

and is in opposition to the conclusions of Losana that four definite lower hydrates of cupric oxide may exist.

2. The spontaneous decomposition of cupric hydroxide gel gives brown to black cupric oxide. The decomposition of the gel is accelerated in contact with solution of dilute alkali. The rate of decomposition of relatively large crystals of cupric hydroxide is very much slower under all conditions than that of the minute crystals constituting the gel.

3. If the ratio of equivalents of cupric sulfate (0.1–1.0 *N*) to alkali (0.1–1.0 *N*) in a mixture is equal to or less than one, the resulting blue precipitate is pure cupric hydroxide; if this ratio is equal to or greater than 1.33, the precipitate is the basic salt, $4\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$, identical with the mineral Brochantite; if the ratio is 1.25, a previously unidentified basic salt of the formula

$5\text{CuO}\cdot\text{SO}_3\cdot x\text{H}_2\text{O}$, is obtained; with ratios between 1 and 1.25, the precipitate is a mixture of cupric hydroxide or oxide and the new basic salt in varying proportions; and with ratios between 1.25 and 1.33, the resulting precipitates are mixtures of the $5\text{CuO}\cdot\text{SO}_3\cdot x\text{H}_2\text{O}$ and $4\text{CuO}\cdot\text{SO}_3\cdot 3\text{H}_2\text{O}$ in varying proportions.

4. The identity of the new basic salt has been established as $5\text{CuO}\cdot\text{SO}_3\cdot x\text{H}_2\text{O}$ by (a) its characteristic X-ray diffraction pattern; (b) the existence of a break in an electrometric titration curve at a ratio of $\text{CuSO}_4:2\text{NaOH} = 1.25$; and (c) the results of chemical analysis of relatively large crystals.

5. The alleged stabilization of blue cupric hydroxide in the presence of low concentrations of heavy metal sulfates is not a stabilization phenomenon but consists in the formation of the blue basic salt, $5\text{CuO}\cdot\text{SO}_3\cdot x\text{H}_2\text{O}$.

HOUSTON, TEXAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Crystal Structure of Diphenylselenium Dichloride¹

BY JAMES D. McCULLOUGH AND GABRIELE HAMBURGER

Introduction

During the recent investigation of the crystal structure of diphenylselenium dibromide² carried out in this Laboratory, X-ray diffraction photographs of diphenylselenium dichloride were prepared in view of a possible isomorphism. Although crystals of the dibromide and dichloride were both reported by Gilta³ to be orthorhombic bipyramidal with similar axial ratios, the space group of the dibromide was found to be D_{2h}^{14} —*Pbcn* with a four molecule unit while that of the dichloride was found to be D_{2h}^{15} —*Pbca* with an eight molecule unit. Because of the above contrast and the general interest in molecules involving central atoms with unshared electron pairs, further work on the dichloride was considered worth while.

Experimental

Diphenylselenium dichloride was prepared by mixing equivalent quantities of Eastman Kodak Co. diphenylselenium and pure chlorine, both being previously dissolved in carbon tetrachloride.

The solid thus formed was recrystallized from carbon bisulfide and crystals to be used in the structure determination were prepared by the slow evaporation of a carbon bisulfide solution. Most of the crystals formed were of the type described by Gilta, but a few were in the form of small needles with the elongation in the direction of the *a* axis (Gilta) which is the *b* axis of the X-ray unit employed later.

Complete sets of oscillation photographs about the *a* and *b* axes of the X-ray unit were prepared using Cu K_α radiation. The crystals chosen were very small and approximately cylindrical so as to minimize differential absorption effects. Measurements on these photographs lead to a unit cell with $a_0 = 7.59 \text{ \AA}$., $b_0 = 17.97 \text{ \AA}$., and $c_0 = 17.77 \text{ \AA}$., all values $\pm 0.03 \text{ \AA}$.. The axial ratios of this cell, $a:b:c = 0.4224:1:0.9888$, when properly transformed to correspond to the axes used by Gilta, give the values $0.5056:1:0.8542$. These are in fair agreement with his ratios, $0.4986:1:0.8531$. In view of the slight difference between the lengths of the *b* and *c* axes of the X-ray unit, one might suspect that an error had been made in performing the transformation, interchanging these two axes. A careful examination of the X-ray photographs

(1) Presented in part at the meetings of the American Association for the Advancement of Science, Pasadena, June, 1941.

