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IONIZATION IN MIXTURES

For the full investigations which involve the properties of solutions containing more than one electrolyte, it is necessary to compute the ionizations of the constituents of the mixture. The isohydric principle is usually employed as the basis for this calculation, and the others* have been suggested their reliability has not been thoroly investigated and they have not come into general use.

In the present state of development of the theory of solutions there is apparently no satisfactory theoretical basis upon which a method for the desired computations may be founded. The chief, if not the only, evidence in favor of the isohydric principle is the fact that the conductances thus calculated for solutions containing two or more electrolytes are in good agreement with the experimentally determined values. It is, therefore, important to investigate whether from other principles also, values may be calculated which agree with the experimental results.

The isohydric principle states that in a mixture the ionization, γ , of each salt is a function of the total ion-concentration. The character of this function is determined for each constituent in its pure solution. In order to calculate the ionization of each electrolyte, it is usual to plot values of γ against $\log c\gamma$, and by a series of approximations to find for each constituent a value of γ which satisfies the required conditions. Thus in the case of mixtures containing two salts with a common ion, the following relations must be satisfied:

* Bray and Hunt, Jour. Am. Chem. Soc. 33, 781.

$$c_1 \gamma_1 + c_2 \gamma_2 = \Sigma i$$

$$\gamma_1 = f_1(\Sigma i)$$

$$\gamma_2 = f_2(\Sigma i)$$

where c_1 and c_2 are the concentrations of the two constituent salts, γ_1 and γ_2 their respective ionizations, and Σi the total ion concentration.

The specific conductance, \bar{L} , is then given by the following relation:

$$1000 \bar{L} = c_1 \gamma_1 \Lambda_{o_1} + c_2 \gamma_2 \Lambda_{o_2}$$

where Λ_{o_1} and Λ_{o_2} are the equivalent conductances of the two salts at infinite dilution.

If, however, the ionization is assumed to be a function of the total salt concentration rather than the total ion concentration, the calculation of \bar{L} is much simpler, for then the following relation holds:

$$1000 \bar{L} = c_1 \Lambda_1 + c_2 \Lambda_2$$

Here Λ_1 and Λ_2 are the equivalent conductances of the separate constituent salts at a concentration Σc equal to $c_1 + c_2$.

TABLE I.

Constituents Mixed in Ratio 1:1		C gr.-equiv. per liter	1000 \bar{L} Calc. = $f(\sum i)$	1000 \bar{L} Calc. = $f(\sum c)$	$\Delta \bar{L}$ %	1000 \bar{L} obs.
KCl)) KBr)	(18°)	.2	21.822	21.822	.00	
KCl)) KIO ₃)	(18°) (25°) (25°)	.2 .1 .01	18.383 11.0614 2.4138	18.385 11.0617 2.4138	.01 .00 .00	11.060* 2.412*
NaCl)) NaIO ₃)	(18°)	.2	14.250	14.253	.02	
NaCl)) HCl)	(25°)	.2 .1 .02 +.01	48.21 11.45 2.721 2.650	48.17 11.45 2.720 2.650	0.1 0.0 0.03 0.00	47.25 ² 11.41 ^{2,3} 2.709 ² 2.632 ²
ZnSO ₄)) CuSO ₄)	(18°)	.1	4.4612	4.4628	.03	³
K ₂ SO ₄)) Na ₂ SO ₄)	(18°)	.1	8.5973	8.5976	.00	³
NaCl)) BaCl ₂)	(18°)	.1	9.1289	9.1359	.08	³
CdSO ₄)) MgSO ₄)	(18°)	.1	4.5402	4.5414	.03	

* Results from this laboratory.

² Bray and Hunt, Jour. Am. Chem. Soc. 33, 781.

³ The results of Archibald and McKay, Trans. N. S. Inst. Sci., 9, 317-333, show the observed and calculated values to agree within their experimental error, about 0.2%.

Table I shows the results of calculations made by each of the above methods. The salts represented in column one are present in equal equivalent concentrations, the total concentration appearing in column two. The next two columns show the conductances of the mixtures calculated on the two assumptions, $\gamma = f(\sum c)$ and $\gamma = f(\sum i)$. The probable error in computation by the graphic method is about 0.02%. Column five shows the percentage differences between the values given by the two methods. Where data for mixtures are available they are given in the last column.

The pairs of salts used as examples represent distinctly different combinations. Thus, since the ionizations of KCl and KBr are practically identical at corresponding concentrations, the two principles stated above must lead to identical ion concentrations in all mixtures of these salts. On the other hand, in the case of mixtures of KCl and KIO_3 , whose degrees of ionization are quite different for uni-univalent salts, the two sets of calculated ion concentrations differ by an appreciable amount, but on account of the fact that the salt with the more mobile ion is ionized to a greater degree the corresponding conductances differ to a slight extent only. In the case of HCl and NaCl the difference between the mobilities of the ions not common is exceptionally large. The remainder of the mixtures represent combinations of ions with different valences. In the last case the ionizations of the salts in their own pure solutions are exceptionally divergent for bi-bivalent salts.

In each instance, $\Delta \bar{L}$, the difference between the specific conductances calculated on the two principles, is within the limit of experimental error of the conductivity determinations.

In a mixture of two salts with no common ion the difference between the specific conductances calculated by the two methods is great enough to be detected. Some of the data of Sherrill* was examined and compared with the values of \bar{L} calculated (a) on the basis $\frac{(B^+)(A^-)}{(BA)} = f(\sum i)$ (isohydric) used by Sherrill, and (b) on the basis $\frac{(B^+)(A^-)}{(BA)} = f(\sum c)$, where (B^+) , (A^-) , and (BA) represent the concentrations of the cation, anion, and undissociated molecules, respectively. In the latter case the solution of the eight condition equations is somewhat simpler.

TABLE II.

Solution	Concentrations in Millequivalents per liter								Specific Conductance X 1000		
	K ⁺	Na ⁺	Cl	SO ₄	of the undissociated molecules				Calculated	Observed	Calculated uncorrected for viscosity.
				KCl	NaCl	K ₂ SO ₄	Na ₂ SO ₄				
No. 1											
$\gamma = f(\sum i)$	75.0	73.2	82.7	65.5	8.5	8.8	16.5	18.0	17.59		17.61
$\gamma = f(\sum c)$	74.9	72.7	83.7	63.8	8.0	8.3	17.1	19.0	17.52	17.52	17.55
No. 2.											
$\gamma = f(\sum i)$	31.8	125.4	131.5	25.7	5.5	23.0	2.6	11.6	17.58		17.59
$\gamma = f(\sum c)$	31.8	125.0	132.1	24.6	5.4	22.5	2.8	12.6	17.52	17.52	17.54
No. 3.											
$\gamma = f(\sum i)$	39.5	38.7	43.0	35.2	3.4	3.6	7.1	7.7	9.371		9.374
$\gamma = f(\sum c)$	39.4	38.5	43.3	34.6	3.2	3.4	7.3	8.0	9.340	9.346	9.346

Table II shows the results of calculations on these solutions.

Sherrill's data were corrected for viscosity in each case, the viscosity of

* Jour. Am. Chem. Soc. 32, 741.

the mixture being estimated from the viscosities of the constituent solutions. The last column, however, shows the specific conductances using ionization values uncorrected for viscosity. Solution No. 1 was made by mixing 0.2 N NaCl and 0.2 N K_2SO_4 in the ratio 1:1, No. 2 by mixing the same solutions in the ratio 4:1, and No. 3 by mixing 0.1 N solutions of each in the ratio 1:1. It will be noted that the concentrations of the various constituents are found by the two methods to be appreciably different and that these differences cancel each other in such a way that the specific conductances are very nearly the same.

In all cases investigated calculations of the specific conductance based on $\gamma=f(\sum c)$ give results differing from those based on the isohydric principle by a very small amount. In the case of mixtures of two electrolytes with a common ion the differences are well within the experimental error. With mixtures involving no common ion the differences are still small, and the conductances calculated on the basis of the principle that the total salt concentration determines the ionizations are in closer agreement with the observed data than are the values calculated by the aid of the isohydric principle. For this reason and also because it is much less laborious it seems desirable to use in the case of strong electrolytes the principle that ionization in mixtures depends upon the total salt concentration.

To further test these two principles mixtures containing a transition electrolyte, one ionized about 15% in 0.1 N solution, were prepared and their conductivities measured. Chloracetic acid was selected as of suitable strength, and its sodium salt used as the other component of the mixtures.

Commercially prepared chloracetic acid was redistilled until the distillate gave no test for chlorid ion. A standard NaOH solution was prepared from the pure metal, care being taken to exclude carbon dioxide from the air. The final solution gave no test for carbonate ions with calcium hydroxid. The NaOH was standardized against standard hydrochloric acid, and the chloracetic acid against the NaOH, using phenolphthalein as the indicator. In preparing the mixtures, equivalent quantities of each solution were mixed and diluted to the desired volume. The specific conductances measured at 25° are given in Table III. HA represents chloracetic acid and NaA its sodium salt.

TABLE III.

SA	Normality .	1000 \bar{L}
HA	0.05	3.177
HA	0.01	1.237
NaA	0.05	3.781
HA	0.01	0.827
HA)	0.025	2.570
NaA)	0.025	
HA)	0.005	0.813
NaA)	0.005	

The value for HA in .05 N solution is somewhat higher than that determined by Ostwald*. Both values for NaA lie close to the data of

* Kohlrausch and Holborn, *Leitvermögen der Electrolyte*.

Ostwald and Bredig*. The values used for the conductivities at infinite dilution are those of Ostwald ² and Bredig ³, the units they give being corrected to reciprocal ohms. They are $\Lambda_{0,HA} = 386$ and $\Lambda_{0,NaA} = 92.2$.

The ionization of each constituent in the mixture was calculated on three assumptions: (1) the ionization of each constituent is controlled by the total ion concentration (isohydric principle), or, $\gamma = f(\sum i)$; (2) the ionization of each component is controlled by the total salt concentration, or, $\gamma = f(\sum c)$; (3) the ionization of the strong electrolyte NaA is controlled by the total salt concentration and that of the weaker electrolyte by the total ion concentration, or, $\gamma_{NaA} = f(\sum c)$, $\gamma_{HA} = f(\sum i)$. The third assumption seems at first sight to be the most reasonable, since it has been shown that for strong electrolytes the principle $\gamma = f(\sum c)$ gives good results, while for weak electrolytes the isohydric principle would be expected to hold. The specific conductivities calculated upon the basis of these assumptions are compared with each other and with the observed values in Table IV.

TABLE IV.

Specific Conductance x 1000 of Mixtures of Chloracetic Acid and Sodium Chloracetate at 25°.

Mixture	Calculated Values			Observed Value
	1. Total Salt.	2. Total Ion.	3. Total salt and Total Ion.	
0.025 N HA + 0.025 N NaA	3.48	2.68	2.63	2.57
0.005 N HA + 0.005 N NaA	1.032	0.846	0.842	0.813

* Kohlrausch and Holborn, *Lutvermogen der Elektrolyte*.

² *Zeit. Phys. Chem.* 3, 176

³ *Zeit. Phys. Chem.* 13, 218

Evidently, none of the principles stated above is in complete agreement with the data: the calculated conductivity is in each case too great. However, the principle that the total salt rather than the total ion concentration controls the ionization of strong electrolytes gives values more nearly in agreement with the observed data.

This result together with that of the comparison of the application of the two methods to mixtures containing only strong electrolytes and with the fact that the application of the method is very simple, makes it desirable to further test the principle that in mixtures the total salt concentration controls the ionization of the strong electrolytes. Meantime it would seem advantageous to accept the above principle provisionally and to employ it, rather than the isohydric principle, in calculating ionization values in mixtures.

ACTIVITIES OF IONS FROM THE SOLUBILITY OF SALTS IN SOLUTIONS OF
ONE ANOTHER.

