[Contribution from the Department of Chemistry and Chemical Engineering of Case Institute of Technology]

Equilibria in Saturated Solutions. III. The Quaternary System $CaCl_2$–$MgCl_2$–KCl–H_2O at 35°

By William J. Lightfoot and Carl F. Prutton

In previous papers,[1,2] the isotherms for the ternary systems, $CaCl_2$–$MgCl_2$–H_2O, $CaCl_2$–KCl–H_2O and $MgCl_2$–KCl–H_2O were reported at 35° and 75°. These investigations were carried out in preparation for study of the quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O.

Experimental Method

The analytical methods and techniques were the same as those used in the investigation of the ternary systems. Solutions and solid phases were brought into equilibrium at 35 ± 0.02°. It was found that six to eight hours was sufficient time for equilibrium to be established.

In the identification of the solid phases present in a four-component system, there are three methods which may be used. The application of the wet residue method used in ternary systems was extended by Schreinemakers[3] to quaternary systems. Igelsrud and Thompson[4] in their study of this system at 0° presented an analytical method for the identification of the solid phases. Microscopic examination of the wet residue quickly establishes the identity of the solid phases. All three of these methods were used.

The Quaternary Isotherm.—In order to represent completely the compositions of the saturated solutions of a quaternary isotherm, a three dimensional coördinate system is required. The space model of the regular tetrahedron is usually employed. In Fig. 1, the upper portion of the quaternary tetrahedron is shown schematically, the relative proportions of the saturation surfaces being indicated.

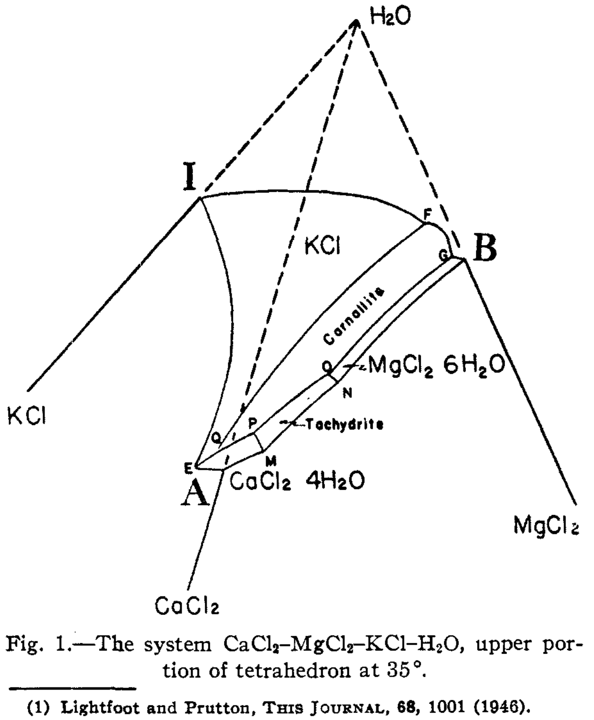

Fig. 1.—The system $CaCl_2$–$MgCl_2$–KCl–H_2O, upper portion of tetrahedron at 35°.

The same characteristic of magnesium chloride solutions is noted in the quaternary system that was found in the ternary systems, carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$, is almost completely insoluble in solutions having $MgCl_2.6H_2O$ as a solid phase. Tachydrite solutions dissolve more carnallite as the calcium chloride content of the solution is increased; with solutions saturated for $CaCl_2 \cdot 4H_2O$ a considerably larger portion of carnallite is dissolved.

The saturation surface of $MgCl_2 \cdot 6H_2O$ is extremely small, with tachydrite, $CaCl_2 \cdot 2MgCl_2 \cdot 12H_2O$, only slightly larger. The surface for $CaCl_2 \cdot 4H_2O$ is next in size with carnallite and KCl occupying the largest portions. The carnallite surface is the most significant in that it is a slice through practically the whole diagram, being in evidence as a solid phase from the ternary system $MgCl_2$–KCl–H_2O where there is no calcium chloride to solutions where the magnesium chloride content has fallen to 1.02% and the calcium chloride content has risen to 49.76%.

