

As to the amount of nitrogen dioxide necessary for the catalysis, it seems probable that a very minute amount is all that is necessary, since Daniels and Johnston in their experiments on thermal decomposition found no evidence that the rate of decomposition increased as the concentration of nitrogen dioxide increased. It should be noted in this connection that the method of removing nitrogen dioxide by the introduction of ozone represents a far more complete removal than the method used by Daniels and Johnston of pumping off the decomposition products from the solid nitrogen pentoxide used in their experiments.

### Summary

Pure nitrogen pentoxide in the presence of excess ozone appears to have a much slower rate of thermal decomposition than nitrogen pentoxide which is already partly decomposed. The decomposition is thus apparently autocatalytic.

Small traces of the decomposition products, however, seem to be all that is necessary to secure a constant specific rate of decomposition.

The authors wish to express their acknowledgment to Dr. Richard C. Tolman, former Director of the Laboratory, for advice and suggestions.

WASHINGTON, D. C.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 19]

## THE CRYSTAL STRUCTURES OF POTASSIUM CHLOROPLATINITE AND OF POTASSIUM AND AMMONIUM CHLOROPALLADITES

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### Introduction

An X-ray examination of the tetragonal crystals of potassium chloroplatinite,  $K_2PtCl_4$ , potassium chloropalladite,  $K_2PdCl_4$ , and ammonium chloropalladite,  $(NH_4)_2PdCl_4$ , has been carried out with the object of comparing the structure of these crystals with those of the cubic crystals of the corresponding salts with 6 halogen atoms. The structure of ammonium chloroplatinate has been found by Wyckoff and Posnjak<sup>2</sup> to be such that it may be regarded as containing chloroplatinate groups in which each platinum atom is surrounded by 6 equidistant and equivalent chlorine atoms at the vertices of an octahedron. It would probably be anticipated that in the chloroplatinites, 4 chlorine atoms would be grouped about each platinum atom; but the form and dimensions of this group as well as its situation in the structure could scarcely be predicted with safety.

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<sup>2</sup> Wyckoff and Posnjak, *THIS JOURNAL*, **43**, 2292 (1921).

### Materials and Method of Experimentation

Crystals of the salts were obtained by slow evaporation of their aqueous solutions at room temperature.

Crystallographic data for potassium chloroplatinite and palladite are available.<sup>3</sup> These are as follows:  $K_2PtCl_4$ ,  $a:c = 1:0.4161$ , density 3.291 – 3.306;  $K_2PdCl_4$ ,  $a:c = 1:0.4098$ . The observed forms are given as  $\{110\}$ ,  $\{001\}$ , and  $\{111\}$  in each case. The face development indicates at least tetragonal bipyramidal symmetry. In view of this fact and the additional one that no evidence of dissymmetry was observed in the Laue photographs (See Fig. 1), the symmetry of the atomic arrangement in these two salts has been assumed to be holohedral.

The crystals of ammonium chloropalladite were similar in appearance to those of the potassium salt and showed a similar strong pleochroism.

The X-ray data were obtained from spectral photographs and unsymmetrical Laue photographs as previously described.<sup>4</sup> The spectral reflections from potassium chloroplatinite were made using large, slightly ground faces. Of the other two salts only small thin plates parallel to (110) were available; hence some of the spectra were obtained by transmission of the incident X-ray beam directly through the crystal. Unsymmetrical Laue photographs were made using a peak voltage of about 54 kv.; for potassium chloroplatinite a crystal section parallel to (001) was used, and for the other two salts sections parallel to (110).

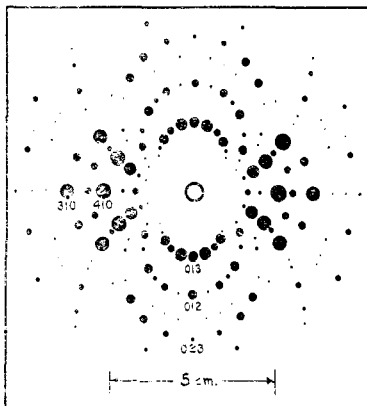


Fig. 1.—Diagram of Laue photograph obtained with  $K_2PdCl_4$ . Incident beam nearly perpendicular to (110) (original axes), or (100) (new axes). Distance from crystal to plate, 5 cm.