(2) McCullough and Hamburger, *THIS JOURNAL*, **63**, 808 (1941).

(3) G. Gilta, *Bull. soc. chim. Belg.*, **46**, 275 (1937).

shows that this is not the case and a goniometric examination of three crystals made by Dr. Joseph Murdoch of the Department of Geology of this University leads to axial ratios in better agreement with the X-ray unit. All indices and axes used hereafter refer to the X-ray unit described above.

The photographs about both axes show planes of symmetry as required by the orthorhombic system. The regular absences noted on indexing the films were $0kl$ with k odd, $h0l$ with l odd and hko with h odd. The space-group is accordingly $D_{2h}^{16}-Pbca$. A rough density determination made by the flotation method gave a value of 1.62 g./cc., which corresponds to 7.8 molecules per unit cell. The calculated density for 8 molecules per unit is 1.662 g./cc.

With eight molecules in the unit cell we must place 8 Se, 16 Cl and 96 C, the hydrogen atoms being omitted from consideration. These atoms are apparently in the general positions: $\pm\{xyz; 1/2 + x, 1/2 - y, \bar{z}; \bar{x}, 1/2 + y, 1/2 - z; 1/2 - x, \bar{y}, 1/2 + z\}$ one set being required for selenium, two for chlorine and twelve for carbon. The two chlorine atoms and the two phenyl groups are accordingly not crystallographically equivalent and the diphenylselenium dichloride molecule is not required to have any symmetry higher than C_1 .

Patterson projections on (100) and (010) were prepared using intensities estimated with the aid of a calibrated comparison strip and corrected by the Lorentz and polarization factor to obtain values of $|F_{hkl}|$.² In the work on the solid solution of diphenylselenium dichloride in the dibromide which is described later on, the multiple film technique employed by de Lange, Robertson and Woodward⁴ was used. These projections show well defined maxima for selenium atoms at positions corresponding to the atomic parameters $x = 0.06$, $y = 0.10$ and $z = 0.13$. The projection on (100) yields good maxima for chlorine atoms at positions corresponding to $y_1 = 0.15$, $z_1 = 0.06$ and $y_2 = 0.05$, $z_2 = 0.19$. The maxima due to chlorine on the (010) projection are not as distinct, but $x = 0.25$ appears to be a likely value.

As a check on these parameters and with the possibility of locating the phenyl groups in mind, Fourier projections on (100) and (010) were carried out. The algebraic signs for F_{hkl} were based on the above positions of selenium and chlorine.

(4) De Lange, Robertson and Woodward, *Proc. Roy. Soc. (London)*, **A171**, 398 (1939).

The summation on (100) is given by the expression

$$\sum_k \sum_l F_{0kl} \cos 2\pi(ky + lz)$$

The results of these summations are indicated in Figs. 1 and 2. All of the previous findings are verified and the x parameters for chlorine are more clearly established.

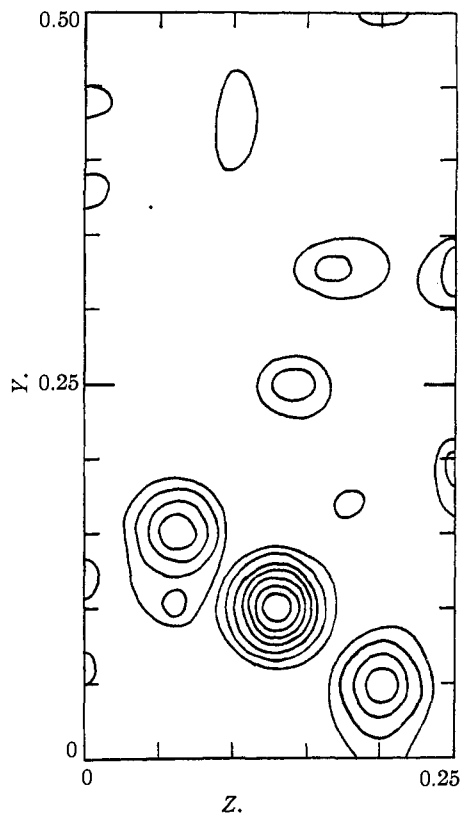


Fig. 1.—Fourier projection on (100).