It is well known that activity data may be obtained from the solubilities of salts in solutions of other salts. For example with a uni-univalent salt such as $TlCl$ the activity of the unionized $TlCl$ is constant because it is in equilibrium with the solid phase. Hence the product of the activities of the ions,

$a_{Tl^+} \times a_{Cl^-}$, = a constant, because the relation $\frac{a_{Tl^+} \times a_{Cl^-}}{a_{TlCl}} = \text{a constant}$ necessarily holds.

Expressing the concentration of the salt, c , in equivalents per liter, and putting the activity coefficient, $\alpha = \frac{a}{c}$, we may write

$$\frac{c_A}{A} \cdot \alpha_A \cdot \frac{c_B}{B} \cdot \alpha_B = \text{a constant,}$$

or

$$\frac{\alpha_A^A \cdot \alpha_B^B}{\alpha_{0A}^A \cdot \alpha_{0B}^B} = \frac{C_{0A}^A \cdot C_{0B}^B}{C_A^A \cdot C_B^B} = \frac{S^2}{C_A^A \cdot C_B^B},$$

where the subscript zero refers to the solution in pure water and S is the solubility of the salt.

For a salt of the type $A_m B_n$, the expression will evidently be

$$\frac{\alpha_A^m \cdot \alpha_B^n}{\alpha_{0A}^m \cdot \alpha_{0B}^n} = \frac{C_{0A}^m \cdot C_{0B}^n}{C_A^m \cdot C_B^n} = \frac{S^{m+n}}{C_A^m \cdot C_B^n}$$

Thus from solubility experiments we can determine how the product of the activity-coefficients of the ions, each coefficient raised to the appropriate power, varies with the concentration of the added salt, or with the total concentration of the solution.

There is a large quantity of data available for this purpose. The most complete for a uni-univalent salt is for $TlCl$; but even here the added salts are not such that the effect of the two added ions can be differentiated. If we know, for example, the

effect upon the solubility of a salt of the added salts: KCl, KNO₃, K₂SO₄, NaCl, NaNO₃, Na₂SO₄, BaCl₂, Ba(NO₃)₂, we can separate the effect of the K ion and Na ion by comparing the effects of their chlorides; or by comparing the effects of their nitrates, or sulfates; and similarly for K and Ba, and for Cl and NO₃, and so on.

Such a series of solubilities were determined for KClO₄, with the above named added salts.

Solubilities were determined at 25° C, using the general method of Noyes and Boggs¹, except that normalities were referred to 1000 grams of water. KClO₄ was recrystallized until no test for Cl⁻ or ClO₃⁻ was obtainable, one recrystallization being usually sufficient. Other salts were carefully recrystallized once, and in salts other than chlorides no chlorid ion could be detected. The strengths of the salt solutions were determined by evaporating a weighed portion on a steam bath and drying to constant weight at 200° C. After being filtered in the thermostat the total salt in the saturated solutions was determined in the same manner. Knowing the amount of salt associated with a given amount of water in the salt solutions the amount of KClO₄ was determined by difference. The results are given in Table I.

The ratio $\frac{\alpha_{K^+} \cdot \alpha_{ClO_4^-}}{\alpha_{K^+} \cdot \alpha_{ClO_4^-}}$ was calculated from these data and plotted against the logarithm of the total equivalent concentration of the solution. The results are shown in Figure I.

It will be seen that there is a specific effect for each ion. For example, K - ion has a greater effect in reducing the activity coefficient product of K - and ClO₄ - ions than has Na - ion, and Na - ion has greater effect in reducing the activity coefficient product than has ^{Ba}NO₃ - ion, and NO₃ - ion more than Cl - ion. This is illustrated in Table II for the total concentration 0.5 normal.

Similar plots were made for such other difficultly soluble salts as TlCl, Ag₂SO₄, PbCl₂, CaSO₄, Ba(BrO₃)₂, Ba(IO₃)₂, Pb(IO₃)₂, and Tl₂SO₄.

¹ J.A.C.S., 33, 1650 (1911)

TABLE I.

Added Salt	Strength of Salt Solution		Average	Solubility of $KClO_4$		Average	Total concentration	$\frac{\alpha_K + \alpha_{CO_3^-}}{\alpha_K + \alpha_{CO_3^-}}$
None				.1490	.1488			
				.1488	.1493			
				.1491	.1492			
				.1491	.1492	.1491	.1491	1.000
NaCl	.1006	.1007		.1567	.1568			
	.1007	.1008	.1007	.1566	.1568	.1567	.2574	.905
	.2995	.2992		.1659				
	.2991	.2991	.2994	.1659	.1657	.1558	.4652	.809
	.5906			.1732	.1732			
	.5903	.5901	.5903	.1732	.1730	.1732	.7635	.741
KCl	.0985	.0980		.1138	.1135			
	.0983	.0984	.0983	.1135	.1136	.1136	.2119	.923
	.2993	.2995		.0758				
	.2995	.2995	.2994	.0757	.0751	.0757	.3751	.783
	.6089	.6089		.0534	.0529			
	.6087	.6090	.6089	.0536	.0535	.0535	.6624	.627
NaClO ₄	.1027			.1117	.1123			
	.1026	.1025	.1026	.1123	.1122	.1122	.2148	.922
	.3091							
	.3088	.3090	.3090	.0751	.0752	.0752	.3842	.769
	.6273	.6273	.6273	.0532	.0535	.0533	.6806	.613
NaNO ₃	.1008	.1007		.1610	.1611			
	.1008	.1008	.1008	.1610	.1612	.1611	.2619	.857
	.3141	.3140		.1789	.1780			
	.3138	.3138	.3139	.1791	.1790	.1790	.4929	.694
	.6218			.1995	.1994			
	.6221		.6220	.1993	.1992	.1994	.8214	.559
Na ₂ SO ₄	.1047	.1047		.1633	.1634			
	.1047	.1048	.1047	.1633	.1626	.1633	.2680	.834
	.3210	.3209		.1801	.1800			
	.3211	.3210	.3210	.1802	.1799	.1800	.5010	.686
	.6610	.6610						
	.6610	.6610	.6610	.1954	.1959	.1957	.8567	.580

TABLE I (Continued)

Added Salt	Strength of Salt Solution		Average	Solubility of $KClO_4$		Average	Total concentration	$\frac{\alpha_K \alpha_{CaO_4}}{\alpha_{OK} \alpha_{OeO_4}}$
KNO_3	.0971	.0971	.0971	.1174	.1173	.1174	.2145	.883
	.0971			.1175	.1175			
	.2955	.2953	.2954	.0844	.0848	.0846	.3800	.691
	.2953			.0847	.0844			
	.6686		.6686	.0641	.0639	.0642	.7307	.490
.6687	.6686	.0654		.0636				
K_2SO_4			¹⁾ .0998*			¹⁾ .1194	.2192	.849
	.3024		.3025	.0857		.0857	.3882	.688
	.3026	.3025		.0857	.0855			
	.6011	.6005	.6008	.0641		.0644	.6652	.519
	.6004	.6012		.0644	.0649			
$BaCl_2$.0991	.0991	.0991	.1569	.1569	.1569	.2560	.903
	.2975	.2974	.2974	.1637	.1638	.1638	.4612	.829
	.2971			.1637	.1638			
	.5996	.5995	.5995	.1692	.1694	.1693	.7688	.776
$Ba(NO_3)_2$.0988	.0991	.0990	.1612	.1612	.1605	.2595	.875
				.1592				
	.3019	.3021	.3019	.1756		.1747	.4766	.728
	.3016	.3018		.1726	.1760			
	.6074	.6076	.6075	.1896	.1907	.1902	.7937	.614
	.6077	.6073		.1896	.1907			

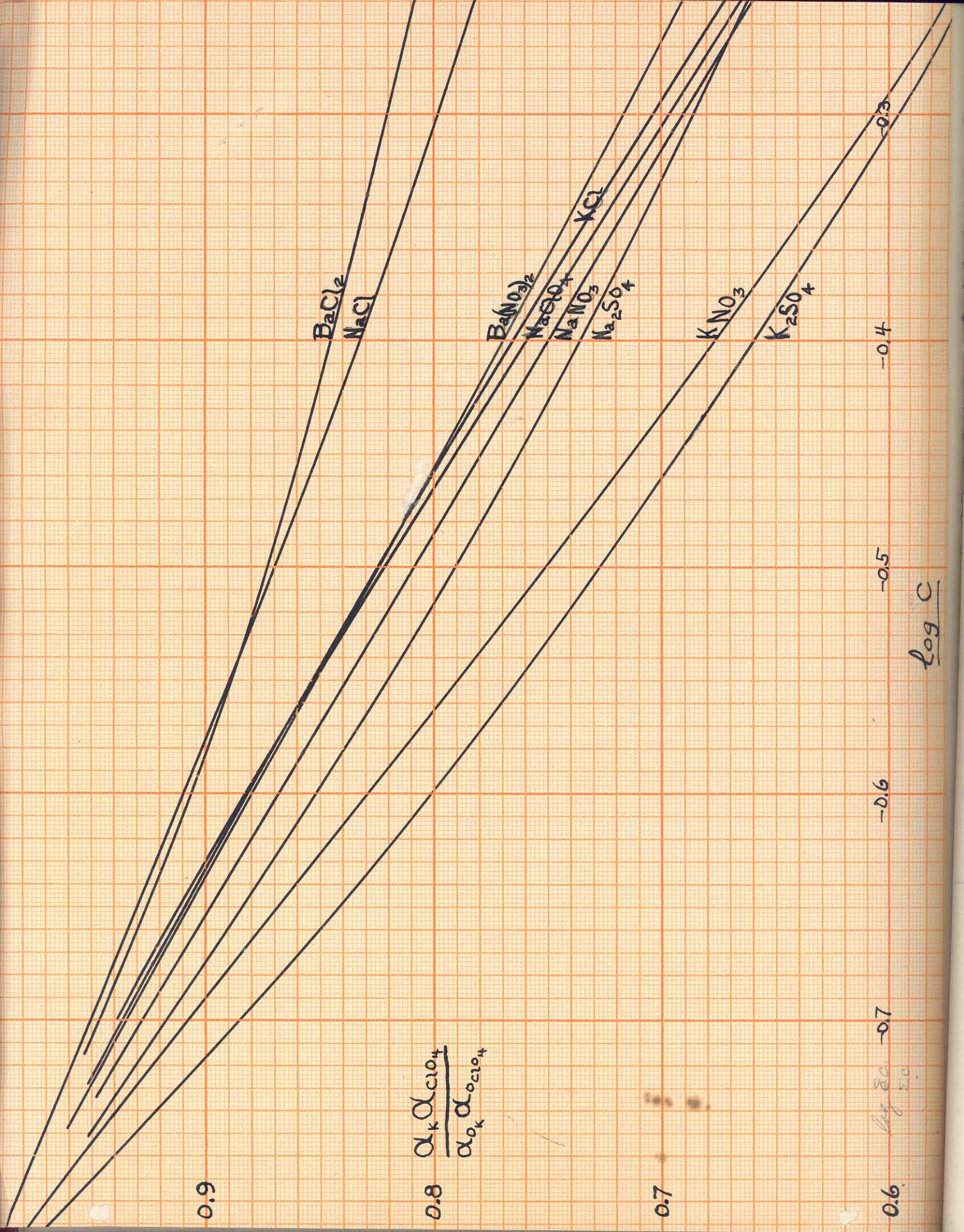
1) ^{Derived from the} Results of Noyes and Boggs, J. A. C. S., 33, 1650 (1911)

Table II.

