using the absorption coefficients where an electron transition is involved, such as in the dissociation of bromine into a normal and an excited bromine atom, show that such dissociations could not be effected in a molecular beam using the most intense sources of light available. Thus the experiments of Kröger, Lewis and Mayer, Mayer and the present investigation are in entire agreement with the theoretical expectations.

Summary

1. In reactions as ordinarily studied there are three factors influencing the decomposition, namely, the absorption and emission of radiation, intermolecular collisions and collisions with the walls. Methods have been discussed for separating these three factors and studying them independently.

2. We have completed experiments on the effect of radiation alone on nitrogen pentoxide by passing a molecular beam of this substance through a furnace containing approximately black body radiation. Even at the lowest temperature only one molecule in 10^{27} should have escaped decomposition if black body radiation alone caused the decomposition under ordinary conditions. We could detect no decomposition in any experiment.

3. We have calculated the probability of absorption of radiation by the nitrogen pentoxide molecule and find the experimental result in agreement with theory.

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[Contribution from the Chemical Laboratory of the University of Illinois]

TRANSFERENCE NUMBERS OF IONS IN SOLID SODIUM CHLORIDE AT HIGH TEMPERATURES

By T. E. Phipps and R. T. Leslie

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For a large number of solid salts it has been shown that the relation between the electrical conductance and the absolute temperature may be represented by an equation of the form:

$$\ln k = A/RT + C \tag{1}$$

where k is the specific conductance, A is a heat quantity designated as the heat of liberation of the ions from the lattice, and R is the gas constant. It has been found, however, that this relation is not linear over the whole temperature range for sodium and potassium chlorides, bromides and iodides. Ussataja and Hochberg[1] have observed this deviation for sodium chloride above 500° and have attempted to apply an equation of the form

$$\ln k = AT + C \tag{2}$$

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[1] Ussataja and Hochberg, *Z. Physik*, **46**, 88 (1927).

above this temperature. Phipps, Lansing and Cooke[2] and Phipps and Partridge[3] have investigated the above salts and have found that the relation between log k and $1/T$ is linear but that the curve shows two slopes. The upper is slightly greater than twice the lower slope for the halides of sodium and potassium mentioned above. The curve for sodium chloride is shown in Fig. 1. On account of the difficulty of measurement in the transition range, due probably to polarization effects, it is not certain whether the change in slope is gradual or abrupt.

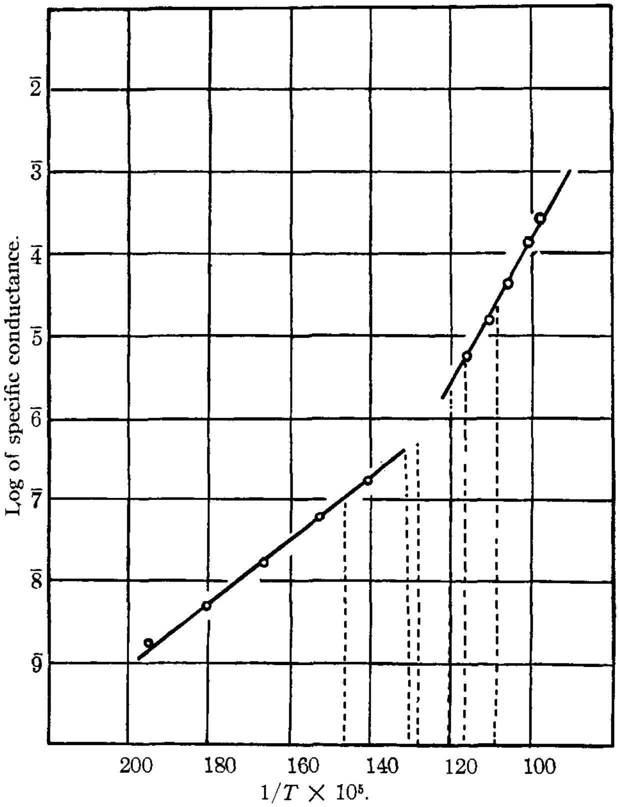

Fig. 1.—Temperature-conductance curve of solid sodium chloride. Dotted lines mark temperatures at which transference experiments were run.