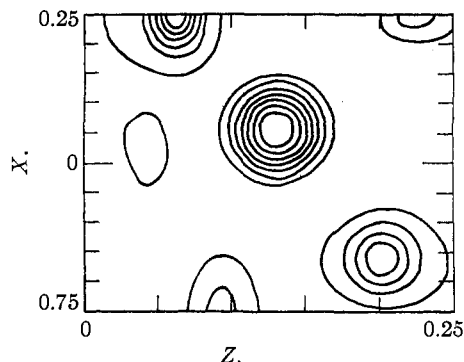


Fig. 2.—Fourier projection on (010).

On the Fourier projection on (100) the selenium maximum appears at the midpoint of a line joining the two chlorine maxima. This is consistent with the observed bond angle of 180° for Br-Se-Br in diphenylselenium dibromide, but

there are other possibilities in this case, that is, the distance Se-Cl_I may be different from that of Se-Cl_{II} or the two chlorine atoms may be both above or both below the selenium atom.

This latter possibility is ruled out by the projection on (010) which indicates one chlorine at $x = 0.83$ and one at $x = 0.25$. A chlorine atom at $x = 0.25$ would lead to a peak twice as large as one at 0.83 due to the space-group symmetry and this is actually observed. The two Se-Cl distances thus indicated are different and lead to a bond angle slightly removed from 180°. A reasonable interpretation leading to equal Se-Cl distances and a bond angle of 180° may be obtained by assuming the x parameter of Cl_I to be 0.28 rather than 0.25. This should lead to two close maxima, one at $x = 0.22$ and the other at $x = 0.28$. Failure to resolve these maxima would not be surprising, especially in view of the small range of indices covered in the x direction.

Although the phenyl groups are not clearly resolved on the Fourier projections, considerable evidence regarding their approximate positions is to be had. One set of phenyl groups appears to be at about $y = 1/4, z = 1/4$ with the plane of the carbon ring parallel to (100). This leads to a superposition of the rings from adjacent molecules in the direction of the x axis. The length of this axis, 7.59 Å. is just slightly greater than twice the van der Waals thickness (3.7 Å.) of an aromatic molecule and lends support to this observation. The x parameters of these carbon atoms, C_I-C_{VI}, are all the same as that for selenium.

The second phenyl group, C_{VII}-C_{XII}, is even less distinct on the projection. The parameters finally chosen for this group were assigned so as to give the molecule a two-fold axis. This can be done in two ways, the way actually chosen being in better agreement with the Fourier projection on (100). The parameters resulting from this treatment are listed in Table I. The values for selenium and chlorine are all considered reliable to 0.003 with the exception of the x parameter for Cl_{II} which may be off 0.01 and that for Cl_I which may be off 0.02. The carbon parameters have been calculated on the assumption of a Se-C distance of 1.39 Å. The tabulated parameters for carbon may be considerably in error, but that they are approximately correct is borne out by the fact that the calculated intensities for reflections of low indices are in much better agreement with

the observed intensities when the phenyl groups are included.