Values of the ratio: $\frac{\alpha_{K^+} \alpha_{CO_3^{2-}}}{\alpha_{K^+} \alpha_{CO_4^{2-}}}$
total concentration.

for different added salts at 0.5 N

<u>Salt</u>	<u>Ratio</u>	<u>Difference</u>	<u>Salt</u>	<u>Ratio</u>	<u>Difference</u>	<u>Salt</u>	<u>Ratio</u>	<u>Difference</u>
KCl	0.705	0.093	KNO ₃	0.600	0.090	K ₂ SO ₄	0.597	0.091
NaCl	0.798	0.020	NaNO ₃	0.690	0.030	Na ₂ SO ₄	0.686	
BaCl ₂	0.821		Ba(NO ₃) ₂	0.717				
<hr/>								
KCl	0.705	0.10 $\frac{1}{2}$	NaCl	0.798	0.11 $\frac{1}{2}$	BaCl ₂	0.821	0.10 $\frac{1}{4}$
KNO ₃	0.600	0.003	NaNO ₃	0.690	0.004	Ba(NO ₃) ₂	0.717	
K ₂ SO ₄	0.597		Na ₂ SO ₄	0.686				
<hr/>								



0.9

$$\frac{\alpha_k \alpha_{c10_4}}{\alpha_0 \alpha_{c10_4}}$$

0.8

0.7

0.6

BaCl₂
NaCl

Ba(NO₃)₂
NaClO₄
NaNO₃
Na₂SO₄

KNO₃
K₂SO₄

KCl

-0.3

-0.4

-0.5

-0.6

-0.7

log C

log 80
5.0

Lewis and Randall³ have put forth the principle that the activity coefficient of every strong electrolyte is the same in all dilute solutions of the ionic strength. He defines ionic strength such that each ion (1, 2, 3, ---) contributes to it proportionally to its stoichiometrical molality (m_1, m_2, m_3, \dots) multiplied by the square of its valence ($v_1^2, v_2^2, v_3^2, \dots$), or ionic strength, $\mu = \frac{1}{2} \sum m_n v_n^2$

This rule, he shows in many cases, applies to solutions as dilute as $\mu = 0.1$. We have tested the rule for higher concentrations. Referring to the graphs, where the ratio of activity coefficients is plotted both against the logarithm of the ionic strength and against the logarithm of the total concentration, it was seen that the lines sometimes coincide more closely on one plot and sometimes on the other, but that the ionic strength rule does not all simplify the situation for these concentrations.

Harned⁴ has stated that in a mixture of two salts with a common ion the activity of the common ion is the same at the same total concentration, with whatever other ions it may be associated. Harned has obtained results only on chlorid ion in mixtures of KCl, NaCl, LiCl and HCl. It seems then, in view of the specific ion effect noted above, that this generalization should be limited to univalent chlorids.

Summary.

1. The available data for solubilities of salts in solutions of other salts has been reviewed, and a series of determinations for $KClO_4$ made including combinations of Na, K, Ba, Cl, NO_3 and SO_4 ions.

2. At the concentrations considered, the effect of added ions is a specific effect, and must be determined for each ion upon each difficultly soluble salt.

³ G. N. Lewis and M. Randall, J.A.C.S. 43, 1137 (1921)

⁴ Harned, J.A.C.S., 42, 1814 (1920)

THE CRYSTAL STRUCTURE OF LEAD MOLYBDATE.

By Roscoe Dickinson and Richard M. Bozorth.

I. Purpose of the Investigation.

The present investigation is a study, with the aid of Laue photographs, of the crystal structure of lead molybdate. The special objects in view were: (1) to determine whether the arrangement of lead and molybdenum atoms previously obtained by one of us¹ with the aid of X-ray spectrometer measurements, is confirmed; (2) to locate the oxygen atoms by departures in the intensities of the photographic spots from what would be expected from the assumed arrangement of lead and molybdenum atoms; previous work had failed to determine the position of the oxygen atoms.

2. Experimental Procedure.

The method used was essentially that of Nishikawa as developed by Wyckoff.²

Two small, clear, orange-colored crystals of the mineral wulfenite were selected and ground mechanically to thin sections on plate glass, using flour emery as an abrasive. The sections, both ground parallel to a (001) face were of thickness 0.4 mm. and 0.2 mm. respectively. The photographs, both somewhat unsymmetrical, were made by passing the small cylindrical beam of X-rays through the sections not quite perpendicularly. The distance of the photographic plate from the crystal was 5 cm.; and the orientation of the crystal with respect to the plate was determined by the preservation of the intensities of the faces (102) and $(10\bar{2})$ in the thin section.

X-rays were produced by a Universal Type Coolidge tube with a tungsten target. The peak voltage estimated by means of a sphere gap when the tube was not operating was 64,000 volts. This estimate is probably approximately correct since the tube consumed only a small fraction of the rated energy output of the transformer. The tube current was 3.5 milli amperes and the exposure with the thinner crystal 8 hours; the exposure with the other crystal was somewhat longer.

¹ Dickinson, J. Am. Chem. Soc. 42, 85, 1920.

² Am. J. Science, 4th series, vol. 50, 317, 1920.

3, Treatment of Observations.

From prints of the photographs were prepared gnomonic projections in the manner described by Wyckoff.² Altho the projections were somewhat unsymmetrical, a knowledge of the axial ratio and the approximate orientation of the crystal enabled the indices of the planes producing each of the spots to be determined without ambiguity. When the projections were prepared, the distance of each photographic spot from the center of the central image was measured on the print and the intensity of the spot estimated on the plate.

For analytical purposes it seems simplest to regard the crystal as built up on a simple tetragonal prism lattice of the dimensions 7.64 x 7.64 x 12.04 Å. According to previous spectrometer results there are 8 lead and 8 molybdenum atoms associated with each unit of this size. Their arrangement is given by the following coordinates:

Pb at $(0,0,0)$ $(\frac{a}{2}, \frac{a}{2}, 0)$ $(0, \frac{a}{2}, \frac{c}{2})$ $(\frac{a}{2}, 0, \frac{c}{2})$

$$(\frac{3a}{4}, \frac{3a}{4}, \frac{3c}{4}) \quad (\frac{a}{4}, \frac{a}{4}, \frac{3c}{4}) \quad (\frac{a}{4}, \frac{3a}{4}, \frac{c}{4}) \quad (\frac{3a}{4}, \frac{a}{4}, \frac{c}{4})$$

Mo at $(\frac{a}{2}, \frac{a}{2}, \frac{c}{2})$ $(0, 0, \frac{c}{2})$ $(\frac{a}{2}, 0, 0)$ $(0, \frac{a}{2}, 0)$

$$(\frac{a}{4}, \frac{a}{4}, \frac{c}{4}) \quad (\frac{3a}{4}, \frac{3a}{4}, \frac{c}{4}) \quad (\frac{a}{4}, \frac{3a}{4}, \frac{3c}{4}) \quad (\frac{3a}{4}, \frac{a}{4}, \frac{3c}{4})$$

where $a = 7.64$ Å and $c = 12.04$ Å.

The shortest distance between two (hkl) planes passing through lattice points is given by the expression³:

$$d_{(hkl)} = \frac{c}{\sqrt{(h^2 + k^2)\frac{c^2}{a^2} + 1^2}}$$

This becomes in the present case, if $d_{(hkl)}$ is expressed in Angstroms:

$$d_{(hkl)} = \frac{12.04}{\sqrt{(h^2 + k^2)2.487 + 1^2}}$$

³ A. W. Hull, Phys. Rev. [2] 10,661,(1917)

The value of $n\lambda$, i.e. order of reflection times wave-length, for any particular spot is then given by:

$$n\lambda = 2d_{(hkl)} \sin \theta = \frac{24.08 \sin \theta}{\sqrt{(h^2 + k^2)2.487 + l^2}}$$

The value of $\sin \theta$ is readily calculated from the distance of the spot from the central image, and the distance of the crystal from the photographic plate.

From the maximum voltage impressed on the tube, the shortest wave-length present in the X-ray spectrum may be calculated from the quantum relation $Ve = h\nu$. In the present case λ was calculated to be 0.193 Å. The smallest value of $n\lambda$ calculated for any spot on the photographs was 0.214 Å. In view of the fact that the intensity of the spectrum close to the short wave-length end is comparatively small⁴ it seems reasonable to assume that values of $n\lambda$ between 0.21 and 0.42 Å correspond to pure first order reflections.

In order to be able to compare the intensities of reflection by a given wave-length for different forms, a plot of $n\lambda$ against intensities was made for each form.

4. Interpretation of the Data.

The symmetry usually assigned to wulfenite is tetragonal pyramidal, this class being characterized by only a tetragonal axis of symmetry. If the arrangement of the atoms correspond to this class of symmetry, the Laue photographs obtained should have symmetry like that obtainable from a crystal having in addition to a tetragonal axis a center of symmetry, that is, like that from a crystal of the bi-pyramidal class. Consequently of the eight planes, (hkl) $(\bar{h}kl)$ $(h\bar{k}l)$ $(\bar{h}\bar{k}l)$ (khl) $(\bar{k}hl)$ $(kh\bar{l})$ $(\bar{k}h\bar{l})$, which might produce spots on the photographs taken, the first four should in general, under the same conditions, reflect with different intensity from the second four. If this takes place the points on an $n\lambda$ -intensity plot will lie on two curves, one containing only points due to the first four planes. Such a distribution was shown with certainty only in the case of the forms $\{511\}$ and $\{151\}$, altho each photograph has about 200 spots. A similar lack of dissymmetry was observed by Jager⁵. One of two possibilities results

⁴ C. T. Ulrey, Phys. Rev. (2) 11, 401 (1918).

⁵ Kon. Ak. v. W., Amsterdam, 18, 1350 (1916)

from this: (1) The entire atomic arrangement has symmetry greater than that even of the bi-pyramidal class. In this case the observed dissymmetry of {511} and {151} must be disregarded. (2) The heavy atoms are arranged with greater symmetry but the oxygens are not. Due to their relatively low weight they have too little effect upon the intensity of reflection for their relative dissymmetry to become evident except in the case of {511} and {151}. In either case the heavy atoms have more than bi-pyramidal symmetry.

If the arrangement of lead and molybdenum atoms is that given in section 3, and the oxygen atoms are for the time neglected, the intensity of reflection of a given wave-length is given by the expression

$$I = k f\left(\frac{d}{n}\right) \cdot (A^2 + B^2)$$

where

$$A = \overline{Pb} \left(\cos 2\pi n \cdot 0 + \cos 2\pi n \frac{h+k}{2} + \cos 2\pi n \frac{k+l}{2} + \cos 2\pi n \frac{h+l}{2} \right. \\ \left. + \cos 2\pi n \frac{3(h+k+l)}{4} + \cos 2\pi n \frac{h+k+3l}{4} + \cos 2\pi n \frac{3h+k+l}{4} + \cos 2\pi n \frac{h+3k+l}{4} \right) \\ + \overline{Mo} \left(\cos 2\pi n \frac{h+k+l}{2} + \cos 2\pi n \frac{l}{2} + \cos 2\pi n \frac{h}{2} + \cos 2\pi n \frac{k}{2} \right. \\ \left. + \cos 2\pi n \frac{h+k+l}{4} + \cos 2\pi n \frac{3h+3k+l}{4} + \cos 2\pi n \frac{h+3k+3l}{4} + \cos 2\pi n \frac{3h+k+3l}{4} \right)$$

B = a similar expression in sine terms.

In what follows k will be treated as constant for a given substance under the same conditions. No assumption will be made concerning $f\left(\frac{d}{n}\right)$ except that the function decreases continuously as $\frac{d}{n}$ decreases. Except where definitely stated no assumption will be made regarding the relative values of \overline{Pb} and \overline{Mo} .

It can be shown that the general expressions for A and B reduce to the following in special cases:

Class I. When one and only one index is odd:

$$\text{If } n = 1 \quad A = 0 \quad B = 0$$

$$n = 2 \quad A = 0 \quad B = 0$$

$$n = 3 \quad A = 0 \quad B = 0$$

$$n = 4 \quad A = 8\overline{Pb} + 8\overline{Mo} \quad B = 0$$

Class II. When two and only two indices are odd:

$$\text{If } n = 1 \quad A = 0 \quad B = 0$$

$$n = 2 \quad A = 8\overline{Pb} + 8\overline{Mo} \quad B = 0$$

Class III. When all three indices are odd:

$$\text{If } n = 1 \quad A = 4\overline{Pb} - 4\overline{Mo} \quad B = 4\overline{Pb} - 4\overline{Mo}$$

Neglecting the effect of the oxygen atoms, planes with one odd index should give no values of $n\lambda$ corresponding to reflections under the fourth order; i.e. if $(n\lambda)_m$ is the smallest value of $n\lambda$ found for any one of these planes $\frac{(n\lambda)_m}{4}$ should be no smaller than about 0.21.