In discussing the associated ternary systems, it was pointed out that both carnallite and tachydrite were incongruently saturating compounds at 35°. No formation of a quaternary compound was found at 35° either through analytical results or by microscopic examination.

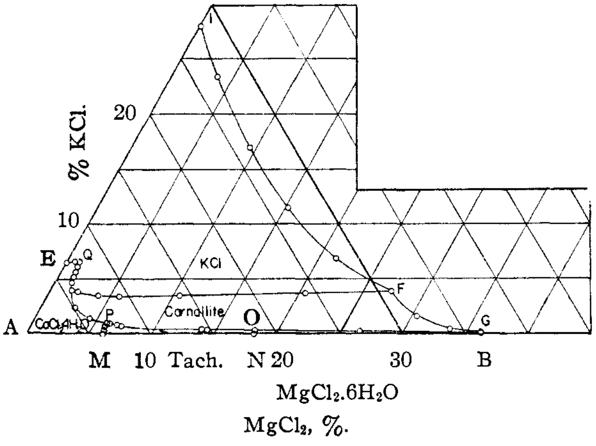

Fig. 2.—Equilibria in the quaternary system, $CaCl_2$–$MgCl_2$–KCl–H_2O at 35°, projection on the $MgCl_2$–KCl–H_2O plane.

In Table I, the data for the quaternary system are given. The isotherm has been projected on the $MgCl_2$–KCl–H_2O plane of the tetrahedron in Fig. 2 using the method suggested by Schreinemakers. This is a projection parallel to a particular and specified edge of the tetrahedron. Points E, F, G, N and M are the invariant points of the associated ternary systems. Area IFQE is the saturation surface of KCl, FGOPQ that of carnallite, GBNO that of $MgCl_2 \cdot 6H_2O$, MNOP that of tachydrite, and AEQPM that of $CaCl_2 \cdot 4H_2O\alpha$. The curve FQ is the intersection of the carnallite surface with the KCl surface and all points on it represent equilibrium between the solid phases carnallite and KCl with saturated solution given by some point on this curve. GO represents solutions saturated with $MgCl_2 \cdot 6H_2O$ and carnallite; OP with tachydrite and carnallite, PQ with $CaCl_2 \cdot 4H_2O\alpha$ and carnallite; NO with $MgCl_2 \cdot 6H_2O$ and tachydrite; MP wih tachydrite and $CaCl_2 \cdot 4H_2O\alpha$; and EQ with KCl and $CaCl_2 \cdot 4H_2O\alpha$.

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(1) Lightfoot and Prutton, This Journal, 68, 1001 (1946).

(2) Lightfoot and Prutton, *ibid.*, 69, 2098 (1947).

(3) Schreinemakers, *Z. Phys. Chem.*, 59, 641 (1907).

(4) Igelsrud and Thompson, This Journal, 58, 2003 (1936).