Tubandt's[4] transference experiments upon salts of the less polar type such as the halides of silver and lead have indicated uni-ionic conduction in practically all cases. For these same halides a single slope is observed

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[2] Phipps, Lansing and Cooke, This Journal, **48**, 112 (1926).

[3] Phipps and Partridge, *Thesis*, University of Illinois, **1927** (to be published).

[4] Tubandt, *Z. anorg. allgem. Chem.*, **115**, 105 (1921).

when log *k* is plotted against $1/T$. The existence of two slopes in the conductance curves for the more polar halides of sodium and potassium led Phipps, Lansing and Cooke[2] to make the suggestion that there may be a change in the mechanism of conduction in the latter case as the temperature is raised, perhaps from uni-ionic to bi-ionic conduction. Smekal[5] interpreted the two-slope behavior just mentioned as supporting the "imperfect lattice" theory, the lower slope being determined by the heat of liberation of "Lockerionen" (that is, ions freer to move due to their position on the "inner surfaces" of the imperfect lattice) while the upper slope is determined by the heat of liberation of the "Gitterionen" (that is, the ions on the interior of units which are small enough to be considered as perfect). Smekal's conclusion rests upon the transference experiment of von Seelen[6] in which it was found that only the sodium ion moved in sodium chloride at 400°. This, however, is below the temperature at which the conductance curve changes slope.

Transference experiments were undertaken to determine if possible whether or not uni-ionic conduction persists at high temperatures in solid sodium chloride. The results may be briefly stated as follows. Transference by the chloride ion is negligible up to approximately 510°. At higher temperatures the chloride ion assumes an important part in the conduction.

Experimental

It has been suggested that the nature of the electrodes determines the mechanism of conduction. Thus Le Blanc and Kröger[7] have attributed the transference number of unity for silver in silver iodide, as observed by Tubandt,[4] to the fact that Tubandt used silver electrodes which provided a "follow-up" ion for the silver but not for the iodide ions of the lattice. In the present investigation it did not seem possible to design an electrode reversible for the chloride ion for use with sodium chloride at high temperatures. A metallic sodium anode and a nickel cathode were used. If Le Blanc and Kröger are correct in their surmise, the movement of the sodium ion would be favored by this choice of electrodes. In spite of the fact that the conditions might be considered adverse to the movement of the chloride ion, the results showed conclusively that the chloride ion took part in the conduction at high temperatures.

The chief difficulty encountered in the work was in the devising of a satisfactory sodium electrode. The final form of the apparatus which was used is shown in Fig. 2. The transference cell proper consisted of a block of rock salt, G, into which a hole was drilled to form a cup for the sodium, and three or four thin plates of salt upon which this cup rested. The cup constituted the anode portion and the plates the cathode portion. Attempts were made at first to use open cups, but the sodium spattered while

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[5] Smekal, *Z. Physik*, **44**, 869 (1927).

[6] v. Seelen, *ibid.*, **29**, 125 (1924).

[7] Le Blanc and Kröger, *Z. Electrochem.*, **30**, 253 (1924).

being introduced and evaporated too rapidly during the run. To obviate these difficulties a salt cover having two small holes, one for the introduction of the sodium and the other for the nickel electrode wire, was finally used. The nickel electrode rested on the cover of the anode cup as may be seen in Fig. 2 (detail). This formed a direct path through the salt to the nickel cathode. However, calculation showed that not more than 3% of the current could have passed by this path instead of through the sodium in the cup. Even if the nickel electrode should force movement of the chloride ion at the expense of the sodium ion, an uncertainty of at most 0.03 in the transference number of either ion would result from this shunt around the sodium. It is thought that the actual error introduced here is much less than 0.03.

The cups were about a centimeter in cross section and two centimeters high, while the plates were from a quarter to a half a square centimeter in area and a tenth of a centimeter thick. The parts were smoothed with fine emery paper. It was found in this connection that fitting together of raw cleaved surfaces resulted in excessive sticking and faulty cleavage at the end of the experiment. All parts were given a preliminary heating to about 400°, cooled in a desiccator and weighed before the experiments.