Likewise planes with two odd indices should not reflect under the second order; and for these $\frac{(n\lambda)_m}{2}$ should be no smaller than 0.21.

Planes having all odd indices may be expected to give values of $n\lambda$ from 0.21 up.

The smallest value of $\frac{n\lambda}{4}$ found for any plane having only one odd index was 0.225. Planes belonging to four forms were found giving values of $\frac{n\lambda}{4}$ between 0.21 and 0.42 viz. $\{201\}$, $\{221\}$, $\{412\}$ and $\{322\}$.

On each photograph planes belonging to nineteen different forms having two odd indices were found with values of $\frac{n\lambda}{2}$ under 0.42. A very few of these gave values of $\frac{n\lambda}{2}$ under 0.21, the smallest being 0.194. This value, although perhaps smaller than would have been expected, is not below the lower limit of wave-lengths calculated from the estimated voltage.

Of planes having all three indices odd, reflections were found on each photograph with values of $n\lambda$ ranging from about 0.21 up. Planes belonging to seven different forms were found reflecting in the first order in the first photograph and eight forms in the second.

Thus no planes were found reflecting lower orders than predicted from the assumed arrangement of lead and molybdenum atoms; moreover all three kinds of planes were found reflecting in ranges of $n\lambda$ indicated as possible.

As previously mentioned, the intensity of these spots were roughly estimated on the

photographic plates, and by means of comparisons between them the arrangement was further tested as mentioned below.

Within each class of planes, the intensity of the reflections of a given wave-length should be uniformly less the smaller the interplanar distance because within each class the values of A and B are the same for each plane.

For the same value of $\frac{d}{n}$, planes of classes I and II should reflect the same wave-length with equal intensities. Reflections from planes of class III, however, should under these conditions be weaker than those of the other classes, for here $\sqrt{A^2 + B^2}$ is proportional to the difference of the reflecting powers of Pb and Mo, instead of to their sum.

These tests were applied in a great many cases, and in each case the structure was confirmed except when comparisons involved the {511} form.

5. Conclusions.

The arrangement of the lead and molybdenum atoms as previously determined spectrometrically has been confirmed by the Laue photographic data. It has not been possible to locate the oxygen atoms; the only data giving any evidence of their reflections is that relating to the {511} form.

Pasadena, March 1922.

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THE CRYSTAL STRUCTURE OF POTASSIUM CYANIDE.

By RICHARD M. BOZORTH.¹

Received December 22, 1921.

I. Introduction.

The purpose of this research was to study by means of X-rays the crystal structure of potassium cyanide, hoping thereby to throw some light on the similarity in properties between this substance and the alkali halides. The crystallographic information is very meagre, nothing having been found in the literature except the statement² that the salt crystallizes from the melt in cubes and from an aqueous solution in octahedra.

This research was carried out in part with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which I wish to express my indebtedness. I also wish to express my thanks to Dr. R. G. Dickinson, under whose immediate direction the work was carried out.

II. Preparation of the Crystals and the Methods of Measurement.

The crystals used in this research were prepared by two methods. Slow evaporation of a saturated aqueous solution in a desiccator yielded crystals with (111) faces large enough for good spectrometer measurements. Cubes large enough for Laue photographs were formed by placing a layer of alcohol over the saturated aqueous solution and allowing diffusion to take place. After several days crystals formed on the sides of the container.

Observation under a polarizing microscope showed optical isotropy, confirming the fact that the crystal has cubic symmetry. A good cubic cleavage was found, but no cleavage was observed parallel to (111) or (110) planes.

Most of the X-ray data were obtained from Laue photographs and from photographs of line spectra from single faces. The apparatus used and the treatment of the spectral photographs were the same as those employed by Dickinson.³ The angles and relative intensities of two reflections from the (111) face were measured on the X-ray spectrometer.⁴

III. The Spectral Measurements and the Unit of Structure.

The values of the angles of reflection for different planes are given in the second column of Table I. The number of molecules per unit of structure and the dimensions of the unit were derived from these data. To

¹ Du Pont Fellow in Chemistry.

² P. Groth, "Chemische Krystallographie," Leipsic, 1906, vol. 1, p. 203.

³ Dickinson, THIS JOURNAL, 44, 276 (1922).

⁴ Dickinson and Goodhue, *ibid.*, 43, 2046 (1921).

find the number m of molecules in the unit of structure, the following well-known equation was employed.

$$\frac{n^3}{m} = \frac{8 \sin^3 \theta \cdot M}{\lambda^3 \rho N} \quad (1)$$

In this equation n denotes the order of reflection, θ the angle of reflection from a (100) plane, M the molecular weight of the substance, λ the wavelength of the X-rays, ρ the density of the substance (1.52), and N the Avagadro number.

The length d_{100} of the unit cube, on the basis that $m = 4$, was calculated by the equation

$$n\lambda = \frac{2 d_{100} \sin \theta}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

The values so calculated in 10^{-8} centimeters are given in the sixth column of Table I.

TABLE I
THE SPECTRAL MEASUREMENTS

Crystal Face	Angle of Reflection	Order of Reflection	Spectral Line	Wave-length	Length of Unit Cube	Intensity of Reflection
(100)	5° 23'	2	<i>Rh</i> α	0.614	6.54	Strong
	10° 51'	4	α	0.614	6.52	Medium
	16° 23'	6	α	0.614	6.53	Weak
	4° 47'	2	β	0.545	6.54	
	4° 40'	2	γ	0.534	6.56	
(110)	7° 39'	2	α	0.614	6.52	Strong
	15° 22'	4	α	0.614	6.55	Weak
	6° 42'	2	β	0.545	6.60	
	6° 35'	2	γ	0.534	6.59	
(111)	5° 24'	1	Mo α	0.710	6.53	100:153
	10° 51'	2	α			
			(Mean)		6.55	

The value of d_{100} calculated directly from the density under the assumption that there are 4 molecules in the unit is 6.55×10^{-8} cm. This is equal to the mean of the above values. This value was used for calculations of the wavelengths from the Laue photographs.

IV. The Laue Photographs.

Laue photographs were taken with the beam of X-rays approximately perpendicular to the (100) face, and also with the beam approximately perpendicular to the (111) face. Gnomonic projections were made from the photographs, and the analysis carried out according to the method described by Wyckoff.⁵ A gnomonic projection of an unsymmetrical photograph taken with the beam making an angle of 4° with the perpendicular to the (111) face, showing the 3-fold axis of symmetry, is repro-

⁵ Wyckoff, *Am. J. Sci.*, 50, 318 (1920).

duced in Fig. 1. The area of each spot is proportional to the intensity estimated directly from the plate.

The smallest value of $n\lambda$ for any plane, as calculated from Equation 2, was found to be 0.24×10^{-8} cm.; consequently it was deemed safe to consider any values of $n\lambda$ between this value and 0.48×10^{-8} cm. to be pure first-order reflections. The forms giving reflections in the first order were: (311), (331), (531), (533), (551), (711), (731), (553), (731), (751), (753). Those appearing in the second order, but not in the first, were: (221), (320), (321).

All of the spots from planes reflecting in the first order on Laue photographs had comparative intensities such that the planes with the greater

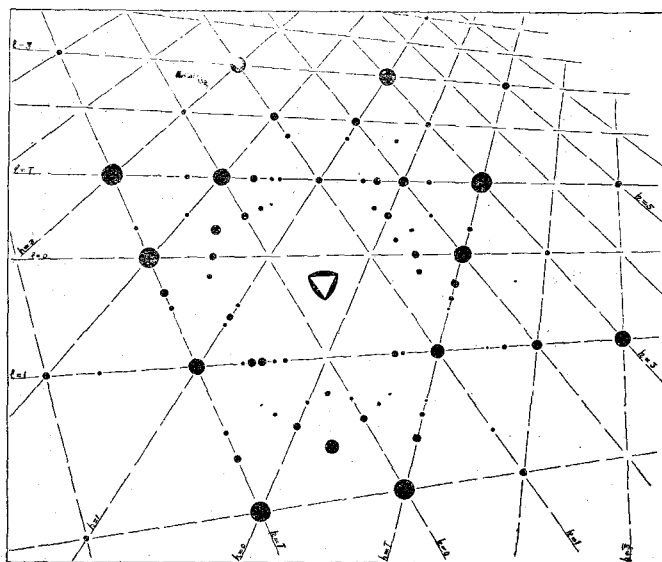


Fig. 1.

interplanar distance always had the greater intensity when reflecting with the same wavelength. Also, spots produced by second-order (221) planes could not be distinguished in intensity from those produced by first-order (531) planes; and second-order (321) reflections could not be distinguished in intensity from first order (731) reflections.

It was possible to obtain one additional piece of information from a powder photograph. From this it was clear that the second-order (100) reflection was more intense than the first-order (111) reflection.

V. Interpretation of the Data.

The relative intensities of reflection of various orders shown in Table I are characteristic of crystals with the sodium chloride structure having

the halogen appreciably, but not too greatly, different in weight from the metal. Thus there is a rapid decline of intensity with increasing order for the planes (100) and (110), and a weaker reflection of the first order from (111) than of the second order. The facts shown by the powder photograph that the second order reflection from (100) was stronger than the first order from (111) in spite of the smaller value of d/n in the former case is also in agreement with a sodium chloride structure. In view of these facts and of the close resemblance between potassium cyanide and the alkali halides, the attempt has been made to satisfy the requirements of the remaining X-ray data on the assumption that the potassium atoms are located in the same way as the metal atoms in sodium chloride, and that the carbon and nitrogen atoms are near the corresponding halogen position. This assumption, whose approximate validity is clear from the above X-ray considerations, simplifies the treatment of the possible structures given below, which would otherwise contain three parameters to be determined.

Magnesium oxide is a crystal having the sodium chloride structure; and the application of the theory of space groups to this substance has been treated in detail by Wyckoff.⁶ All the possible positions for the atoms of potassium cyanide are included in the possibilities given by Wyckoff for magnesium oxide. There are two possible arrangements for a substance having 4 molecules in the unit and 3 atoms in the molecule. These are,

- (a) K at : (u, u, u) (u, \bar{u} , \bar{u}) (\bar{u} , u, \bar{u}) (\bar{u} , \bar{u} , u)
 C at : (v, v, v) (v, \bar{v} , \bar{v}) (\bar{v} , v, \bar{v}) (\bar{v} , \bar{v} , v)
 N at : (w, w, w) (w, \bar{w} , \bar{w}) (\bar{w} , w, \bar{w}) (\bar{w} , \bar{w} , w)
- (b) K at : (u, u, u) ($\frac{1}{2} + u, \frac{1}{2} - u, \bar{u}$) ($\frac{1}{2} - u, \bar{u}, \frac{1}{2} + u$) ($\bar{u}, \frac{1}{2} + u, \frac{1}{2} - u$)
 C at : (v, v, v) ($\frac{1}{2} + v, \frac{1}{2} - v, \bar{v}$) ($\frac{1}{2} - v, \bar{v}, \frac{1}{2} + v$) ($\bar{v}, \frac{1}{2} + v, \frac{1}{2} - v$)
 N at : (w, \bar{w} , w) ($\frac{1}{2} + w, \frac{1}{2} - w, \bar{w}$) ($\frac{1}{2} - w, \bar{w}, \frac{1}{2} + w$) ($\bar{w}, \frac{1}{2} + w, \frac{1}{2} - w$)

The arrangement (a) has tetrahedral symmetry, while (b) has tetartohedral symmetry. The first can be made to approximate the sodium chloride structure by giving u the value 0.25, and v and w values on either side of 0.75. The second can be made to approximate the sodium chloride structure by giving u the value zero and v and w values on either side of 0.50. Since the reflecting powers of carbon and nitrogen are probably about the same, these two arrangements are indistinguishable by the present methods of analysis, provided the atoms are in the positions indicated above. There is, moreover, a holohedral arrangement (Wyckoff's (j)), having 32 molecules in a unit (the d_{100} for which is 13.10×10^{-8} cm.), derivable from the space group O_h^5 ; but this would also be indistinguishable from these. It suffices, therefore, to consider only the first arrangement.