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### Derivation of the Structure

In the second column of Table I are given the angles of reflections found for the rhodium line,  $K\alpha_1$  (wave length,  $\lambda$ , 0.6121 Å.). Application of the equation,  $n\lambda = 2d \sin \theta$ , shows that  $d_{001}$  is 4.13 Å. or an integral multiple of this value, and  $d_{110}$ , 6.99 Å. or a multiple of this. Measurements for the line  $K\beta$  gave results concordant with these. From the density of potassium chloroplatinite and the weight of a single molecule, the number of molecules in a tetragonal unit of structure of the dimensions  $6.99 \times 6.99 \times 4.13$  Å. is readily calculated to be 0.97. This unit corresponds to a rotation of the original axes through  $45^\circ$  about the tetragonal axis,

<sup>3</sup> Groth, "Chemische Kristallographie," Engelmann, Leipzig, 1906, vol. 1, p. 351.

<sup>4</sup> Dickinson, THIS JOURNAL, 44, 276 (1922).

so that the original forms  $\{110\}$ ,  $\{001\}$  and  $\{111\}$  become  $\{100\}$ ,  $\{001\}$  and  $\{101\}$ , respectively. The spots occurring on the various Laue photographs were assigned indices referred to these axes (as in Fig. 1), and values of  $n\lambda$  were calculated for them on this basis; all classes of planes were

TABLE I  
REFLECTION DATA FOR POTASSIUM CHLOROPLATINITE

$hkl$	Observed angle of reflection	$\frac{d_{hkl}}{n}$	Intensity
(001)	4° 15'	$1 \times 4.13$	strong
	8 32	$\frac{1}{2} \times 4.13$	strong
	12 51	$\frac{1}{3} \times 4.13$	medium
	17 15	$\frac{1}{4} \times 4.13$	medium
(110)	2° 33'	$(1 \times 6.88)$	strong
(original axes)	5 2	$\frac{1}{2} \times 6.98$	medium
(100)	7 33	$\frac{1}{3} \times 6.99$	medium
(new axes)	10 5	$\frac{1}{4} \times 6.99$	strong
	12 38	$\frac{1}{5} \times 7.00$	medium

found with values of  $n\lambda$  well below 0.48 and none below 0.24. The lower limit of the spectrum corresponding to the peak voltage is about 0.23 Å.; the unit containing one molecule is therefore possible. *All of the tetragonal crystallographic indices used in the remainder of this paper refer to the axes of this unit.*

The dimensions of the unit in the other two salts were determined by similar measurements. For potassium chloropalladite,  $d_{100} = 7.04$ ,  $d_{001} = 4.10$ , calculated density = 2.66, observed density = 2.67. For ammonium chloropalladite,  $d_{100} = 7.21$ ,  $d_{001} = 4.26$ , calculated density = 2.12, observed density = 2.17. The second order from (001) was about as strong as the first order with the potassium salt but weaker than the first with the ammonium salt; the third order was weaker than either in both cases. From (100) both showed a strong fourth order as compared with the third and second.

The location of the atoms within the unit may now be considered. The only holohedral space-group<sup>5</sup> providing position for the single platinum or palladium atom is  $D_{4h}^1$ . This space-group gives, however, a considerable variety of ways of arranging the other atoms; for instance, on the assumption that all of the chlorine atoms occupy equivalent positions as well as the potassium atoms, 28 distinct arrangements are possible. A discussion of all the possible arrangements will not be entered into here. Consideration of the X-ray data eliminates all these arrangements except the following one: K or N at  $(0\frac{1}{2}\frac{1}{2})$   $(\frac{1}{2}0\frac{1}{2})$ ; Pt or Pd at (000); Cl at  $(uu0)$   $(\bar{u}u0)$   $(u\bar{u}0)$   $(\bar{u}\bar{u}0)$ .