TABLE I
PARAMETER VALUES FOR DIPHENYLSELENIUM DICHLORIDE

	x	y	z
Se	0.055	0.100	0.130
Cl _I	.28	.152	.062
Cl _{II}	.83	.049	.201
C _I	.055	.19	.19
C _{II}	.055	.26	.16
C _{III}	.055	.32	.21
C _{IV}	.055	.31	.28
C _V	.055	.24	.31
C _{VI}	.055	.18	.27
C _{VII}	.92	.10	.04
C _{VIII}	.99	.07	.98
C _{IX}	.88	.07	.92
C _X	.71	.10	.92
C _{XI}	.65	.13	.98
C _{XII}	.75	.13	.04

Values of F_{hkl} were calculated by use of the above parameters and Pauling-Sherman atomic scattering factors. In order to minimize the effect of large probable errors in the carbon parameters, a temperature factor was applied to the phenyl groups in calculating the amplitude. The F values so calculated are compared with the observed values in Table II.

Solid Solutions of Diphenylselenium Dibromide in Diphenylselenium Dichloride.—During the early stages of this investigation it was observed that diphenylselenium dibromide forms solid solutions in the dichloride, the crystals formed having the structure of the dichloride in the range from the pure dichloride up to more than 50 mole % of the dibromide. As an interesting and valuable check on the structure of the dichloride, an X-ray investigation of a crystal containing approximately 50 mole % of dibromide was carried out. These crystals were prepared by dissolving an equimolar mixture of the pure dichloride with pure dibromide in carbon bisulfide and permitting the solvent to evaporate. The crystals formed cover only a small range in composition as shown by the fact that random samples show nearly the same density by the flotation method. In color they are intermediate between the red-orange color of the dibromide and the pale yellow color of the dichloride. Work is in progress on the phase relationships involved in the dichloride-dibromide system.

In the case of the solid solution, photographs were prepared about the a axis only, using CuK $_{\alpha}$ radiation as before. The cell size found is just

TABLE II
COMPARISON OF CALCULATED WITH OBSERVED AMPLITUDES
FOR DIPHENYLSELENIUM DICHLORIDE

(hkl)	F_{hkl}		(hkl)	F_{hkl}	
	Calcd.	Obs.		Calcd.	Obs.
002	-3	0	041	-20	18
004	-12	20	043	9	11
006	3	3	045	21	23
008	-5	10	047	4	0
0.0.10	-4	8	049	-7	10
0.0.12	-30	23	0.4.11	-18	15
020	4	7	061	4	0
022	7	8	063	25	26
024	-9	10	065	-2	0
026	5	10	067	-10	13
028	7	5	069	21	17
0.2.10	7	14	081	7	12
0.2.12	-10	8	083	8	15
040	-37	22	085	-27	22
042	-25	20	087	-16	14
044	16	18	089	25	24
046	7	5	0.10.1	-1	0
048	14	12	0.10.3	-1	0
0.4.10	15	15	200	20	32
0.4.12	17	16	202	-21	16
060	-20	17	204	-17	36
062	0	0	206	13	20
064	26	25	208	29	29
066	-11	5	400	8	13
068	-23	23	402	12	9
0.6.10	-2	0	404	1	0
080	-2	0	406	5	0
082	16	14	408	-1	0
084	-12	9	600	-5	0
086	3	7	602	-5	0
088	9	8	604	14	9
0.10.0	7	6	606	5	7
0.10.2	-1	0	102	-20	25
0.10.4	-24	21	104	-25	40
021	-33	21	106	-13	7
023	-23	25	302	-18	25
025	11	17	304	10	7
027	-2	0	306	33	42
029	-15	15	502	-30	23
0.2.11	-5	0	504	6	0
0.2.13	30	25	506	-10	20

slightly larger than that of the pure dichloride, the measurements leading to $a_0 = 7.65 \text{ \AA}$., $b_0 = 18.1 \text{ \AA}$. and $c_0 = 17.8 \text{ \AA}$. A completely independent estimation of intensities was made, using the multiple film technique. The F values so obtained were used as coefficients in a Fourier summation and the projection which resulted was identical in every important detail with that of the pure dichloride with the exception of slight differences in the halogen parameters and differences in the relative heights of the peaks. The halogen maxima in this case are relatively higher by about the anticipated amount, and are almost exactly equal

to each other. The y and z parameters found in this case are shown in Table III.