For the intensity, I , of reflection of a given wavelength from any plane

⁶ Wyckoff, *Am. J. Sci.*, 1, 138 (1921).

we may write: $I = f(d/n) (A^2 + B^2)$, where A is given by the following equation and B by a similar expression in sine terms.

$A = \bar{K} [\cos 2\pi n(h+k+1)u + \cos 2\pi n(-h+k-1)u + \cos 2\pi n(-h-k+1)u + \cos 2\pi n(h-k-1)u] + \bar{C}$ [a similar expression in v] + \bar{N} [a similar expression in w]. \bar{K} , \bar{C} , and \bar{N} , the reflecting powers of the atoms, were placed equal to the atomic numbers of potassium, carbon, and nitrogen, respectively; u was placed equal to 0.25, while v and w were independently varied by steps of 0.020 between 0.625 and 0.875. With these various values $\sqrt{A^2 + B^2}$ was calculated for the planes for which data are available.

It was found on the Laue photographs that planes with all odd indices reflecting a given wavelength in the first order gave smaller intensities the smaller the value of d/n . Assuming that $f(d/n)$ has smaller values the smaller d/n is, a satisfactory set of values of $\sqrt{A^2 + B^2}$ should show no great variation, especially for planes having nearly equal values of d/n . It was also found that planes with any even index reflected in the second order with about the same intensity as planes with all odd indices in the first order when the values of d/n were the same. These planes with even indices should give about the same values of $\sqrt{A^2 + B^2}$ as the other planes.

The best correspondence with the data seems to be obtained by placing $v = 0.70$ and $w = 0.80$. The values of $\sqrt{A^2 + B^2}$ calculated with these parameters, together with the values calculated for other parameters, are given in Table II for all of the planes whose calculated and observed intensities can be compared. Values of d/n in 10^{-8} centimeters are given in Col. 3.

TABLE II
CALCULATED VALUES OF $\sqrt{A^2 + B^2}$

Order of Reflection	Plane	Value of d/n	Values of $\sqrt{A^2 + B^2}$ for		
			$u = 0.25$ $v = 0.70$ $w = 0.80$	$u = 0.25$ $v = 0.65$ $w = 0.85$	$u = 0.25$ $v = 0.75$ $w = 0.75$
1	(311)	1.97	48	86	24
1	(331)	1.50	59	72	24
1	(531)	1.11	76	63	24
2	(221)	1.09	80	87	128
1	(533)	0.99	76	82	24
1	(551)	0.92	76	34	24
1	(711)	0.92	104	65	24
2	(320)	0.91	71	116	128
2	(321)	0.88	72	86	128
1	(553)	0.85	76	94	24
1	(731)	0.85	93	71	24
1	(751)	0.76	76	61	24
1	(753)	0.72	76	82	24

It will be seen that the values of $\sqrt{A^2 + B_2}$ calculated for $u = 0.25$, $v = 0.70$, $w = 0.80$, correspond satisfactorily with the observations. The only exception is that the calculated value for (711) is (104/76) or 1.4 times that calculated for (551), while the observed intensities of the (711) and (551) spots were the same as nearly as could be determined.

The intensities obtained from spectrometer measurements and from reflection photographs are in good agreement with the calculated values. The relative intensities of the spectra from a simple face can be estimated by assuming the normal decline to be 100:20:7. Values of the intensities so calculated are compared with the observations in Table III.

TABLE III
CALCULATED AND OBSERVED INTENSITIES

Plane	Relative Intensities Calculated for			Observed Intensities
	$u = 0.25$ $v = 0.70$ $w = 0.80$	$u = 0.25$ $v = 0.65$ $w = 0.85$	$u = 0.25$ $v = 0.75$ $w = 0.75$	
(100)	100:10:3	100:2:1	100:20:7	Rapid decline for the three orders
(110)	100:11	100:17	100:20	First order much stronger
(111)	100:218	100:51	100:570	100:153

VI. Representation of the Crystal Structure.

Figure 2 represents $1/8$ of the unit of structure, with the atoms placed in accordance with the values of the parameters, $u = 0.25$, $v = 0.70$, $w = 0.80$. The potassium atoms are represented by the larger circles, and the carbon and nitrogen atoms by the smaller ones. These latter atoms are equidistant from the corners of the cube not occupied by potassium atoms. Since the measurements do not serve to distinguish between the carbon and nitrogen atoms, both of these kinds of atoms are represented by the same sized circle.

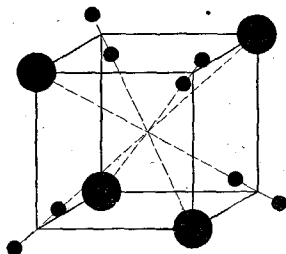


Fig. 2.

Table IV gives the distances between the centers of the atoms, together with the sum of the corresponding Bragg radii,⁷ both in 10^{-8} centimeters.

TABLE IV
DISTANCES BETWEEN THE ATOMS

	Distance	Sum of Bragg Radii
Carbon to nitrogen.....	1.15	1.4
Potassium to carbon.....	3.0	2.8
Potassium to nitrogen.....	3.0	2.7

⁷ Bragg, *Phil. Mag.*, 40, 180 (1920).

Langmuir has suggested⁸ that in the cyanide radical the carbon and nitrogen atoms possess in common an outer shell of electrons. If in accordance with this hypothesis the cyanide radical be regarded as a single atom for crystal structure purposes, potassium cyanide can be given the holohedral sodium chloride structure with four molecules in the unit; but if this be done, the values of $\sqrt{A^2 + B^2}$ for (711) and (320) will, on the same assumptions used previously, be 24 and 128, respectively, and this would make the intensity of the (320) reflection $(128/24)^2$ or 28 times as strong as that of the (711) reflection. This great discrepancy might be overcome by assuming the reflecting power of the cyanide radical to drop off much more rapidly than that of the potassium atom with decreasing values of d/n ; but there seems to be little present justification for such an assumption.

VII. Summary.

The crystal structure of potassium cyanide has been studied with X-rays making use of the Laue photographic method, the spectrometric method, and the powder method. The X-ray data show conclusively that the structure of this substance approximates the sodium chloride structure. Consequently, the potassium atoms were placed at the sodium atom positions and the carbon and nitrogen atoms near the chlorine atom positions. The positions of carbon and nitrogen atoms which give the best agreement with the data place these atoms 1.15×10^{-8} cm. apart, equidistant from the position of the chlorine atom. The structure is represented in Fig. 2.

PASADENA, CALIFORNIA.

⁸Langmuir, THIS JOURNAL, 41, 905 (1919).

THE CRYSTAL STRUCTURE OF AMMONIUM FLUOSILICATE

By RICHARD M. BOZORTH¹

Received March 22, 1922

1. Introduction

Ammonium fluosilicate, $(\text{NH}_4)_2\text{SiF}_6$, exists in two crystalline forms,² cubic and hexagonal. The cubic form is the stable one at ordinary temperatures, while the hexagonal form has been obtained³ below 5°. It seemed probable that the cubic form has the same structure as ammonium chloroplatinate studied by Wyckoff and Posnjak,⁴ and ammonium and potassium chlorostannate studied by Dickinson;⁵ but complete evidence of iso-morphism was lacking.⁶ It was therefore desirable to study its crystal structure, not only to determine whether it is the same as that of these other salts, but also to measure the size of the unit of structure and the distances between the centers of the various atoms.

Crystals of the fluosilicate were prepared by the spontaneous evaporation at room temperature of an aqueous solution containing an excess of hydrofluoric acid.

The methods employed for obtaining the X-ray data and for the interpretation of these data are essentially those used by Wyckoff and Posnjak and by Dickinson, to whose articles reference may be made for more detailed information.

I wish to express my thanks to Dr. R. G. Dickinson for valuable advice during the progress of this research.

2. Determination of the Size of the Unit-cube and the Number of Molecules in It

Photographs of line spectra from the (111) face of a crystal showed

¹ DuPont Fellow in Chemistry.

² Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 485.

³ Gossner, *Z. Kryst. Mineral.*, **38**, 147 (1904).

⁴ Wyckoff and Posnjak, *THIS JOURNAL*, **43**, 2292 (1921).

⁵ Dickinson, *ibid.*, **44**, 276 (1922).

⁶ Ref. 2, p. 466.

five orders of reflection. From the values of the angles of the reflections and the density of the salt, determined to be 2.01, the smallest possible number of molecules in the unit of structure was found in the usual way to be 4, as in the other salts mentioned above.

Table I gives the angles of reflection, the orders of the reflections, and the length in Ångstrom units of the unit-cube based on this conclusion. In calculating the number of molecules in the unit and the length of the unit-cube the wave length⁷ of the rhodium α_1 line was taken to be 0.6121 Ångstrom units.

TABLE I
THE X-RAY REFLECTIONS OF THE RHODIUM α_1 LINE FROM THE (111) FACE

Angle of reflection	Order of reflection	Length of unit-cube	Intensity of reflection
3° 38'	1	8.37	strong
7° 15'	2	8.40	strong
10° 56'	3	8.38	medium weak
14° 39'	4	8.38	medium weak
18° 26'	5	8.38	weak
From the density 8.37			
Final value		8.38	

3. The Laue Photographic Data

Laue photographs were then taken with a beam of X-rays passing through the (111) face, and these photographs analyzed by the usual methods.

The data which were useful in determining the positions of the fluorine atoms are given in Table II. The interplanar distances and wave lengths are expressed in Ångstroms. The smallest wave length calculated for any spot on a Laue photograph was 0.27 Ångstrom units. Wave lengths lower than 0.26 were considered to be absent from the spectrum.

TABLE II
DATA FROM THE LAUE PHOTOGRAPHS
Photograph No. 1. Photograph No. 2. Photograph No. 3

Reflecting plane	Inter-planar distance	Wave length of reflected X-rays		Wave length of reflected X-rays		Wave length of reflected X-rays		Calculated amplitude for $\mu=0.205$
		Intensity of spot produced	Intensity of spot produced	Intensity of spot produced	Intensity of spot produced	Intensity of spot produced	Intensity of spot produced	
First-Order Reflections								
(135)	1.42	0.40	0.9	0.47	3	1.2
(531)	1.42	0.49	1.0	1.2
(335)	1.28	0.48	0.3	0.50	0.4	0.2
(353)	1.28	0.46	0.5	0.2
(155)	1.17	0.52	1.5	0.49	4	2.8
(117)	1.17	0.46	0.6	0.4
(535)	1.09	0.46	2.5	1.8
(731)	1.09	0.31	0.0	0.42	0.05	0.5
(373)	1.02	0.47	0.4	0.37	0.4	1.5

⁷ Duane, *Bull. Nat. Research Council*, 1, No. 6 (1920).