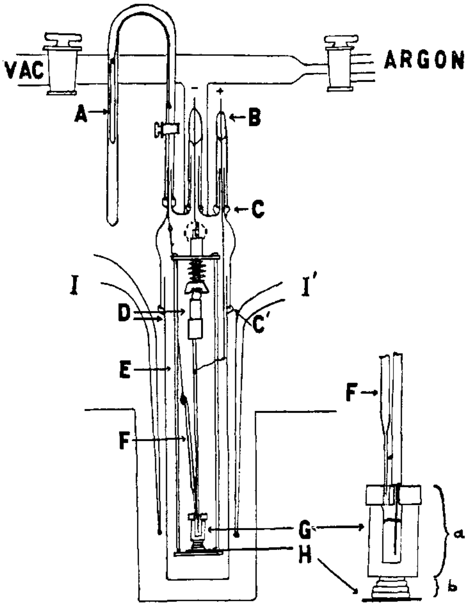

Fig. 2.—Apparatus used in determining transference numbers. A, brass counterpoise; B, tungsten-to-glass seals; C, C′, sealing wax seals; D, quartz; E, nickel frame; F, pyrex capsule filled with sodium; G, rock salt transference cell; H, removable nickel; I, I′, thermocouples; a, anode portion; b, cathode portion.

The lower part of the frame, E, in which the crystals were held was constructed entirely of nickel in order to withstand the sodium vapor. The nickel plate cathode, H, was removable so that it could be washed separately from the rest of the frame, and the washings analyzed for salt in case the crystals stuck to it. This frame was suspended from the negative terminal in such a way that it could be removed to facilitate mounting the crystals before the run.

The tube inclosing the whole apparatus was of quartz to allow visibility during the introduction of the sodium into the anode cup and to withstand the high temperatures. The tube was considerably attacked by the sodium vapor at the high temperatures and became coated with the usual brown deposit of silicon together with a layer of soda glass, which had to be removed by treatment with hydrofluoric acid after each run. Failure to do this led to cracking of the tube when it was next heated. The quartz tube was joined at C′ with a sealing wax seal to the Pyrex cap shown in Fig. 2.

The glass capsule, F, was filled with sodium by the method described by Gibson and Phipps[8] and was suspended in the position shown in the figure with the brass counterpoise, A, drawn up and clamped by means of the stopcock.

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[8] Gibson and Phipps, This Journal, **48**, 312 (1926).

To start the run the apparatus was evacuated to 10^{-5} or 10^{-6} mm. of mercury, and the temperature of the furnace surrounding the quartz tube was raised to about 150°. This caused the sodium to melt and run out of the capsule into the cup. The stopcock holding the counterpoise was then opened so that the capsule was drawn up into the cool part of the tube where it was not attacked by the sodium vapor. The stopcock to the vacuum pump was then closed and the apparatus filled with argon to about two atmospheres' pressure. This decreased the rate of evaporation of the sodium. Before the argon entered the apparatus it was passed through an alloy of sodium and potassium and through forty centimeters of magnesium perchlorate trihydrate in a vacuum-tight, all-glass train which was joined to the argon tank by a copper-to-glass seal.

The temperature was then brought up to the desired point and regulated automatically by a potentiometer, contact galvanometer and stick-relay system which was actuated by the thermocouples, I, I′, shown in the figure. This regulator had been previously calibrated in a blank run by inserting a Pt, Pt-Rh thermocouple in the position occupied by the crystals in an actual run. Regulation was found to be within a degree.

The total current through the crystals was measured by a silver coulometer and was kept below a milliampere to prevent heating. At high temperatures the sodium evaporated rapidly from the cup and it was necessary to determine by trial how long the run could be continued without losing all of the sodium.

The cathode crystals were colored blue in all of the runs above 410° except in the experiments where artificially grown sodium chloride plates were used, in which case a brown color resulted. All of the other parts remained colorless. The amount of sodium which diffused into the cathode plate was doubtless negligible, as shown by the work of Phipps and Mason.[9] Its presence could not have given rise to metallic conductance since only the end crystal was colored. A layer of metallic sodium was generally found between the cathode crystal and the nickel plate. Much of the sodium liberated at this interface distilled to the cooler parts of the apparatus.

Immediately after the apparatus was opened the cup and the cover were separated from the salt plates. The two parts were dropped as quickly as possible into separate portions of absolute alcohol and the sodium allowed to dissolve. The crystals were then rinsed with alcohol, the rinsings being added to the proper washings, and dried at 130° for several hours. The cup and cover were weighed together as anode portion. The plates remained stuck together and were weighed as cathode portion.