TABLE I

THE QUATERNARY SYSTEM $MgCl_2$–$CaCl_2$–KCl–H_2O AT 35°

Point or line	Saturated solution, weight per cent.			Wet residue			Solid phase
	$MgCl_2$	$CaCl_2$	KCl	$MgCl_2$	$CaCl_2$	KCl	
F	27.33	...	3.81	...	...	...	Carnallite + KCl
FQ	20.61	9.12	3.69	20.13	5.59	24.67	Carnallite + KCl
FQ	10.59	23.57	3.47	...	...	...	Carnallite + KCl
FQ	5.83	31.66	3.37	...	...	...	Carnallite + KCl
FQ	4.07	35.51	3.44	...	...	...	Carnallite + KCl
FQ	4.01	35.60	3.43	...	...	...	Carnallite + KCl
FQ	2.31	41.00	3.80	...	...	...	Carnallite + KCl
FQ	1.30	45.85	4.71	5.73	34.99	17.16	Carnallite + KCl
FQ	1.15	48.34	5.69	...	...	...	Carnallite + KCl
FQ	1.17	48.89	6.04	5.69	38.50	15.96	Carnallite + KCl
Q	1.04	49.74	6.49	2.81	48.61	7.29	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\alpha$
Q	1.01	49.78	6.45	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\alpha$
Q	1.01	49.74	6.46	2.23	51.40	6.36	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\alpha$
Q	1.03	49.78	6.45	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\alpha$
Q mean	1.02	49.76	6.46				Carnallite + KCl + $CaCl_2 \cdot 4H_2O\alpha$
G	36.17	...	0.14	...	...	...	Carnallite + $MgCl_2 \cdot 6H_2O$
GO	26.66	12.97	.16	31.75	8.43	4.48	Carnallite + $MgCl_2 \cdot 6H_2O$
O	18.06	26.76	.23	25.66	19.29	5.53	Carnallite + $MgCl_2 \cdot 6H_2O$ + Tachydrite
O	18.07	26.74	.23	...	...	...	Carnallite + $MgCl_2 \cdot 6H_2O$ + Tachydrite
O	18.10	26.73	.23	25.39	21.15	3.35	Carnallite + $MgCl_2 \cdot 6H_2O$ + Tachydrite
O mean	18.07	26.74	.23	...	...	...	Carnallite + $MgCl_2 \cdot 6H_2O$ + Tachydrite
OP	14.23	32.01	0.32	21.40	24.24	5.67	Carnallite + Tachydrite
OP	13.83	32.60	.33	...	...	...	Carnallite + Tachydrite
OP	7.28	42.75	.71	...	...	...	Carnallite + Tachydrite
OP	6.98	43.27	.76	13.26	34.98	5.11	Carnallite + Tachydrite
OP	6.15	44.44	.97	...	...	...	Carnallite + Tachydrite
P	5.89	45.32	1.00	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$ + Tachydrite
P	5.90	45.31	0.99	9.06	42.50	2.41	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$ + Tachydrite
P	5.93	45.26	.99	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$ + Tachydrite
P mean	5.91	45.30	.99	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$ + Tachydrite
PQ	4.42	46.65	1.33	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	2.69	48.40	2.28	5.04	47.81	3.96	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	1.72	49.25	3.92	8.76	39.28	8.29	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	1.36	49.54	5.10	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
E	...	50.45	6.48	...	...	...	KCl + $CaCl_2 \cdot 4H_2O\alpha$
EQ	0.71	50.06	6.46	0.23	51.57	9.72	KCl + $CaCl_2 \cdot 4H_2O\alpha$
EQ	0.93	49.83	6.45	...	...	...	KCl + $CaCl_2 \cdot 4H_2O\alpha$
M	6.20	45.03	..	...	...	...	Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
MP	6.13	45.18	0.33	5.75	51.34	0.13	Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
MP	5.82	45.43	0.70	4.53	51.99	0.31	Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
N	18.18	26.68	..	...	...	...	Tachydrite + $MgCl_2 \cdot 6H_2O\alpha$
					Metastable		
OP′	4.34	48.18	1.41	...	...	...	Carnallite + Tachydrite
OP′	4.22	48.63	1.53	...	...	...	Carnallite + Tachydrite
OP′	3.97	49.24	1.64	...	...	...	Carnallite + Tachydrite
P′	3.38	50.50	2.09	...	...	...	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\gamma$
P′	3.38	50.49	2.09	...	...	...	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\gamma$
P′	3.38	50.51	2.11	...	...	...	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\gamma$
P′	3.42	50.47	2.09	...	...	...	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\gamma$
P′ mean	3.39	50.49	2.10	...	...	...	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\gamma$
P′Q′	3.06	50.81	2.10	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\gamma$
P′Q′	2.05	51.78	3.91	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\gamma$
P′Q′	1.51	52.05	4.53	...	...	...	Carnallite + $CaCl_2 \cdot 4H_2O\gamma$
Q′	0.86	50.68	6.97	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$
Q′	.86	50.68	7.02	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$
Q′	.92	50.71	7.02	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$
Q′	.92	50.71	7.01	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$
Q′	.89	50.71	7.02	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$
Q′ mean	.89	50.70	7.01	...	...	...	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$

There are three quaternary isothermal invariant points in the system: P, Q and O. At Q the three solid phases in equilibrium with the fixed composition of saturated solution are $CaCl_2 \cdot 4H_2O\alpha$, KCl, and carnallite; at P, $CaCl_2 \cdot 4H_2O\alpha$, tachydrite, and carnallite. Actually the carnallite area is not pinched off as is shown in this projection. It is due to the fact that the left-hand portion of FQ superimposes part of the curve PQ.