TABLE II (continued)
 Photograph No. 1. Photograph No. 2. Photograph No. 3

Reflecting plane	Inter-planar distance	Photograph No. 1		Photograph No. 2		Photograph No. 3		Calculated amplitude for $\mu=0.205$
		Wave length of reflected X-rays	Intensity of spot produced	Wave length of reflected X-rays	Intensity of spot produced	Wave length of reflected X-rays	Intensity of spot produced	
First-Order Reflections								
(557)	0.84	0.46	0.4	0.47	0.6	1.7
(359)	0.78	0.36	0.2	0.40	0.3	0.9
(593)	0.78	0.32	0.1	0.46	0.5	0.9
(775)	0.76	0.50	0.0	0.44	0.0	0.0
(1-1-11)	0.76	0.46	0.4	1.2
(559)	0.73	0.45	0.3	0.49	0.5	3.0
(197)	0.73	0.44	0.1	0.41	0.1	0.7
(11-13)	0.73	0.46	0.05	0.52	0.1	0.2
(11-15)	0.69	0.46	0.2	0.47	0.2	1.8
(759)	0.67	0.46	0.1	0.41	0.1	1.3
(5-5-11)	0.64	0.44	0.2	0.47	0.3	2.4
Second-Order Reflections								
(121)	3.42	0.40	0.4	0.3
(212)	2.79	0.48	0.2	0.0
(123)	2.24	0.35	0.4	0.41	0.9	1.1
(043)	1.68	0.45	0.1	0.41	0.1	0.5
(324)	1.56	0.52	0.0	0.47	0.0	0.1
(350)	1.44	0.48	0.5	0.41	0.5	3.2

4. Interpretation of the Data

The possible arrangements for ammonium fluosilicate permitted by the theory of space groups are those considered for ammonium chloroplatinate by Wyckoff and Posnjak, and for ammonium chlorostannate by Dickinson. The correct arrangement in this case is the same one that they have found, and can be proved in the same way. The intensity functions are accordingly of the same form.

For purposes of comparing intensities, planes may be divided into three classes, namely: (1) planes all of whose indices are odd; (2) planes having two odd indices and one even; (3) planes having one odd index and two even. Planes of Classes 2 and 3 reflect only in even orders.

The value of the parameter μ , which fixes the position of the fluorine

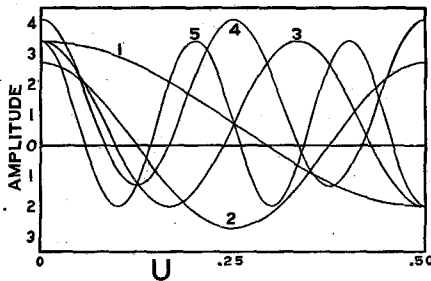


Fig. 1.

atoms, was first limited to the region between 0.19 and 0.25 by the following method. It was observed on the spectral photographs that the fourth-order reflections from the (111) face were as strong as the third-order reflections. It was therefore concluded that the fourth-order amplitude must be greater than the third-order ampli-

tude. The amplitudes calculated for all five orders from the (111) face are plotted for all distinct values of u in Fig. 1. The regions which show a greater fourth-order than third-order amplitude can be noted. It was concluded

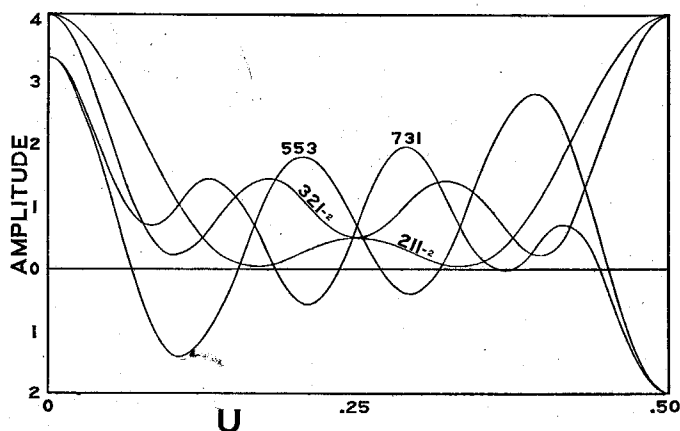


Fig. 2.

from Laue photographic data that (553) must have a larger amplitude than (731) in the first order, and (321) a larger amplitude than (211) in the second order. The calculated amplitudes of these forms are plotted for all distinct values of u in Fig. 2. It will be seen from Figs. 1 and 2 that the only values of u which account for these data are those between 0.19 and 0.25. To limit further the value of u a plot was made showing the amplitudes of planes of Class 1 for values of u between 0.19 and 0.25. The original plot included all planes having an interplanar distance of more than 0.64 Ångstrom units, which is the interplanar distance for (11·5·5), the most complex plane observed. In Fig. 3 are reproduced only those curves which were most useful. Certain inequalities in amplitude were established from the Laue photographic data, and the value of u more definitely determined with the aid of the figure. For example, since $(11·5·1) > (971)$, $u < 0.218$;

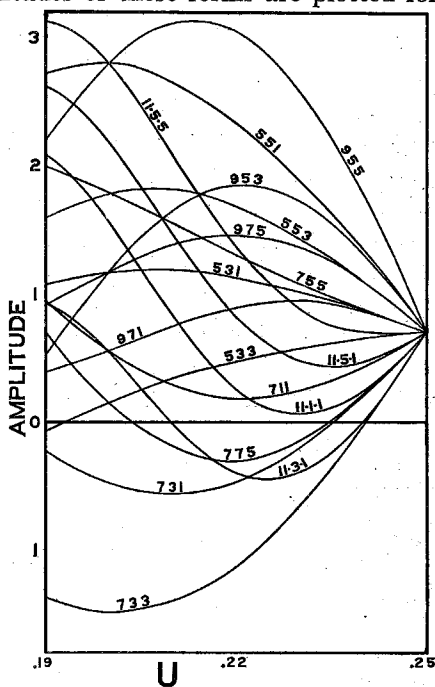


Fig. 3.

since $(11\cdot5\cdot1) > (975)$, $u < 0\cdot211$; since $(711) < (533)$, $u < 0\cdot218$; since $(955) > (11\cdot5\cdot1)$, $u > 0\cdot195$; and since $(971) \geq (11\cdot3\cdot1)$, $u > 0\cdot200$. The value of u , therefore, lies between 0.200 and 0.208. The best value is considered to be 0.205.

In calculating the amplitudes given in the last column of Table II it has been assumed that the reflecting power of each atom is proportional to its atomic number; but the determination of u based on the comparisons that have been made is largely independent of this assumption, since any reasonable values of the reflecting powers would lead to the same conclusion. However, comparisons between planes of different classes, or even between planes of the same class where at least one of the amplitudes is small or opposite in sign to the other, can be made properly only with a good knowledge of reflecting powers. In view of these limitations all the comparisons which have been properly made are satisfied remarkably well when $u = 0\cdot205$. Many of these comparisons may be made with the data of Table II, using the calculated amplitudes given in the last column.

5. Conclusions as to the Structure

Summary

The crystal structure of ammonium fluosilicate has been shown to be like that of ammonium chloroplatinate, ammonium and potassium chlorostannates, namely the structure is that⁸ of calcium fluoride, CaF_2 , in which each fluorine atom is replaced by an ammonium group, and each calcium atom by a fluosilicate group with the 6 fluorine atoms equidistant from the silicon atom in the directions of the axes of the crystal. The length of the cube constituting the unit of structure containing 4 molecules was found to be 8.38 Ångstrom units; the corresponding lengths for the three other complex salts just mentioned are 9.84 for ammonium chloroplatinate, 10.05 for ammonium chlorostannate, and 9.96 for potassium chlorostannate. The shortest distance between the centers of the atoms of fluorine and silicon is 1.72 Ångstrom units, while the sum of the Bragg radii⁹ for these atoms is 1.84. The corresponding distances between the platinum or tin and the chlorine atoms in the other three salts are 2.3 Ångstrom units for ammonium chloroplatinate, 2.46 for ammonium chlorostannate and 2.44 for potassium chlorostannate.

PASADENA, CALIFORNIA

⁸ See W. H. and W. L. Bragg, "X-Rays and Crystal Structure," G. Bell and Sons, Ltd., London, 1916, p. 107.

⁹ W. L. Bragg, *Phil. Mag.*, **40**, 180 (1920).

THE CRYSTAL STRUCTURE OF CADMIUM IODIDE.

1. Introduction.

The purpose of this work was to determine by means of X-rays the positions of the atoms in crystalline cadmium iodide, CdI_2 . Crystals were prepared by spontaneous evaporation at room temperature of a saturated solution. The crystals are light yellow, hexagonal tablets, described crystallographically by Groth¹ as belonging to the hexagonal system.

The X-ray data were obtained in two ways: (1) from photographs of line spectra from the principal faces, using rhodium as the target, and (2) from Laue photographs.

2. Spectral Photographs and the Unit of Structure.

Photographs were taken of line spectra reflecting from (00.1), (10.0) and (11.0) planes. The first was taken by reflecting the X-rays from the (00.1) face, while for the other two measurements the X-rays were passed thru a thin crystal in such a way that the (10.0) or (11.0) planes could reflect. The angles of reflection and the estimated intensities of the reflected beam are given in Table 1. Measurements are for the rhodium line, wave-length 0.6121 angstroms.²

The value of $\frac{d}{n}$, where d is the interplanar distance and n the order of reflection, may be calculated from these data. If the reflections occurring at the smallest angles from the (00.1) and (11.0) planes be regarded as first order reflections, the dimensions of the corresponding hexagonal unit of structure are found to be 6.84 angstroms in height and 4.24 angstroms along one side of the base. (see Figure 2). Combining these measurements with the density, 5.644 as quoted by Groth¹, this unit is found to contain one molecule, CdI_2 . on this basis the (00.1) reflections will be the first to eighth orders, the (11.0) re-

¹ P. Groth, "Chemische Krystallographie" Leipzig, 1906, vol. 1, p. 213.

² Duane, Bull. Nat. Research Council, I, No. 6 (1920).

Table 1.

Data from the Spectral Photographs.

Reflecting plane	Angle of reflection	$\frac{d}{n}$	Order of intensities
(00.1)	2° 34'	6.83	3 ^d
			2 ^d
			4 th
			1 st
			7 th
	15° 35'	1.14	5 th
			8 th
			5 th
(10.0)	14° 26'	1.23	
(11.0)	8° 18'	2.12	1 st
	16° 53'	1.05 ₅	2 nd

flections the first to third orders, and the (10.0) reflection will be the third order.

3. Discussion of the Possible Structures.

A symmetrical Laue photograph showed that cadmium iodide is not hexagonal but trigonal. An examination of all the spots showed that the symmetry of the photograph corresponds to that of the point group, D_{3d}^3 , and that therefore the arrangement of the atoms is given by a specialization of the point groups D_{3d} or C_{3v} . If there is but one molecule in the unit the possible arrangements are all included in the following:

- I. Cd at $00\frac{1}{2}$, I at $\frac{1}{3} \frac{2}{3} u$, $\frac{2}{3} \frac{1}{3} \bar{u}$
 II. Cd at $00u$, I at $\frac{1}{3} \frac{2}{3} 0$, $\frac{2}{3} \frac{1}{3} 0$
 III Cd at 000 , I at $00u$, $00\bar{u}$.

Arrangement III places the three atoms in a straight line parallel to the axis of the crystal; consequently the spectrum from any prism face would show a regular decline of intensity with order of reflection. Since the (10.0) spectrum shows a third order much stronger than the first or second orders, these arrangements may be ruled out.

To distinguish between arrangements I and II, use was made of the intensities of the (00.1) reflections. For the intensity, I , of reflection of a given wavelength from any plane we may write: $I = f(d/n) \cdot S^2$, where for arrangement I, $S = \bar{C}d \cdot \cos \frac{nl}{2} + 2\bar{I} \cdot \left[\cos n\left(\frac{h+2k}{3} + lu\right) \right]^*$. $\bar{C}d$ and \bar{I} , the reflecting powers of the atoms, were taken to be proportional to their atomic numbers, and were put equal to 10 and 11, respectively. $f(d/n)$ is considered to be a function decreasing continually with decreasing values of (d/n) . h , k and l are the Bravais-Miller indices of the reflecting plane.

3

Notation of Schönfleis "Krystallsysteme u. Krystallstruktur" Teubner, Leipzig, 1891.

*"Equation (1)"

For the reflections from the (00.1) face S becomes $10 + 22 \cos nu$ for arrangement I while for arrangement II, $S = \sqrt{[(10 \cos nu + 22)^2 + (10 \sin nu)^2]}$. Plots were constructed showing the value of S for all distinct values of the parameter, u , for each of these arrangements.