The possibility of serious error due to faulty cleavage made necessary the following rather elaborate procedure. To determine the cleavage

[9] Phipps and Mason, *Ill. Acad. of Science,* **18,** 304 (1925).

error in the weight of the anode and cathode crystals, the plate next to the cathode was first split off and the remaining block of crystals again weighed. The change in weight due to transference should have occurred in this first plate. The next plate in order was then split off and the remainder weighed. This was continued until all the plates had been separated. The group of plates which included the plate next to the anode cup and which changed weight the least is shown in Table I as "middle section." In some experiments this middle section showed a change in weight and in such cases it was assumed that the change was entirely due to faulty cleavage between the middle section block and the cathode plate. Accordingly, such change was included in the change in weight of the cathode plate. However, part or all of this change of weight might have arisen from faulty cleavage between the anode cup and the middle section. The change in the transference number which would result if the change in weight of the middle portion were ascribed entirely to faulty cleavage between the anode cup and the middle section is shown in parentheses after each transference number in Table I.

The alcohol washings from the anode and cathode portions were analyzed separately and the weights of these portions were corrected for the salt which had dissolved. This correction was not apportioned among the plates in finding the change in the middle section because it was suspected that most of the salt in the alcohol washings came from the plate next to the cathode as a result of the rather violent reaction between the layer of sodium and the alcohol at this surface. In fact the alcohol washings from the cathode crystal and the nickel cathode nearly always showed small chips of undissolved salt at the bottom in amount considerably exceeding the solubility of the salt in absolute alcohol. These chips undoubtedly came from the cathode–cathode crystal interface and comprised by far the greater part of the sodium chloride in the washings. This will explain the very large correction of the cathode crystals for weight lost in washings, which in an extreme case (No. 14, Table I) amounted to 5 mg. That the middle plates contributed practically nothing to the alcohol washings was proved by the fact that in nearly every run at least one plate in the middle section was found after the washing to check to a tenth of a milligram with its original weight. The error in imputing the solubility losses of the middle plates to the cathode plate affects the transference numbers indirectly if at all by affecting the magnitude of the possible cleavage errors (the values in parentheses, Table I). The weight of the cathode portion was further corrected for the salt which stuck to the nickel cathode. The nickel frame and the inside of the quartz tube were also washed and the salt found was added to the weight of the cup and cover. This was justified by the fact that the exposed area of the anode cup and cover was about ten times that of the cathode portion so that the error caused by attributing all of this salt to evaporation from the anode is less than the uncertainty due to cleavage. At the highest temperature, 655°, the error in the transference number which might have resulted from this approximation was 0.01 unit.

Results

The pole reactions may be written

$$\mathrm{Na} \longrightarrow \mathrm{Na}^+ + \ominus \text{ anode}$$
$$\mathrm{Na}^+ + \ominus \longrightarrow \mathrm{Na} \text{ cathode}$$

On the passage of C equivalents of current through the cell there is a net loss of C $(1 - t_+)$ equivalents of sodium and C t_- equivalents of chlorine, that is to say, C t_- equivalents of sodium chloride from the cathode portion.

TABLE IA

DATA FROM TRANSFERENCE EXPERIMENTS IN DETAIL

Expt.	Sample No.	Temp., °C.	Voltage	Time, hours	Weight of crystals, g.					
					(1) Cathode Before	(1) Cathode After	(2) "Middle" Before	(2) "Middle" After	(3) Anode Before	(3) Anode After
14	1	580	110	15	1.7851	1.7746	0.7944	0.7941	3.4706	3.4728
24	3	580	110	19	1.4741	1.4642	.2850	.2855	....	....
25	3	580	110	20	1.8727	1.8576	.8719	.8713	4.1312	4.1379
26	2	510	310	46	1.6539	1.6506	.7192	.7197	....	....
29	2	490	220	59	0.6231	0.6306	.3292	.3298	....	....
33	[a]	490	220	38	.2764	.2746	.0934	.0934	....	....
34	2	410	220	161	.1879	.1873	.0800	.0801	....	....
36	3	655	70	10	.5772	.5690	.1107	.1100	6.6489	6.6453
38	3	558	220	46	.3163	.3068	.0684	.0684	....	....
39	3	655	70	16	.5174	.5100	.0669	.0664	....	....