TABLE III
PARAMETER VALUES FOR SOLID SOLUTION

	y	z
Se	0.100	0.130
X _I	.154	.061
X _{II}	.045	.200

Values of F_{0kl} were calculated for the solid solution using the mean of the scattering factors for chlorine and bromine for the halogens X_I and X_{II}. The phenyl groups were treated as before. These calculated values are compared with the observed values in Table IV.

TABLE IV
COMPARISON OF CALCULATED WITH OBSERVED AMPLITUDES
FOR SOLID SOLUTION

(hkl)	F_{hkl}		(hkl)	F_{hkl}	
	Calcd.	Obs.		Calcd.	Obs.
002	-4	0	0.10.0	-9	12
004	-14	25	0.10.2	-2	0
006	-1	0	0.10.4	-27	23
008	-10	7	021	-37	34
0.0.10	-1	0	023	-27	31
0.0.12	-35	20	025	5	9
020	7	10	027	3	0
022	3	3	029	-10	7
024	-7	8	0.2.11	-2	0
026	7	10	0.2.13	-39	22
028	7	7	041	-23	21
0.2.10	16	20	043	19	21
0.2.12	-14	12	045	28	31
040	-19	23	047	2	0
042	-35	34	049	3	0
044	22	24	0.4.11	-29	21
046	12	9	061	-3	0
048	-14	14	063	32	37
0.4.10	23	21	065	-1	0
0.4.12	15	15	067	-13	19
060	-10	11	069	27	25
062	0	0	081	-5	0
064	26	28	083	7	13
066	-13	6	085	-34	23
068	-36	35	087	-24	17
0.6.10	-3	0	089	37	36
080	2	0	0.10.1	-5	0
082	16	14	0.10.3	5	0
084	-11	9	0.10.5	2	0
086	1	3			
088	10	10			

Discussion of the Structure

Projections of the structure on (100) and (010) of the unit cell are shown in Figs. 3 and 4. The molecular structure indicated is identical to that of diphenylselenium dibromide. This conclusion

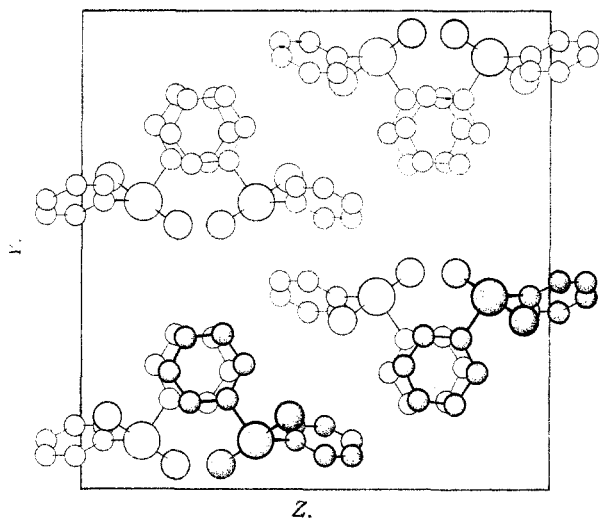


Fig. 3.—Projection of the structure of diphenylselenium dichloride on (100) of the unit cell. Circles represent in order of decreasing radius, selenium, chlorine and carbon atoms.

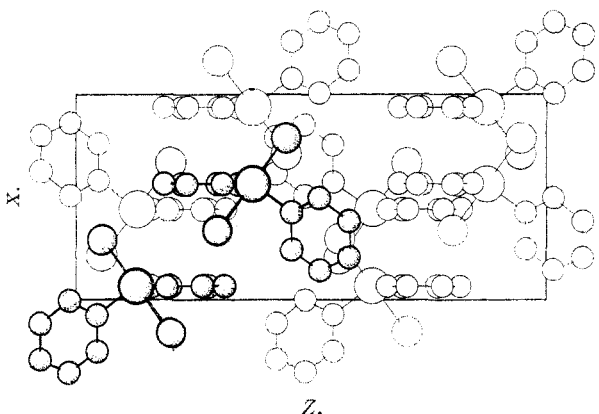


Fig. 4.—Projection of the structure of diphenylselenium dichloride on (010) of the unit cell.

is supported by the fact that the two substances form solid solutions in the form of the dichloride over a wide range of composition. The difference between the crystal structures of the two pure substances is accordingly in the manner in which the molecules pack together.