In a manner similar to that employed with potassium chlorostannate,<sup>4</sup>

<sup>5</sup> Niggli, "Geometrische Krystallographie des Diskontinuums," Gebrüder Borntraeger, Leipzig, 1919, p. 408.

it can be shown that the strength of the fourth-order reflection from (100) as compared with that of the third and second, necessitates giving  $u$  a value near  $1/4$ . Data from the Laue photographs make possible a more precise determination of the value of  $u$  as well as a thorough testing of the structure. As usual, the following principle has been employed in considering the X-ray data; when, under comparable conditions of wave length, a plane is observed to reflect more strongly than a second plane with the same or a larger interplanar distance, the value of  $\sqrt{A^2 + B^2}$  must be larger for the first plane than for the second. For the present structure  $B = 0$ , and when  $n = 1$ ,  $A$  is given by the expression:

$$A = 2a\bar{K} + \bar{P}t + 2\bar{C}l [\cos 2\pi (h + k) u + \cos 2\pi (h - k) u]$$

The coefficient  $a$  has the following values: Class 1:  $h$ ,  $k$ , and  $l$  all odd;  $a = 1$ . Class 2:  $h$  and  $k$  one odd and one even,  $l$  odd or even;  $a = 0$ . Class 3:  $h$  and  $k$  odd,  $l$  even, or  $h$  and  $k$  even,  $l$  odd;  $a = -1$ .

It is evident from the expression for  $A$  that no abnormal intensity relations should occur among planes of the same class having the same value of  $h$  and  $k$ . The unsymmetrical photographs, especially those through (100), gave opportunity to test this, and none were found.

The values of  $A$  for some planes of potassium chloroplatinite, calculated on the assumption of proportionality of reflecting power to atomic number,<sup>6</sup> are shown plotted against values of  $u$  in the neighborhood of  $1/4$  in Fig. 2.

By reference to these curves, the following intensity relations may be seen to place the value of  $u$  close to 0.235:  $\{541\} > \{521\}$ ,  $u < 0.250$ ;  $\{10.2.1\} >> \{932\}$ ,  $u > 0.215$ ;  $\{812\} > \{831\}$ ,  $u > 0.220$ ;  $\{10.2.1\} >> \{10.0.1\}$ ,  $u > 0.225$ ;  $\{10.2.1\} \geq \{10.1.1\}$ ,  $u \geq 0.233$ ;  $\{721\} \geq \{711\}$ ,  $u \leq 0.238$ . From similar considerations the value of  $u$  in the palladium salts has been taken as 0.23.

The chief test of this structure is its ability to account for the large number of abnormal intensity relations to be found on the Laue photo-

<sup>6</sup> Because of the great incompleteness of our present knowledge of the reflecting powers, the question as to whether they should be more properly taken proportional to the probable number of non-nuclear electrons associated with the atom need hardly arise; an examination of the calculation of  $A$  for values of  $u$  slightly below  $1/4$  shows that for the purposes of the present paper the reflecting powers need, in most cases, be only roughly correct.

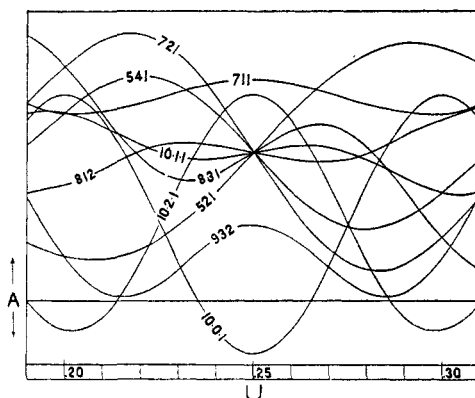


Fig. 2.—Values of  $A$  plotted against  $u$  for some planes of  $K_2PtCl_6$ .

graphs. Data furnishing a number of typical examples are given in Tables II and III. In this tabulation no effort has been made to eliminate

TABLE II  
LAUE PHOTOGRAPHIC DATA FROM POTASSIUM CHLOROPLATINITE  
Incident beam  $7^\circ$  from perpendicular to (001)

Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$ $u=0.235$	Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$ $u=0.235$
$\bar{3}\bar{5}1$	1.15	0.36	6	107	$\bar{6}41$	0.95	0.47	0.1	13
$0\bar{6}1$	1.12	0.35	0.3	17	$7\bar{2}1$	0.94	0.45	2.6	119
$1\bar{6}1$	1.11	0.36	3	73	811	0.85	0.46	0.6	83
$2\bar{6}1$	1.07	0.35	4	96	821	0.83	0.46	0.1	9
$\bar{7}01$	0.97	0.36	0.8	36	$\bar{5}\bar{6}2$	0.82	0.46	0.3	52
$5\bar{5}1$	0.96	0.36	3	130	831	0.80	0.45	0.4	64
$7\bar{3}1$	0.90	0.37	2.6	128	$1\bar{8}2$	0.80	0.45	0.6	83
$\bar{7}41$	0.85	0.37	0.4	39	$\bar{7}42$	0.80	0.47	0.2	39
$8\bar{2}1$	0.83	0.37	0.2	9	091	0.76	0.46	1.0	129
901	0.76	0.36	1.2	129	191	0.76	0.46	0.6	121
$\bar{5}81$	0.73	0.36	0.5	101	$\bar{5}72$	0.76	0.46	0.1	21
$0\bar{9}2$	0.73	0.35	0.6	129	$\bar{9}12$	0.72	0.45	0.2	45
$1\bar{9}2$	0.72	0.36	0.3	45					
$2\bar{9}2$	0.71	0.35	0.1	28					
941	0.70	0.36	0.6	126					
$\bar{9}\bar{3}2$	0.70	0.35	0.1	26					
$\bar{2}.10.1$	0.68	0.36	0.3	79					
951	0.68	0.35	0.4	139					

TABLE III  
LAUE PHOTOGRAPHIC DATA FROM POTASSIUM CHLOROPALLADITE  
Incident beam  $8^\circ$  from perpendicular to (100)

Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$ $u=0.230$	Plane	Spacing	$n\lambda$	Estimated intensity	$\sqrt{A^2 + B^2}$ $u=0.230$
$\bar{3}02$	1.55	0.38	0.8	21	$21\bar{2}$	1.72	0.47	4	38
213	1.25	0.39	1.6	38	$\bar{1}1\bar{3}$	1.31	0.46	6	85
$52\bar{2}$	1.10	0.39	0.1	7	$\bar{3}1\bar{3}$	1.17	0.47	3	81
621	1.08	0.39	1.6	56	522	1.10	0.47	0.1	7
$\bar{1}14$	1.00	0.39	faint	9	730	0.93	0.47	0.5	27
523	0.95	0.39	0.1	7	731	0.90	0.46	1.6	103
$\bar{4}14$	0.88	0.39	0.4	54	$\bar{6}13$	0.88	0.45	0.25	40
$\bar{7}13$	0.80	0.40	0.4	77	$\bar{8}10$	0.87	0.46	0.6	51
125	0.79	0.38	0.1	38	$\bar{8}11$	0.85	0.45	0.4	51
$\bar{9}10$	0.78	0.39	faint	45	$03\bar{5}$	0.77	0.45	faint	21
$\bar{9}11$	0.76	0.39	0.4	92	$\bar{1}3\bar{5}$	0.77	0.47	0.4	81
$23\bar{5}$	0.75	0.38	0.2	70	$84\bar{1}$	0.77	0.46	0.2	40
940	0.72	0.39	0.4	100	$54\bar{4}$	0.75	0.47	0.2	81
$\bar{7}2\bar{4}$	0.70	0.38	0.15	97	$\bar{3}3\bar{5}$	0.74	0.47	0.25	93
$\bar{9}2\bar{3}$	0.67	0.39	0.0	14	$\bar{7}24$	0.70	0.45	0.1	97
$\bar{1}1.2.0$	0.63	0.40	0.1	109	$\bar{1}0.2.1$	0.68	0.45	faint	28
$\bar{1}1.2.1$	0.62	0.39	0.1	109					

comparisons for which the calculations require a fairly accurate knowledge of the relative reflecting powers of the atoms. The agreement is, however,

good except in some cases involving planes of Class 3 having neither  $h + k$  nor  $h - k$  divisible by 4. For instance, with potassium chloroplatinite (0.10.1) certainly reflected although it has a comparatively small spacing and is calculated  $\sqrt{A^2 + B^2}$  is nearly zero; and with potassium chloropalladite, (025) with almost as great a spacing as ( $\bar{8}$ 12) reflected considerably less strongly than the latter plane, although the calculated values of  $\sqrt{A^2 + B^2}$  are 58 and 51 respectively. Agreement in these cases would be obtained without disturbing any others that were observed, by assuming that the platinum or palladium atoms reflect more strongly relative to the other atoms than in proportion to the atomic numbers. In view of the fact that the same structure accounts for the general character of the great majority of the different data afforded by the 3 salts, and that the few inconsistencies occur precisely in those cases where our ability to use the data is weakest, the confirmation of the structure is regarded as satisfactory. This structure is the simplest one which is capable of accounting for the X-ray data.