In Figs. 3 and 4, the quaternary isotherm has been projected on the $CaCl_2$–KCl–H_2O plane and the $CaCl_2$–$MgCl_2$–H_2O plane, respectively. A consistent notation of the curves and points has been followed to facilitate the location of the same point on the different projections. In the projection on the $CaCl_2$–KCl–H_2O plane, the saturation curve for KCl in the ternary system superimposes the saturation curve for carnallite and KCl, FQ. Recognition of this aids in visualizing the surfaces in the space model. When the isotherm is projected on the $MgCl_2$–$CaCl_2$–H_2O plane, a considerable portion is superimposed by the ternary curves. This is probably the least useful diagram of the three, but it presents relationships which are not so easily seen from the other two projections.

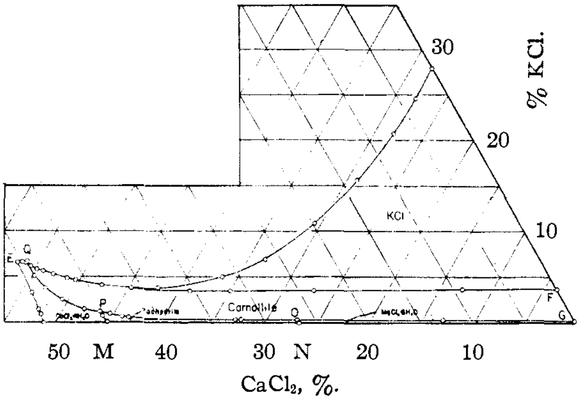

Fig. 3.—Equilibria in the quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 35°, projected on the $CaCl_2$–KCl–H_2O plane.

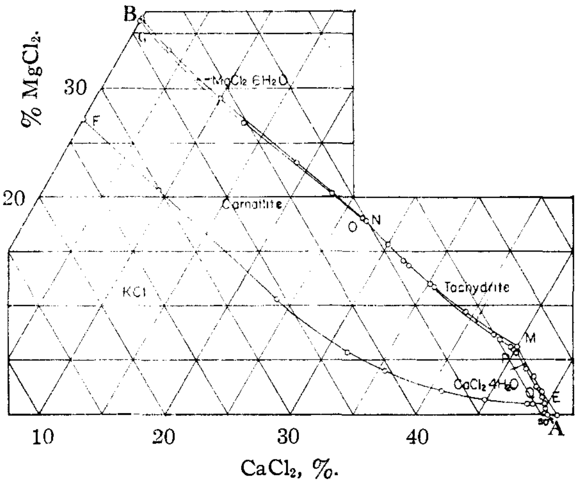

Fig. 4.—Equilibria in the quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 35°, projection on the $CaCl_2$–$MgCl_2$–H_2O plane.

In the experimental work, there was some difficulty at first in obtaining solutions saturated with the stable form of calcium chloride tetrahydrate. Samples quite frequently indicated on microscopic examination that $CaCl_2 \cdot 4H_2O\gamma$ was the solid phase. Analyses of these samples were made and the invariant points and saturation curves for the metastable form in relation to the quaternary system were determined. The results are plotted in Fig. 3, the projection on the $CaCl_2$–KCl–H_2O plane. Comparison with the same projection showing stable equilibrium show that a marked change has taken place. The left-hand portion of the carnallite area has been broadened and the area of existence of tachydrite as a solid phase increased. Points Q′ and P′ are now the invariant points, where $CaCl_2 \cdot 4H_2O\alpha$ is replaced with $CaCl_2 \cdot 4H_2O\gamma$. Points M and E represent the iso-

Table II

The Quaternary System $MgCl_2$–$CaCl_2$–KCl–H_2O at 35°, Basis of Zero Per Cent. Water Content