The observed Se-Cl separation, 2.30 ± 0.05 Å., is, as would be expected by analogy with the Se-Br distance in diphenylselenium dibromide, longer than the sum of the covalent radii for selenium and chlorine, 2.16 Å. It is interesting to compare the bond distances in these two dihalides with the metal-halogen separations in $(\text{CH}_3)_3\text{SbCl}_2$ and $(\text{CH}_3)_3\text{SbBr}_2$ found by Wells.⁵ This comparison is made in Table V where the calculated distances are the sum of the covalent radii.

(5) A. F. Wells, *Z. Krist.*, **99**, 367 (1938).

TABLE V
M-X DISTANCES IN $(\text{C}_6\text{H}_5)_2\text{SeX}_2$ AND IN $(\text{CH}_3)_3\text{SbX}_2$

	Observed (Å.)	Calculated (Å.)
Se-Cl	2.30	2.16
Se-Br	2.52	2.31
Sb-Cl	2.49	2.40
Sb-Br	2.63	2.55

The molecular structure of the trimethylantimony dihalides is the same as that of the diphenylselenium dihalides in every respect if one replaces two of the methyl groups by phenyls and the third methyl by an unshared pair of electrons. Both structures have the linear X-M-X arrangement. The greater lengthening of the M-X bonds over the calculated value in the selenium compounds is to be attributed largely to the presence of an unshared electron pair.

Observed packing distances in diphenylselenium dichloride are: $\text{Cl}_{\text{I1}}-\text{Cl}_{\text{I2}}$, 4.16 Å., to be compared with 3.60 Å., which is twice the van der Waals radius for chlorine and $\text{Phenyl}_{\text{I1}}-\text{Phenyl}_{\text{I1}}$, 3.80 Å., just slightly greater than the van der Waals thickness, 3.70 Å., of an aromatic molecule. Distances involving the second phenyl group, $\text{C}_{\text{VII1}}-\text{C}_{\text{XII1}}$, are not reliably enough determined to be significant.

The large elective dipole moment (3.47D) found by Smyth, Grossman and Ginsburg⁶ for diphenylselenium dichloride in benzene solution may be satisfactorily accounted for in terms of the structure reported in the present investigation if one assumes the resonating polar forms suggested by Smyth and co-workers.

The authors wish to acknowledge with thanks the cooperation of the National Youth Administration in providing the services of Miss Roxie Wittenberg, who carried out some of the calculations. We also wish to thank Professor Linus Pauling for reading and criticizing the manuscript.

Summary

An X-ray investigation of orthorhombic crystals of diphenylselenium dichloride shows a unit cell with $a_0 = 7.59$ Å., $b_0 = 17.97$ Å. and $c_0 = 17.77$ Å. all values ± 0.03 Å. The unit contains eight molecules and the space group symmetry is $D_{2h}^{15}-Pbca$. With the aid of Patterson and Fourier projections, a structure was deduced which accounts rather well for the observed intensities.

The structure of the diphenylselenium dichloride molecule is the same as that found previously

(6) C. P. Smyth, A. J. Grossman and S. R. Ginsburg, *THIS JOURNAL*, **62**, 192 (1940).

for the diphenylselenium dibromide² molecule. This similarity of molecular structure is in keeping with our observation that the dibromide forms solid solutions with the dichloride having the crystal form and structure of the pure dichloride. This is an interesting fact in view of the lack of isomorphism between the two pure crystalline sub-

stances. An X-ray investigation of a solid solution having 50 mole % of each constituent present shows complete identity of structure with the dichloride.

The observed Se-Cl distance is 2.30 ± 0.05 Å. and the Cl-Se-Cl bond angle is $180 \pm 5^\circ$.