However, the space-group symmetry cannot be considered determined. For this same arrangement of atoms is compatible with the symmetry of other space-groups if a larger unit of structure containing more molecules is assumed, or if lower symmetry is assumed. Indeed a tetrahedral ammonium group, situated as indicated, cannot arise from  $D_{4h}^1$ ; so that this space-group probably does not represent the symmetry, at least of the ammonium salt.

### Discussion of the Structure

The structure arrived at above is shown in Fig. 3. In this diagram OA corresponds to the length  $d_{100}$  and OC to the length  $d_{001}$ . Each platinum or palladium atom is surrounded by 4 equidistant chlorine atoms lying on one plane, and nearer to this platinum or palladium atom than to any other. The distance from the platinum atom to a chlorine atom in potassium chloroplatinite is  $2.33 \pm 0.05 \text{ \AA}$ . In ammonium chloroplatinate this distance has been found<sup>7</sup> to be  $2.26 \text{ \AA}$ . The difference between these two is scarcely outside the error of the measurements.

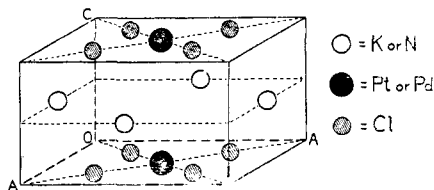


Fig. 3.—Arrangement of the atoms (except hydrogen) in  $K_2PtCl_4$ ,  $K_2PdCl_4$ , and  $(NH_4)_2PdCl_4$ .

The arrangement of the chloroplatinite groups in a basal plane is the same as the arrangement of chloroplatinate groups in a cube plane of potassium chloroplatinate (the latter being assumed to be like the analogous ammonium salt with which it is isomorphous). Moreover, the basal planes of chloroplatinite groups have potassium atoms arranged with re-

<sup>7</sup> Ref. 2, p. 2307.

spect to them in the same manner as the cube planes of chloroplatinate groups. But the manner of repetition of the platinum planes is not the same<sup>8</sup> in the two compounds. These relations are illustrated in Fig. 4,

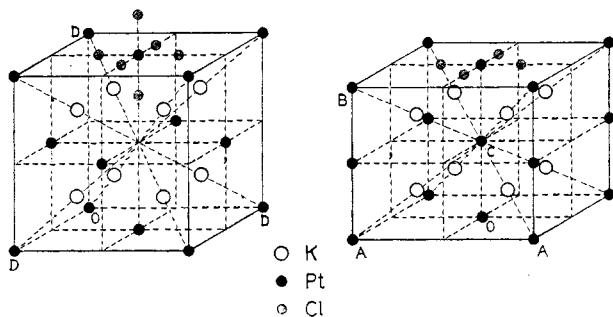
Fig. 4a.— $K_2PtCl_6$ .Fig. 4b.— $K_2PtCl_4$ .

Fig. 4.—Arrangement of the atoms in  $K_2PtCl_6$ , and in  $K_2PtCl_4$  drawn to the same scale. OA, CA, and OC are the tetragonal axes used in this paper. In each compound each platinum atom is surrounded by chlorine atoms in the same manner as the ones shown.

in which the cube representing the structure of potassium chloroplatinate has the edge  $d_{100}$ , and the parallelepiped representing the structure of potassium chloroplatinite has the dimensions  $d_{100}\sqrt{2} \times d_{100}\sqrt{2} \times 2d_{001}$ . The tetragonal structure is only slightly larger than the cubic one in its horizontal dimensions, but considerably shorter vertically. These facts which are also true for other pairs of salts, are shown<sup>9</sup> by Table V.