[a] Artificial plates.

TABLE IB

DATA FROM TRANSFERENCE EXPERIMENTS IN DETAIL

Expt.	Curr. approx. M.A.	Equivs. of curr.	NaCl in washings, g. (4) Cathode portion	NaCl in washings, g. (5) Anode portion	(6) Frame and tube	Loss by cathode portion[a]	Gain by anode portion[b]	t_- from cathode[c]	t_- from anode[d]
14	0.75	0.000233	0.0055	0.0024[d]	...	0.0049	0.0046	0.36(−0.02)	0.34(+0.02)
24	.75	.000421	.0020	...	...	.0079	...	.32(+.02)	....
25	.75	.000554	.0026	.0037	0.0036	.0125	.0140	.38(−.02)	.43(+.02)
26	.1	.000386	.0027	...	...	.0005	...	.03(+.02)	....
29	.1	.000115	.0023	...	...	.0002	...	.03(+.09)	....
33	.1	.00054	.0020	...	...	−.0002	...	−.06(.00)	....
34	.1	.000137	.0007	...	...	.0	...	.00(+.01)	....
36	1.2	.000476	.0003	.0055	.0055	.0079	.0074	.28(−.025)	.27(+.025)
38	.5	.000375	.0001	..	...	.0094	...	.43(.0)	....
39	1.0	.000407	.0007	...	...	.0067	...	.28(−.02)	....

[a] (Loss in 1) − (4).

[b] (Gain in 3) + (5) + (6).

[c] Figures in parentheses are corrections which would result in t_- if changes in weight of middle section were calculated as due to sticking of the cup to the middle section rather than as a change due to transference.

[d] + Frame and tube.

An equal gain should be observed at the anode. To obtain the value of the transference number, the net loss in weight of the cathode portion or the net gain of the anode portion is reduced to equivalents and divided by the total number of equivalents of current passed.

The results of ten out of thirty-nine runs are given in detail in Table I and summarized in Table II. The missing runs suffered mishaps chiefly from the following causes: (1) poor temperature control, (2) leaks or breaks in the vacuum line causing oxidation of the sodium and serious contamination of the crystals, (3) failure of the sodium to run out of the capsule into the anode cup in sufficient quantity, (4) complete evaporation of the sodium from the cup, (5) faulty cleavage after the runs, (6) failure to take complete data (thus in the earlier runs the loss of sodium chloride in the alcohol washings was not determined), (7) cracking of the crystals on heating up the apparatus at the beginning of the run, (8) the use of too high a potential across the cell, causing arcing.

TABLE II

SUMMARY OF TRANSFERENCE NUMBERS

Temp., °C.	No.	Transference number of chloride ion From anode	From cathode	Average
410	34	...	0.00	0.00
490	29	...	.03	−.01
	33	...	−.06[a]	
510	26	...	.03	.03
558	38	...	.43	.43
580	14	0.34	.36	.36
	24	...	.32	
	25	.43	.38	
655	36	.27	.28	.28
	39	...	.28	

[a] In this case the negative value is probably due to the fact that small errors in manipulation and weighing were of great importance on account of the small amount of current transferred.

Best results were obtained from the cathode portions. In three cases satisfactory checks were obtained from analysis of both anode and cathode portions. The complete removal of the sodium from the anode cup was difficult, and even with the best vacuum conditions and the purest argon the anode cover showed a small amount of black contamination, presumably from the interaction of oxidized sodium with the nickel. This made it impossible in most cases to get a satisfactory determination of transference numbers from the weight of the anode cup.

Material from four sources was used. Sample 1, which was the same material used by Phipps, Lansing and Cooke in the determination of the conductance curves, was natural halite from Navarre, Michigan. Sample 2 was a second specimen from Navarre, Michigan. Sample 3 came from Heilbronn, Germany. In run No. 33 (Table I) the anode cup was made from Sample 3, while the plates were grown from a melt. The material of the melt was Mallinckrodt's "Reagent Quality" sodium chloride, thrice recrystallized from conductivity water. It is apparent from the data that the source of the sodium chloride had no appreciable effect upon the transference numbers.