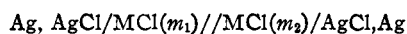
LOS ANGELES, CALIFORNIA RECEIVED NOVEMBER 24, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

The Thermodynamics of Aqueous Solutions of Potassium Chloride at Temperatures from 15–45° from E. m. f. Measurements on Cells with Transference

BY W. J. HORNIBROOK, G. J. JANZ AND A. R. GORDON

Of the thermodynamic investigations by the e. m. f. method of aqueous sodium and potassium chloride solutions, unquestionably the most accurate for the dilute range of concentrations have been those of MacInnes and his associates^{1,2} who employed cells of the type



So far such cells with transference have been used only for 25°; recent determinations in this Laboratory of the transport numbers of potassium chloride³ and of sodium chloride⁴ for temperatures from 15–45° now permit similar measurements for temperatures other than 25°. This paper gives the data for potassium chloride and provides (we believe) a satisfactory isotonic standard for dilute solutions for this temperature range. Moreover, thermal and heat capacity data may now be used as an independent check on the self-consistency of the results. Similar measurements on sodium chloride solutions are now under way; we hope to report them in the not too distant future.

Experimental

The cell, illustrated in Fig. 1, differs from that of Shedlovsky and MacInnes³ only in the mounting of the electrodes. In our cell, the electrodes are heavy disks of platinum, mounted horizontally in ground glass joints. The disks are about 1 cm. in diameter and 1 mm. thick; in this way, a rigid backing is provided for the active surface of the electrode, while at the same time the electrodes can be silver-plated and chloridized outside the cell. The method of preparing the electrodes was essentially that of Brown and MacInnes.¹ The highly polished surface of the platinum was plated with silver for five hours

at a current of 0.7 ma., the electrolyte being a 10 g. p. l. solution of potassium silver cyanide from which excess cyanide had been precipitated by addition of silver nitrate. After standing in concentrated ammonia and washing in water, the silver surface was chloridized anodically in tenth normal hydrochloric acid for twenty-five minutes at 0.7 ma. To obtain reproducible results we found it necessary during both plating and chloridizing to have a uniform current density over the electrode; this was ensured by the design of the siphon leading into the vessel in which the electrolysis was being carried out. We also found it desirable to keep the solutions well stirred during the electrolyses. After chloridizing, the electrodes were allowed to stand in conductivity water (which was frequently replaced) for twenty-four hours, and then were kept until required in a twentieth molal solution of potassium chloride.

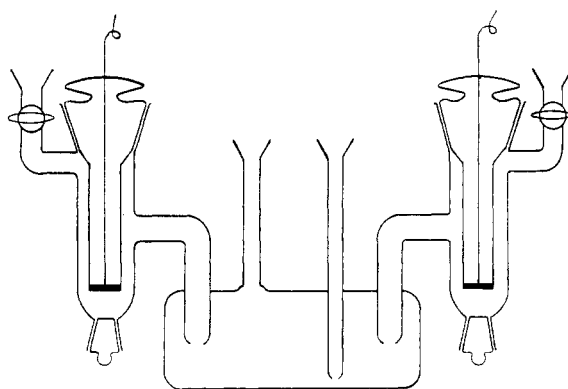


Fig. 1.

The technique of filling the cell has been adequately described by Shedlovsky and MacInnes³ and need not be discussed here. The solutions were made up gravimetrically from conductivity water (specific conductance 1.5×10^{-8} at 25°) and twice recrystallized B. D. H. Analar potassium chloride which had been fused rapidly in platinum in an atmosphere of dry carbon dioxide-free nitrogen. In computing concentrations, all weights were corrected to vacuum. After filling, the cell was placed in an oil-bath whose temperature was controlled to $\pm 0.005^\circ$, bath temperature being read on Beckmann thermometers

(1) A. S. Brown and D. A. MacInnes, *THIS JOURNAL*, **57**, 1356 (1935).

(2) T. Shedlovsky and D. A. MacInnes, *ibid.*, **59**, 503 (1937).

(3) R. W. Allgood, D. J. Le Roy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

(4) R. W. Allgood and A. R. Gordon, to appear shortly.