Consideration of the comparative intensities of the different orders of reflection given in Table 1, and of the nature of the intensity function, leads to the conclusion that certain inequalities exist in the values of S . If S_n be the value of S for the n^{th} order, $S_2 > S_1$, $S_4 > S_2$, $S_4 > S_3$, $S_6 > S_5$, $S_8 > S_6$, and $S_8 > S_7$. It was determined from the plots that these conditions are never satisfied for arrangement II, and therefore this arrangement is impossible. These conditions are satisfied for arrangement I only in the region between $u = 0.23$ and 0.253 . Because the sixth order reflection is several times as strong as the seventh, and since S_6 is calculated as described above to be greater than S_7 only above 0.248 , the best value of u is considered to be 0.250 . Deviations of the reflecting powers of the atoms from strict proportionality to their atomic numbers would not require the value of u to lie within these limits, but a large deviation would not permit a value of u very far removed from 0.25 .

4. Confirmation of the Structure by the Laue Photographs.

Unsymmetrical Laue photographs were examined to confirm the structure given by arrangement I. Two photographs having over 150 spots each were analyzed, the intensity of each spot estimated and its wave-length calculated on the basis of the unit previously chosen. The smallest wave-length found for any spot was 0.26 angstroms, a value consistent with the voltage applied to the tube, about $53,000$ volts. Figure 1 is a gnomonic projection of one of the photographs, with the Laue photograph represented diagrammatically in the center. The area of each spot is proportional to the intensity estimated from the photographic plate.

The structure was tested most satisfactorily by comparing the intensities

of spots produced by planes having the same interplanar distances and reflecting with the same wave-length. Forms as $\{h k l\}$ and $\{k h l\}$ have the same calculated value of S when $(h + 2k)/3$ is an integer, but otherwise S is different for the two forms. In no case where $(h + 2k)/3$ is an integer could differences in intensities be established when comparisons were made in the manner just described. When $(h + 2k)/3$ is not an integer, the intensities never failed to correspond as well as could be expected to the values of S calculated by means of equation (1) for $u = 0.25$. Comparisons were also made between all forms having interplanar distances nearly equal, and found to be satisfactory.

5. Discussion of the Structure. Summary.

All the data obtained from three spectral photographs and two unsymmetrical Laue photographs confirm the structure of cadmium iodide represented in Figure 2. The positions of the iodine atoms were determined by comparing observed intensities of reflections with the intensities predicted assuming the reflecting powers of the atoms to be proportional to their atomic numbers. But with any reasonable assumption regarding reflecting powers the atoms would be placed close to the positions that have been chosen. This arrangement has been shown to be the only possible one if there is only one molecule in the unit. Arrangements involving more than one molecule in the unit, or involving a rhombohedral lattice have not been investigated.

In this arrangement the shortest distance between the centers of cadmium and iodine atoms is 3.00 angstroms; this happens to be exactly the sum of the Bragg radii⁴ for these atoms. The shortest distance between iodine atoms is 4.21 angstroms, a value much larger than that given by Bragg as the "diameter" of the iodine atom, namely 2.80.

⁴ W. L. Bragg, Phil Mag. 40. 180 (1920).

It is interesting to note that this arrangement is that found for Pyrochroit $\text{Mn}(\text{OH})_2$, by G. Aminoff⁵, who estimates the value of u to be $\frac{2}{9}$.

Pasadena, May 1922.

⁵ Zeit. für Krystallographie, 56, 127 (1921).

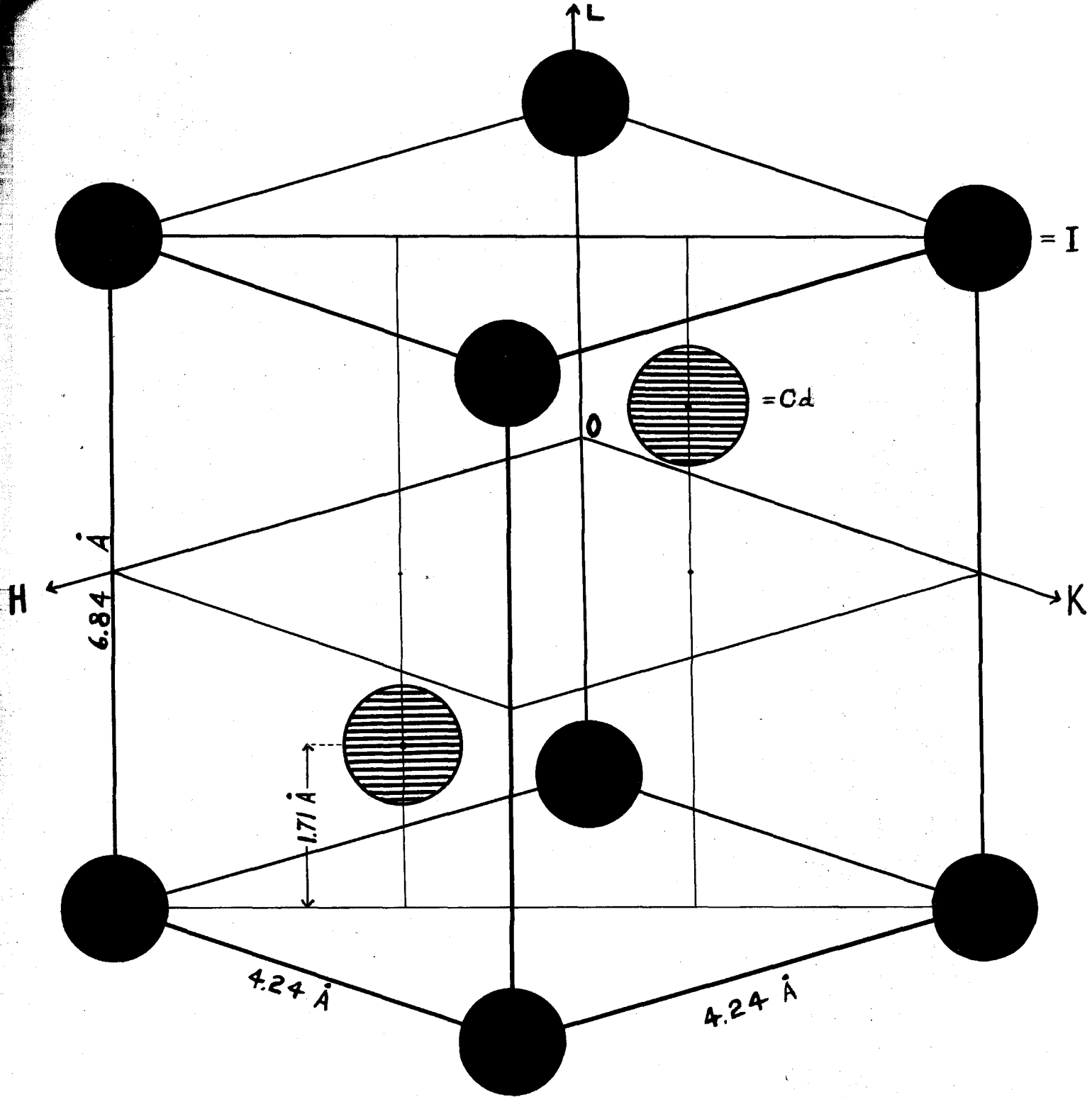


FIGURE 2

Arrangement of the atoms in cadmium iodide.

MONOGRAPH ON THE SEPARATION OF THE ISOTOPES

Richard M. Bozorth

I. Introduction

The existence of isotopes among non-radioactive elements was first discovered by J. J. Thomson¹ during his experiments on positive rays. When his discharge tube contained Neon, he found beside the line corresponding to an atomic weight 20, a faint line corresponding to an atomic weight 22. It has since been shown that Neon is really a mixture of two isotopes, and more recently Aston² has investigated a great number of elements and found that a large proportion of these are in reality mixtures of two or more isotopic forms.

Since the discovery of the two forms of Neon attempts have been made to separate those elements which are mixtures into their constituents. It is the purpose of this monograph to discuss the methods of separation which have been proposed, and the actual attempts at separation which have been made.

II. Properties.

The only properties in which isotopes differ distinctly are mass, and corresponding velocity of translation or agitation of the molecules. The other properties which have been investigated are enumerated below.

1. Atomic volume. Richards and Wadsworth³ found the density of lead to change with the atomic weight so that the atomic volume remained the same within the limits of experimental error, about 0.01%.

2. Solubility. Richards and Schumb⁴ determined the molecular solubilities of lead nitrates from ordinary lead and from radium lead, and found them to be the same within the limit of experimental error, less than 0.01%.

3. Electrochemical equivalence. Van Hevesy and Paneth⁵ measured the potential of the cell, Hg_2Cl_2 , $\text{Pb}(\text{NO}_3)_2$, PbO_2 , using a solution of $\text{Pb}(\text{NO}_3)_2$ from ordinary lead and then replacing this by a solution prepared from radium lead. When one $\text{Pb}(\text{NO}_3)_2$ solution

was substituted for the other he found no difference in the potential of the cell within 10 microvolts.

4. Absorption in charcoal. Aston⁶ absorbed neon in charcoal cooled by liquid air, then sucked off the gas from the charcoal after it had been warmed somewhat. He hoped that the first fraction which came off would be richer in the lighter isotope, but after 3000 distillations found no difference in density.

5. Spectral Properties. Harkins⁸ ^{and Cronberg⁷} ~~has~~ detected a difference in the wave lengths of the lead 4058 line in ordinary lead and radium lead. The difference in atomic weights of the two kinds of lead was 0.9, and the shift in the spectrum 0.0044 angstrom. Merton⁸ has confirmed this fact, finding a shift of 0.0050 ± 0.0007 angstrom, and finding also a shift in the other direction of 0.0022 ± 0.0008 angstrom for thorite lead having an atom weight about 0.6 unit greater than ordinary lead.

Loomis⁷ has suggested that in the absorption spectra of the hydrogen halides there is a difference in wave-length for isotopes, and he believes he has identified one line which is due to HCl_{35} alone, and one due to HCl_{37} . These are supposed to correspond to the frequencies of vibration of the hydrogen and chlorine nuclei along their line of centers.

In general, it is interesting to note that Baxter¹⁶ found the atomic weight of meteoric nickel to be 58.68, a value the same within the experimental error as the atomic weight of terrestrial nickel, 58.70, which he determined in the same manner. It seems likely; then, that elements are mixtures of isotopes in the same proportions throughout the solar system, and that no natural mechanical process exists which separates them.

III. Methods of Separation Dependent upon a Difference in Mass.

(1) By Positive Rays.

Aston⁶ estimates from the dimensions of his positive ray apparatus, that he could

construct a new apparatus which would separate the two isotopes of neon, in which 0.0005 of the total tube current of 10 milliamperes would be carried by the positive rays reaching the receiver. For such an apparatus, the volume of gas collected per hour, measured at 0° and 760 mm. would be

$$\frac{.0005 \times 0.010}{96500} \times 22400 \times 3600 = 0.004 \text{ cc.}$$

But it would be extremely difficult to fix even this small amount once it was separated into its components. It would be diluted by the gas which is present in the tube even at the low pressure attainable, and would require extreme cold to prevent its diffusing away.

(2.) In a Gravitational Field.

The presence of the isotopic mixture neon, in the atmosphere, suggests that at a great height above the surface of the earth the isotopes do not exist in the same relative proportions that they do at the surface. An approximation to the ratio of the two isotopes existing at any height can be calculated by assuming a constant temperature, say 250° K.