Discussion

From a consideration of all the sources of error it is concluded that the transference numbers summarized in the last column of Table II are accurate to ±0.05 unit. At 580°, where the greatest number of determinations was made, the mean value of five determinations is 0.36 for the chloride ion. It appears certain that there is a change in the mechanism of electrolytic conduction through the salt very near to the temperature at which the extrapolated slopes of the conductivity curve shown in Fig. 1 intersect.

The decrease in the value of t_- with increasing temperature in the upper range was unexpected. It might have been due to leakage of the current through the sodium vapor at the high temperature, which increased with the temperature. Saha and Sur[10] have stated that the specific resistance of sodium vapor at 900° is about 13,000 ohms. At 600° calculation shows that conduction through the vapor would be insignificant compared with conduction through the salt. It seems more probable that the direct current produces a polarization of the crystal, which reacts upon the mechanism of conduction so as to affect unequally the mobilities of the two ions of the lattice. It is perhaps predictable from the behavior of the transference numbers that with very small currents passing for long periods of time the transference number of the chloride ion would approach 0.50. If this is correct, the absolute values of the transference numbers given in Table II have little significance except as an indication of the degree of polarization of the crystal under the stated conditions. From the point of view of the lattice theory the significant fact appears to be that at sufficiently high temperatures both ions of the sodium chloride lattice acquire the freedom which only the sodium ion possessed at lower temperatures. Similarity between the conductance curves (log k *vs.* $1/T$) of the chlorides, bromides and iodides of sodium and potassium indicates that this phenomenon is general among uni-univalent polar salts. The fluorides may prove exceptional.

Summary

Transference experiments were performed on sodium chloride at temperatures varying from 410 to 655°, using a reversible sodium anode and a nickel cathode.

The fraction of the current carried by the chloride ion is practically zero between 410 and 510°. Between 558 and 655° chloride ion carries a

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[10] Saha and Sur, *Quart. J. Indian Chem. Soc.*, **1**, 10 (1924).

considerable part of the current. It is significant that the temperature region in which the change from uni-ionic to bi-ionic conduction occurs is the same as the temperature region in which the slope of the conductance curve (log k *vs.* $1/T$) doubles its value.

In the temperature range 558 to 655° the fraction carried by the chloride ion appears to decrease with increasing temperature. This is thought to be a polarization effect.

[CONTRIBUTION FROM THE MISSOURI SCHOOL OF MINES AND METALLURGY]

THE SOLUBILITY OF ALUMINUM BROMIDE IN CARBON DISULFIDE

BY H. H. KAVELER AND C. J. MONROE

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Carbon disulfide as a solvent of inorganic salts was first studied by Arctowski,[1] who found the mercury halides slightly soluble, but the common inorganic salts insoluble. Kohler[2] found that aluminum bromide and iodide are rather soluble. Qualitative data of various investigators on the solubilities of various salts in this solvent have been compiled by Walden.[3]

As aluminum bromide dissolves in carbon disulfide to the extent that various inorganic salts dissolve in water, quantitative determinations of its solubilities at various temperatures were made.

Preparation of the Reagents

The carbon disulfide was purified by the method of Sidot,[4] with modifications of Arctowski, as follows. Commercial carbon disulfide was shaken with mercury until the surface of the metal was no longer tarnished and was then distilled from anhydrous calcium chloride. It was kept in contact with phosphorus pentoxide until ready for use, when it was decanted into a dry flask containing a little paraffin, from which it was distilled out of contact with air. The product, which had a sweet, pleasant odor, was used immediately.

Aluminum bromide was prepared from the purest commercial aluminum and c. p. bromine purified by distilling from chromic acid and from potassium hydroxide and potassium bromide.

As the extreme solubility of the salt made it desirable to prepare as much as 700 g. at one time, a somewhat different apparatus than that of Kohler, Richards,[5] and others was used, as shown in Fig. 1.

A combustion tube (c), of 12 mm. diameter and 1 meter length, resting in an electric furnace (E), was fused onto a train of three 750cc. distilling flasks. It was charged

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[1] Arctowski, *Z. anorg. Chem.*, **6**, 267, 404 (1894).

[2] Kohler, THIS JOURNAL, **22**, 387 (1900).

[3] Walden, "Electrochemie Nichtwassrigen Lösungen," **1924**, p. 480–481.

[4] Sidot, *Compt. rend.*, **69**, 1303 (1869).

[5] Richards, THIS JOURNAL, **42**, 2222 (1920).