60·5°	79·5°
γ	44·81	42·26	39·41	37·84
D	1·358	1·335	1·315	1·296
$[P]$	444·7	445·7	444·6	446·7

Mean 445·6

Diphenyl diselenide, $(C_6H_5)_2Se_2$, $M = 312·5$, m. p. $63°$. Densities determined : $D_4^{79·5°}$ 1·557 ; $D_4^{115·0°}$ 1·518 ; $D_4^{153·5°}$ 1·477 ; whence $D_4^{t°}$ 1·644 $- 0·00109t$.

t	77·0°	97·5°	119·1°	139·2°
γ	40·02	38·49	36·64	34·32
D	1·556	1·538	1·514	1·492
$[P]$	505·2	506·1	507·9	507·0

Mean 506·5

Phenyl selenium bromide, $C_6H_5·SeBr$, $M = 236·2$, m. p. $61°$. Densities determined : $D_4^{65·5°}$ 1·898 ; $D_4^{77·5°}$ 1·875 ; $D_4^{87·5°}$ 1·861 ; $D_4^{97·5°}$ 1·845 ; whence $D_4^{t°} = 2·001 - 0·0016t$.

t	71·5°	80·5°	90·5°	103·0°
γ	43·18	41·55	40·29	38·39
D	1·876	1·862	1·856	1·836
$[P]$	322·7	322·0	320·6	320·2

Mean 321·4

p-*Chlorophenyl selenocyanate*, $C_6H_4Cl·SeCN$, $M = 216·7$, m. p. $53·5—54·5°$. Densities determined : $D_4^{57·5°}$ 1·590 ; $D_4^{68·5°}$ 1·579 ; $D_4^{77·5°}$ 1·570 ; $D_4^{89·0°}$ 1·557 ; whence $D_4^{t°} = 1·650 - 0·00104t$.

t	58·0°	65·5°	76·5°	85·5°
γ	43·02	42·29	41·12	40·03
D	1·590	1·582	1·570	1·561
$[P]$	349·0	349·3	349·5	349·2

Mean 349·3

p-*Bromophenyl selenocyanate*, $C_6H_4Br \cdot SeCN$, $M = 261 \cdot 2$, m. p. $70 \cdot 5$—$71 \cdot 5°$. Densities determined : $D_4^{75 \cdot 5°}$ $1 \cdot 842$; $D_4^{80°}$ $1 \cdot 830$; $D_4^{86 \cdot 0°}$ $1 \cdot 814$; whence $D_4^{t°} = 2 \cdot 042 - 0 \cdot 00264t$.

At $90°$ decomposition became perceptible, so the measurements were confined to lower temperatures.

t	$76 \cdot 0°$	$80 \cdot 5°$	$85 \cdot 5°$	$91 \cdot 0°$
γ	$43 \cdot 6$	$43 \cdot 1$	$42 \cdot 3$	$41 \cdot 6$
D	$1 \cdot 841$	$1 \cdot 833$	$1 \cdot 816$	$1 \cdot 801$
$[P]$	$364 \cdot 6$	$365 \cdot 0$	$366 \cdot 6$	$368 \cdot 0$
				Mean $366 \cdot 1$

Diphenyl selenoxide, $(C_6H_5)_2 SeO$, $M = 249 \cdot 3$, m. p. $108°$. Densities determined : $D_4^{116 \cdot 0°}$ $1 \cdot 382$; $D_4^{126 \cdot 0°}$ $1 \cdot 375$; $D_4^{137 \cdot 0°}$ $1 \cdot 364$; $D_4^{147 \cdot 5°}$ $1 \cdot 335$; whence $D_4^{t°} = 1 \cdot 487 - 0 \cdot 00089t$.

t	$121 \cdot 0°$	$133 \cdot 0°$	$143 \cdot 0°$	$151 \cdot 5°$
γ	$42 \cdot 32$	$41 \cdot 07$	$40 \cdot 21$	$39 \cdot 31$
D	$1 \cdot 379$	$1 \cdot 368$	$1 \cdot 359$	$1 \cdot 351$
$[P]$	$461 \cdot 0$	$461 \cdot 4$	$462 \cdot 0$	$462 \cdot 2$
				Mean $461 \cdot 6$

Phenylseleninic acid, $C_6H_5 \cdot SeO_2H$, $M = 189 \cdot 2$, m. p. $122°$. This substance decomposed rapidly a few degrees above its m. p., so one observation only was made at $123 \cdot 0°$ (Found : $\gamma = 46 \cdot 7$; $D = 1 \cdot 652$; whence $[P] = 299 \cdot 5$).