Point or line	Saturated solution, weight per cent. $MgCl_2$	$CaCl_2$	Solid phase
F	87.76	...	Carnallite + KCl
FQ	61.67	27.29	Carnallite + KCl
FQ	28.14	62.64	Carnallite + KCl
FQ	14.27	77.48	Carnallite + KCl
FQ	9.46	82.54	Carnallite + KCl
FQ	9.32	82.71	Carnallite + KCl
FQ	4.90	87.03	Carnallite + KCl
FQ	2.51	88.41	Carnallite + KCl
FQ	2.08	87.60	Carnallite + KCl
FQ	2.09	87.15	Carnallite + KCl
Q mean	1.78	86.93	Carnallite + KCl + $CaCl_2 \cdot 4H_2O$
G	99.61	...	Carnallite + $MgCl_2 \cdot 6H_2O$
GO	67.00	32.60	Carnallite + $MgCl_2 \cdot 6H_2O$
Q mean	40.12	59.37	Carnallite + $MgCl_2 \cdot 6H_2O$ + Tachydrite
OP	30.56	68.75	Carnallite + Tachydrite
OP	29.58	69.72	Carnallite + Tachydrite
OP	14.35	84.25	Carnallite + Tachydrite
OP	13.68	84.83	Carnallite + Tachydrite
OP	11.93	86.19	Carnallite + Tachydrite
P mean	11.32	86.87	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	8.44	89.03	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	5.04	90.69	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	3.13	89.72	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
PQ	2.43	88.46	Carnallite + $CaCl_2 \cdot 4H_2O\alpha$
E	...	88.62	KCl + $CaCl_2 \cdot 4H_2O\alpha$
EQ	1.24	87.47	KCl + $CaCl_2 \cdot 4H_2O\alpha$
EQ	1.63	87.10	KCl + $CaCl_2 \cdot 4H_2O\alpha$
M	12.10	87.90	Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
MP	11.87	87.49	Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
MP	11.20	87.44	Tachydrite + $CaCl_2 \cdot 4H_2O\alpha$
N	40.53	59.47	Tachydrite + $MgCl_2 \cdot 6H_2O$
			Metastable equilibrium
OP′	8.05	89.34	Carnallite + Tachydrite
OP′	7.76	89.43	Carnallite + Tachydrite
OP′	7.24	89.77	Carnallite + Tachydrite
P′ mean	6.04	90.21	Carnallite + Tachydrite + $CaCl_2 \cdot 4H_2O\gamma$
P′Q′	5.47	90.78	Carnallite + $CaCl_2 \cdot 4H_2O\gamma$
P′Q′	3.55	89.68	Carnallite + $CaCl_2 \cdot 4H_2O\gamma$
P′Q′	2.60	89.60	Carnallite + $CaCl_2 \cdot 4H_2O\gamma$
Q′ mean	1.49	86.55	Carnallite + KCl + $CaCl_2 \cdot 4H_2O\gamma$

thermal invariant points in the ternary systems where the stable form of $CaCl_2 \cdot 4H_2O$ is one of the solid phases. The effect of metastable form in these ternary systems was not determined. Hence MP′ and EQ′ are not true saturation curves for the metastable equilibria. However, it is possible to make an assumption as to the general effect of $CaCl_2 \cdot 4H_2O\gamma$ on the ternary systems. In the ternary system $CaCl_2$–KCl–H_2O the invariant point would be of slightly higher calcium chloride content with the potassium chloride content remaining about the same. The effect on the $CaCl_2$–$MgCl_2$–H_2O system would be more pronounced in that the tachydrite area would be larger, occupying some of the space now covered by $CaCl_2 \cdot 4H_2O$ α. The $CaCl_2 \cdot 4H_2O$ γ field would be very small.

In Table II the data for the quaternary isotherm are given based on the salt content of the saturated solution exclusive of water. The plot of the data is shown in Fig. 5. Coexistent solid phases have been connected by straight lines and the triangles outlined by them represent the three solid phases present at the invariant points. The lines and points follow the consistent notation used in the other projections. The Jänecke diagram for the metastable relations is very similar to Fig. 5.