TABLE IV

COMPARATIVE DISTANCES IN THE CUBIC AND TETRAGONAL CRYSTALS				
Hexachlorides	$d_{100}$	Tetrachlorides	$d_{100}\sqrt{2}$	$2d_{001}$
	OD(Fig. 4a)		AA(Fig. 4b)	AB(Fig. 4b)
$K_2PtCl_6$	9.59	$K_2PtCl_4$	9.87	8.26
$(NH_4)_2PtCl_6$	9.84	....	...	...
$K_2PdCl_6$	9.82	$K_2PdCl_4$	9.96	8.20
$(NH_4)_2PdCl_6$	9.90	$(NH_4)_2PdCl_4$	10.20	8.52

### Summary

Tetragonal crystals of potassium chloroplatinite and potassium and ammonium chloropalladites have been investigated by X-ray methods using spectral photographs and symmetrical and unsymmetrical Laue photographs. The simplest structure which will account for the X-ray data has been described. In this structure each platinum or palladium

<sup>8</sup> If the two structures were alike in this respect also, complete absence would be expected of the reflections from (110) (original axes) given in Table I as occurring at  $2^\circ 33'$ ,  $7^\circ 33'$  and  $12^\circ 38'$ .

<sup>9</sup> As X-ray measurements of the cubic salts (except  $(NH_4)_2PtCl_6$ ) are not available, the values of  $d_{100}$  for these have been calculated from the densities given by Groth, Ref. 3, p. 488, on the safe assumption of isomorphism of these salts with  $(NH_4)_2PtCl_6$ .

atom is surrounded by 4 equidistant and equivalent chlorine atoms lying in 1 plane. The close relation of this structure to that of the cubic crystals of the corresponding hexachlorides is pointed out.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY, STATE UNIVERSITY OF IOWA]

## THE FREE ENERGY OF DILUTION OF ALCOHOLIC SOLUTIONS OF LITHIUM CHLORIDE AND THE EFFECT OF SOLVENT UPON THE ACTIVITY OF THE IONS

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While numerous electrometric investigations have been made of the activity and energy relations of electrolytes in aqueous solutions, almost no attempt has been made to apply this method to the study of non-aqueous solutions.

The present paper contains the results of a study of the electromotive forces of concentration cells, using lithium chloride in ethyl and methyl alcohol as solvents. The cells studied were of the types:  $\text{Ag} | \text{AgCl}, \text{LiCl} (c_1) | \text{Li.Hg}_x - \text{Li.Hg}_x | \text{Li.Cl} (c_2), \text{AgCl} | \text{Ag}$ ; and  $\text{Ag} | \text{AgCl}, \text{LiCl} (c_1) | \text{LiCl} (c_2), \text{AgCl} | \text{Ag}$ .

In addition to determining the electromotive forces of concentration cells using one alcohol as solvent we have also studied some cells of the type  $\text{Ag} | \text{AgCl}, \text{LiCl} (c_1) | \text{Li.Hg}_x - \text{Li.Hg}_x | \text{LiCl} (0.1 M), \text{AgCl} | \text{Ag}$ .  
(alcoholic) (aqueous)

In each case the alcoholic cell was opposed to a cell containing an exactly 0.10 *M* aqueous solution of the salt. This cell differs from that used by Jones<sup>1</sup> and by Kahlenberg<sup>2</sup> in that ion-transference and solvent diffusion are both eliminated. The electromotive forces of these cells give us the data for calculating the free-energy changes involved in the transfer of one mole of the solute from its solution in one pure solvent to its solution in a second solvent, provided, of course, that the simple reaction that we believe to be taking place in the cell is the only one possible.

### Materials and Apparatus

**Solvents.**—Ordinary 95% ethyl alcohol which had been allowed to stand over quicklime for several weeks and then over anhydrous copper sulfate was successively refluxed over and distilled from metallic calcium and pure dry silver nitrate. Only the middle fraction was collected and this was carefully protected from moisture. The methyl alcohol was purified in a similar way except that the treatment with lime was omitted.

**Lithium Chloride.**—A very pure sample of the salt was recrystallized 4 times from distilled water and 3 times from conductivity water. The hydrated crystals were trans-

<sup>1</sup> Jones, *Z. physik. Chem.*, **14**, 346 (1894); *Am. Chem. J.*, **23**, 397 (1900).

<sup>2</sup> Kahlenberg, *J. Phys. Chem.*, **3**, 379 (1899).