Let p_{20} = the partial pressure of Ne_{20} at a height, h , and ρ_{20} = density of Ne_{20} at a height, h ,

$$\text{then } dp_{20} = -dh \rho_{20} g, \text{ and } p_{20} \frac{M}{RT} = \rho_{20}$$

$$\text{Combining these, } -dh \rho_{20} g = d p_{20} \frac{RT}{M}, \text{ or } \rho_{20} = C e^{-\frac{gM}{RT} \cdot h}$$

$$\text{Let } \rho_{20} = \rho_{20}^0 \text{ when } h = 0,$$

$$\text{then } \rho_{20} = \rho_{20}^0 e^{-\frac{g \cdot 20 \cdot h}{RT}}$$

$$\text{Similarly, for } \text{Ne}_{22}, \rho_{22} = \rho_{22}^0 e^{-\frac{g \cdot 22 \cdot h}{RT}}$$

$$\text{and } \frac{\rho_{20}}{\rho_{22}} = \frac{\rho_{20}^0}{\rho_{22}^0} e^{\frac{2g}{RT} \cdot h}$$

At the surface of the earth, the molecular weight of Ne is 20.2, and $\frac{\rho_{20}}{\rho_{22}}$ is sup-

posedly $\frac{22 - 20.2}{20.2 - 20} = 9$. If a sample of air could be obtained from a height of 20 miles, or 1.2×10^6 cm., $\frac{P_{20}}{P_{22}}$ would be $9 \frac{2 \times 980 \times 3.3 \times 10^6}{8.3 \times 10^7 \times 250} = 12.27$, whence the molecular weight M given by $\frac{22 - M}{M - 20} = 12.27$ is 20.151 which differs from 20.2 by only 0.25%.

(3). By Centrifuging.

A centrifugal field is similar to a gravitational field and the equation which applies here may be obtained from the one just developed by replacing the acceleration g by $\omega^2 r$, where ω is the angular velocity and r the radius of the centrifuge. The relation may be derived also by equating the terms, $RT \ln \frac{P_0}{p}$ and $\frac{1}{2} M v^2$, which represent the work necessary to transfer a mole of gas from the center, where the pressure is P_0 , to the periphery, where the pressure is p . The equation obtained is

$$\frac{P_1}{P_2} = \frac{P_{0_1}}{P_{0_2}} \mathcal{Q}^{\frac{v^2}{2RT} (M_1 - M_2)}$$

where v is the peripheral velocity, and the subscripts refer to the two components of the mixture.

$$\text{For the gas HCl, } M = 36.46, \quad \frac{P_{0_1}}{P_{0_2}} = \frac{38 - 36.46}{36.46 - 36} = 3.3478.$$

For a centrifuge with an arm 30 cm. long, whirling at the rate of 5000 R. P. M., $v = 15,700$ cm. per second. This is about the speed ^{used} by Tolman^{10a} in his apparatus for producing electromotive force in solutions.

In this case $\frac{P_1}{P_2}$ at 300° K is $3.3478 \times \mathcal{Q}^{-0.01} = 3.3143$ whence at the periphery $M = 36.4636$, a difference of 0.01%. If a peripheral velocity 10^5 cm. per sec. can be obtained, $M = 36.62$, an increase of 0.5%. This large increase over the value 36.4636 is due to the fact that the value of the velocity appears as the square in the exponent of \mathcal{Q} .

Calculation of the equilibrium concentrations for a centrifuged liquid mixture is more difficult than that for a gas, for here the molecules are practically incompressible. Poole¹¹ has considered this problem, and gives an approximate solution which can be put into the form $\frac{c_1}{c_2} = \frac{c_{o1}}{c_{o2}} e^{\frac{v^2}{RT} (M_1 - M_2)}$, where ~~the~~ c_1 and c_2 refer to the molar concentrations at the periphery, and c_{o1} and c_{o2} are the average concentrations along the tube.

IV. Methods of Separation Dependent upon a Difference in the Speed of the Molecules.

(1) Effusion. If a mixture of gases is allowed to effuse from a small hole, the number of molecules of each kind which flow out is proportional to the number impacts per cm^2 . per sec. made by the molecules of that kind. The number of impacts $\frac{\text{per}}{\text{cm}^2} \frac{\text{per}}{\text{sec}}$ for any gas ~~is~~ determined by the kinetic theory is $1/4 n \bar{c}$ where n is the number of molec/cc. and \bar{c} is the mean velocity. Since for two gases $\frac{\bar{c}_A}{\bar{c}_B} = \sqrt{\frac{M_B}{M_A}}$, the ratio of the concentrations of two isotopes, A and B, in the gas which has flowed thru the opening, is $\frac{n_A}{n_B} \sqrt{\frac{M_B}{M_A}}$. For HCl, $\sqrt{\frac{M_B}{M_A}} = 1.028$, and the corresponding molecular weight of the effluent gas is 36.450.

(2) Rapid Evaporation. If the pressure of the vapor above a liquid could be kept at zero, the number of molecules evaporating from the liquid would be equal to the number of impacts of the molecules of the liquid upon the surface layer. When a liquid and its vapor are in equilibrium, the number of impacts of molecules upon the surface layer from the vapor and liquid sides must be equal. Consequently when there is no vapor phase present, the number of molecules evaporating per sq. cm. per sec. is equal to the number of impacts per cm^2 . $\frac{\text{per}}{\text{sec}}$ calculated for the vapor, namely $1/4 n \bar{c}$. This expression can be evaluated in terms of p , T and M , and it can be easily shown that the number of moles, N , evaporating per sq. cm. per sec. is $\frac{p}{\sqrt{2\pi RTM}}$. This relation has been derived and tested experimentally at low pressures by Volmer and Estermann.¹² For two isotopes,

$\frac{N_1}{N_2} = \frac{p_1}{p_2} \sqrt{\frac{M_2}{M_1}}$, or if x_1 and x_2 are mole-concentrations in the liquid state, $\frac{N_1}{N_2} = \frac{x_1}{x_2} \sqrt{\frac{M_2}{M_1}}$. A separation could thus be obtained by collecting very quickly the vapor from a rapid evaporation.

(3) Diffusion. The Rayleigh diffusion theory¹³ assumes that the diffusion coefficient of each gas is inversely proportional to its molecular weight. Then if x and y are the

molar concentrations of the two gases in the residue and x and y the initial concentrations, the following equations hold:

$$dy = ky \frac{1}{\sqrt{M_y}}$$

$$dx = Kx \frac{1}{\sqrt{M_x}}$$

$$\text{therefore } \frac{dy}{dx} = \frac{y \sqrt{M_x}}{x \sqrt{M_y}}$$

This may be put into the form:

$$\frac{x+y}{x_0+y_0} = \frac{x_0}{x_0+y_0} \left(\frac{y/x}{y_0/x_0} \right)^{\frac{\sqrt{M_x}}{\sqrt{M_y}-\sqrt{M_x}}} + \frac{y_0}{x_0+y_0} \left(\frac{y/x}{y_0/x_0} \right)^{\frac{-\sqrt{M_y}}{\sqrt{M_y}-\sqrt{M_x}}}$$

For an equimolar mixture of two isotopes, this may be approximately expressed as follows:

$$\frac{y/x}{y_0/x_0} = \sqrt{\frac{x+y}{x_0+y_0}} = \frac{\text{final volume}}{\text{initial volume}}$$

or, the ratio of the two constituents after diffusion, divided by the ratio before diffusion, is proportional to M^{th} root of the ratio of the volumes before and after diffusion.

For mixtures not equimolecular, the more general equation above must be used.

The diffusion coefficients are inversely proportional to the molecular weights only as a first approximation. Using Boynton's expression for the diffusion coefficient, and assuming equal diameters for the two isotopes, the ratio of the diffusion coefficients

is found to be $\frac{m_2}{m_1} \cdot \frac{\sqrt{2m_1} + \frac{m_1}{m_2} \sqrt{m_1+m_2}}{\sqrt{2m_2} + \frac{m_2}{m_1} \sqrt{m_1+m_2}}$ This differs

appreciably from $\frac{\sqrt{m_2}}{\sqrt{m_1}}$; for example for HCl when $n_1 = n_2$ $\frac{\sqrt{m_2}}{\sqrt{m_1}} = 1.027$, while the above expression gives 1.070. This is a large discrepancy, and if the latter value is really the correct one Rayleigh's theory makes the separation seem much slower than it really is.

(4) Thermal Diffusion. Chapman¹⁵ has calculated the separation of isotopes in a mixture under a temperature gradient instead of a pressure gradient. He finds for the same values of $\frac{P_1}{P_2}$ and $\frac{T_1}{T_2}$ that thermal diffusion is about three times as efficient as pressure diffusion. According to his formulae, the atomic weight of neon could be changed by 0.001 unit by one diffusion, keeping the extreme temperatures 80° and 800° K.

V A Method Dependent upon a Difference in Light Absorption Spectra.

This method has been suggested by Merton and Hartley,¹⁶ and depends for success upon a difference in the absorption spectra of the two isotopes of HCl, HBr, or HI. Suppose there is a narrow band of light of wave-length λ_1 , absorbed by HCl₃₇ but not by HCl₃₅; and a corresponding band of equal width of wave-length λ_2 , absorbed by HCl₃₅ but not by HCl₃₇. The law of light absorption may be expressed $I = I_0 e^{-\alpha x}$, where I_0 is the original intensity of the beam, and I is the intensity after it has passed through a thickness, x , of material whose absorption coefficient is α . Let a beam of white light pass thru a column of ordinary chlorine until all but 0.001 of the light of wave-length λ_1 has been absorbed; i.e., until $\frac{I_{\lambda_1}}{I_0} = 10^{-3}$. Since there is about three times as much Cl₃₅ as Cl₃₇ in ordinary chlorine, light of wave-length λ_2 will be absorbed by 3 times as much material. This is equivalent to saying that x for λ_2 is 3 times x for λ_1 . Then $\frac{I_{\lambda_2}}{I_0} = e^{-\alpha(3x)} = \left(\frac{I_{\lambda_1}}{I_0}\right)^3 = (10^{-3})^3 = 10^{-9}$ and $\frac{I_{\lambda_2}}{I_{\lambda_1}} = 10^{-6}$

Upon passing this filtered light thru a mixture of hydrogen and chlorine, the light of wave-length λ_1 will activate H and Cl₃₇ while H and Cl₃₅ will not combine appreciably because the activating wave-length, λ_2 , is almost entirely absent. The resulting HCl will then be almost entirely HCl₃₇.

VI. Actual Attempts to Separate Isotopes.

Besides the experiments described in Section II, there have been several more serious attempts to obtain actual separation. These are enumerated below in the order in which the experiments were performed.

(1) By Diffusion. Aston¹⁷ diffused neon thru clay pipstem and obtained a difference in density between the light and heavy fractions of 0.7%. Repeated experiments showed a difference of but 0.3%.

Harkins¹⁸ diffused HCl in a similar way and obtained a difference in density of about, 0.1%

(2) By Centrifuging. Joly and Poole¹⁹ centrifuged molten lead, attaining a peri-

pheral velocity of 10^4 cm. per sec., but could detect no separation. They calculate a difference in density of only 0.005%, too small for their methods to detect.

(3) By Rapid Evaporation. Bronsted and von Hevesy²⁰ distilled mercury at about 50° in a high vacuum, condensing the vapor on the surface of a flask filled with liquid air. By repeating this process many times these men succeeded in obtaining a difference in density between the final distillate and residue of 0.05%, corresponding to 0.1 unit in atomic weight. In all they distilled 2700 cc. of mercury, obtaining 650 cc. of distillate and 2050 cc. of residue.

Bronsted and von Hevesy²¹ have by this same method separated the isotopes of chlorine, by evaporating a strong solution of HCl at -50° C. They obtained a difference in the atomic weights of the lighter and heavier portions of 0.02 unit.

Millikan and Harkins²² have separated mercury in essentially the same way that Bronsted and von Hevesy have. Their separation corresponds to 0.03 unit in atomic weight.

(4). By Effusion. Bronsted and von Hevesy²⁰ passed a stream of mercury vapor thru a tube in the wall of which was inserted a platinum disc perforated by 1000 holes having a diameter of 0.15 mm. The fraction of the mercury passing thru these holes was found to differ in density from ordinary mercury by 0.001%.

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