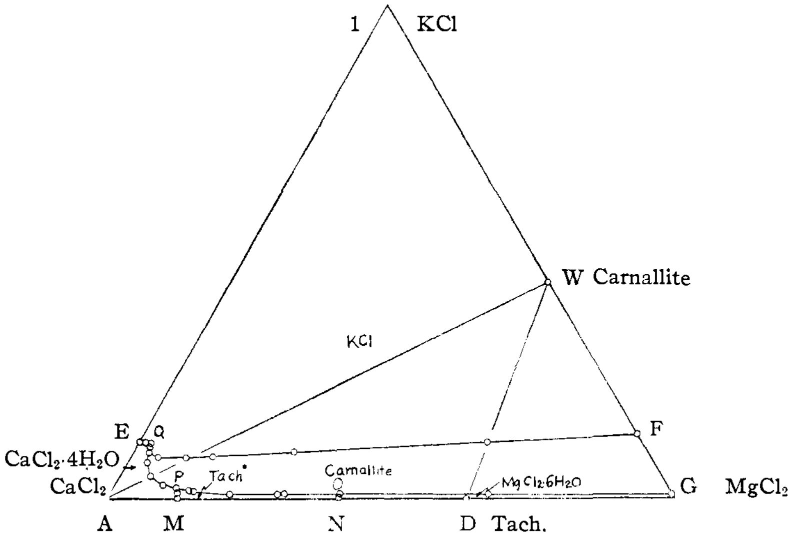

Fig. 5.—Quaternary system $CaCl_2$–$MgCl_2$–KCl–H_2O at 35°, projected on base of tetrahedron.

Summary

1. Isotherms have been determined at 35° for the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Polarography of Selenium and Tellurium. I. The −2 States

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Investigations of the polarographic behavior of the −2 oxidation states of selenium and tellurium have not been reported in the literature. In the case of sulfide ion in 1 *N* sodium hydroxide Revenda,[2a] and Kolthoff and Miller,[2] observed a single, well-developed anodic wave due to the reaction $Hg + S^{=} = HgS + 2e$. We have found that selenide and telluride ions produce similar anodic waves. The reaction of selenide ion is analogous to that of sulfide ion, *i. e.*, primary oxidation of the mercury of the dropping electrode and the subsequent precipitation of mercuric selenide. In the case of telluride ion, however, we have obtained evidence that the anodic wave results from oxidation of the telluride ion itself to the element, rather than "depolarization" of the dropping mercury anode.

Experimental

The selenide and telluride solutions used for these experiments were obtained by controlled potential electrolytic reduction at a mercury cathode of the purified dioxides whose preparations have been previously described.[3] The reductions were performed in the diaphragm cell shown in Fig. 1 and the cathode potential was controlled against a saturated calomel reference electrode by an automatic potentiostat.[4] The reduction of tellurium(IV) was performed in 1 *N* sodium hydroxide at a potential of −1.7 v. *vs.* the S.C.E., while the selenium(IV) was reduced in a 1 *M* ammoniacal chloride buffer at *p*H 8.0 and a potential of −1.8 v. The reduced solution in the cell was sometimes used directly for the polarographic measurements, while in other cases aliquots were transferred to supporting electrolytes in a conventional H-type cell.

The diaphragm cell in Fig. 1 has been modified from that previously described[5] to incorporate a reference electrode as an integral part so that polarograms could be recorded without disturbing the contents of the cell. The cathode chamber is a 250-cc. wide-mouthed erlenmeyer flask, which is joined to the anode chamber and the reference electrode through 30 mm. and 10 mm. medium porosity sintered-glass disks, respectively. Provision is also made for sweeping the solution with an inert gas and for electrical contact with the mercury cathode. The four-hole rubber stopper accommodates the dropping mercury electrode, a propeller type glass stirrer which agitates the mercury-solution interface as well as the solution, an additional gas entry, and a salt bridge to an external reference electrode for use during the electrolysis. To minimize the inclusion of *iR* drop in the measured cathode potential the tip of the salt bridge must be as close to the mercury as is physically possible.[5] A carbon rod served as anode. A layer of agar saturated with potassium chloride was placed on the anode side of the

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[1] Allied Chemical and Dye Corporation Fellow, 1947–48.

[2] (a) J. Revenda, *Coll. Czechoslov. Chem. Commun.*, **6**, 453 (1934); (b) I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 1405 (1941).

[3] J. J Lingane and L. W. Niedrach, *ibid.*, **70**, 1997 (1948).

[4] J. J. Lingane, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 332 (1945).

[5] J. J. Lingane, C. G. Swain and M. Fields, THIS JOURNAL, **65**, 1348 (1943).