Selenium oxychloride, $SeOCl_2$, $M = 166 \cdot 1$. This substance was prepared as described by Lenher (*loc. cit.*) and purified by distillation and repeated freezing. The specimen used had b. p. $181°$ (slight decomp.), and the m. p. ($10°$, corr.) was unchanged by four successive freezings in each of which half of the substance was removed as a "more fusible" fraction. Densities determined : $D_4^{16 \cdot 0°}$ $2 \cdot 445$; $D_4^{38 \cdot 5°}$ $2 \cdot 398$; $D_4^{59 \cdot 5°}$ $2 \cdot 356$; $D_4^{77 \cdot 5°}$ $2 \cdot 314$; whence $D_4^{t°} = 2 \cdot 478 - 0 \cdot 00208t$.

t	$17 \cdot 0°$	$41 \cdot 5°$	$62 \cdot 5°$	$80 \cdot 5°$
γ	$48 \cdot 1$	$45 \cdot 8$	$43 \cdot 4$	$41 \cdot 7$
D	$2 \cdot 443$	$2 \cdot 392$	$2 \cdot 348$	$2 \cdot 310$
$[P]$	$179 \cdot 1$	$180 \cdot 7$	$181 \cdot 6$	$182 \cdot 8$

Another specimen, purchased from British Drug Houses and frozen out once, had m. p. $8°$ (corr.). Densities determined : $D_4^{14 \cdot 5°}$ $2 \cdot 443$; $D_4^{40 \cdot 5°}$ $2 \cdot 390$; $D_4^{54 \cdot 5°}$ $2 \cdot 359$; $D_4^{72 \cdot 0°}$ $2 \cdot 322$; whence $D_4^{t°} = 2 \cdot 475 - 0 \cdot 00212t$.

t	$15 \cdot 0°$	$44 \cdot 5°$	$60 \cdot 5°$	$80 \cdot 5°$
γ	$48 \cdot 8$	$45 \cdot 0$	$43 \cdot 3$	$41 \cdot 3$
D	$2 \cdot 443$	$2 \cdot 380$	$2 \cdot 346$	$2 \cdot 303$
$[P]$	$179 \cdot 7$	$180 \cdot 8$	$181 \cdot 7$	$182 \cdot 8$

The Molecular Weight of Selenium Oxychloride.—The usual Beckmann apparatus was employed. The solvent used was A. R. benzene, dried with phosphorus pentoxide, and a little fresh pent-

oxide was added to the solution before each determination. Occasionally some difficulty was found in the formation of an ice-like solid form of benzene which gave a freezing point $0.2°$ too high; once the shower of small crystals had been obtained, it was easy to obtain readings to within $\pm 0.002°$. To test the calibration of the thermometer, determinations were made with naphthalene and camphor as solutes at concentrations of about 4%. Found: naphthalene 127·4 (calc. 128), camphor 149·3 (calc. 152). The data found for selenium oxychloride ($M = 166.1$) were:

Conc.		Molecular weight.		Conc.		Molecular weight.	
(g./100 g.).	ΔT.	R.	B. & J.	(g./100 g.).	ΔT.	R.	B. & J.
1·925	0·578°	166·5	172·4	10·66	2·757°	193·0	193·6
4·713	1·345	175·3	179·3	14·61	3·75	194·3	191·6
6·06	1·641	184·6	188·1	19·83	4·95	195·7	189·3

The figures in the column headed R are calculated by Raoult's simple formula $M = KC/\Delta T$, in which the constant K is taken as 50. The last column gives the molecular weight from the equation of Bury and Jones (J., 1924, **125**, 2219; 1925, **127**, 1947), viz., $M = 0.78C(66.95 - \Delta T)/\Delta T$. The latter expression gives a maximum in the molecular weight–concentration curve; this can scarcely be taken to have any physical significance but is a consequence of the mathematical form of the empirical equation. Both methods of calculation lead, however, to the conclusion that selenium oxychloride is appreciably associated in benzene solution at concentrations greater than 2% by weight, so the pure substance must be regarded as a highly associated liquid.

Selenium oxychloride monohydrate, $SeOCl_2,H_2O$, $M = 184.1$, was prepared from selenium oxychloride (m. p. 8°) and water. Densities determined: $D_4^{14.8°}$ 2·253; $D_4^{42.3°}$ 2·202; $D_4^{63.6°}$ 2·160; $D_4^{79.6°}$ 2·134; whence $D_4^{t°} = 2.282 - 0.00189t$.

t	16·2°	43·1°	61·45°	77·1°	94·4°
γ	52·48	49·62	46·73	45·78	43·70
D	2·251	2·200	2·165	2·136	2·103
$[P]$	220·1	222·1	222·5	224·2	225·1
					Mean 222·8

BIRKBECK COLLEGE (UNIVERSITY OF LONDON),
FETTER LANE, E.C. 4.