

dom from the necessity of electrodeposition of a metal, apparent absence of poisoning effect, freedom from both manipulation and control of a gas phase.

Summary

1. The antimony electrode made of commercial stick antimony was a satisfactory substitute for the hydrogen electrode in the electrometric estimation of magnesium in its salts and in mixtures of calcium and magnesium salts.

2. Calcium could be present to the extent of eight to twenty-five times the amount of magnesium.

3. The minimum concentration of MgO was 0.10 g. in 150 cc. of solution. At low dilutions the results were unsatisfactory if calcium was present in any appreciable amount, or was even equivalent in amount to the magnesium.

COLUMBUS, OHIO

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 306]

THE FREE ENERGY, HEAT CONTENT AND ENTROPY OF IODINE MONOCHLORIDE

BY JOHN McMORRIS AND DON M. YOST

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Introduction

The absorption bands of iodine monochloride have been studied by Gibson and Ramsperger,¹ Wilson,² Curtis and Darbeyshire³ and Curtis and Patkowski;⁴ and from the results of this work the thermodynamic constants of iodine monochloride may be computed. The uncertainties in interpretation of these spectroscopic data, however, make it desirable that the thermodynamic constants be also derived from some entirely independent source. Two separate chemical studies of this problem are presented in this paper.

The combination in the vapor phase of iodine and chlorine to form iodine monochloride is not accompanied by a change in the total number of molecules. Since there is no total pressure change, the methods employed in this research for studying the reaction are necessarily indirect.

The first method used depends upon the presence of solid barium chloroplatinate which is in equilibrium with the chlorine, barium chloride and platinum, of which only the chlorine reacts with iodine. The dissocia-

¹ Gibson and Ramsperger, *Phys. Rev.*, **30**, 598 (1927).

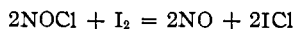
² Wilson, *ibid.*, **32**, 611 (1928).

³ Curtis and Darbeyshire, *Trans. Faraday Soc.*, **27**, 77 (1931).

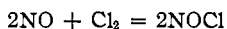
⁴ Curtis and Patkowski, *ibid.*, **25**, 725 (1929); *Nature*, **127**, 707 (1931).

tion pressures of barium chloroplatinate as a function of temperature have already been determined by Gire.⁵ Starting with pure iodine and barium chloroplatinate, two molecules of iodine monochloride will result for each molecule of iodine reacting and the equilibrium state can then be determined by measuring the resulting pressure increase. This will be designated in the later discussion as Method I.

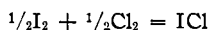
A study was also made of the reversible gas phase reaction



and the results were combined with the data of Dixon⁶ for the reaction



thus making it possible to calculate the equilibrium constants at various temperatures for the reaction



This will be designated as Method II. In all cases iodine monochloride was observed in the reaction vessels at the conclusion of the experiments.

An attempt was also made to study the reaction between phosgene (COCl_2) and iodine, but it was found to be immeasurably slow at temperatures below 200°.

Experimental Method I

A Pyrex bulb of known volume was charged with about seven grams of very dry barium chloroplatinate. One side arm of small bore Pyrex tubing connected the reaction bulb to a glass diaphragm click gage which was in turn connected to the manometer system. Another side arm contained an evacuated glass capsule within which was an accurately weighed amount of pure iodine. The capsule had a tip which could be broken readily by means of a glass-inclosed iron plunger and an external solenoid. A tube by-passing the click gage was provided so that, in evacuating the reaction vessel, no excess pressure would be exerted on either side of the diaphragm. An electric furnace, built according to the recommendations of Gray,⁷ surrounded the reaction bulb. Since the temperature required for the reaction to be conveniently measurable was in the region of 400°, the inclusion of the click gage within the furnace was impracticable. The gage was therefore allowed to project a few centimeters from the furnace and was separately heated to a constant temperature of 150° by a small second furnace immediately adjoining the larger one.

The click gage was accurately calibrated before connecting the gage to the reaction bulb. The constants for the gage used were found to be independent of the temperature over the range from 25 to 175°. After sealing on the click gage, the system was evacuated and the large furnace brought to a temperature of 300°. The system was re-evacuated every few hours for a period of three days, after which time the gain in pressure in the system overnight was less than 0.1 mm. The furnace was then heated to 490°, producing a pressure of chlorine from barium chloroplatinate of about 20 mm., the click gage was heated to 150° and the chlorine was pumped off several times. The by-pass tube was then sealed off, the furnace cooled, and the constants of the click gage re-

⁵ Gire, *Ann. chim.*, 4, 186 (1925).

⁶ Dixon, *Z. physik. Chem.*, Bodenstein Festband, 679 (1931).

⁷ Gray, Publication of Bureau of Standards, S219.

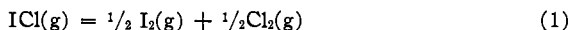
determined. All experiments were carried out at a temperature below 490°; the prolonged baking out doubtless prevented any interference from the presence of water vapor or other foreign gas at the lower temperatures. During these preliminary manipulations, the temperature variation over the length of the large furnace was also determined and the ends were found to be less than one degree cooler than the center. The temperatures were measured by means of chromel-alumel thermocouples calibrated against standardized thermometers, the boiling point of purified naphthalene and the freezing point of zinc.

When the furnace had cooled to room temperature, the iodine capsule was broken by means of the magnetic device. The iodine was driven over into the reaction bulb and the side arm was then sealed off and removed. The furnace surrounding the click gage was heated to 150° and the reaction bulb was heated to the temperature of the experiment.

The chemicals used were of high quality. The iodine was of analytical quality marked 99.97% pure. The barium chloroplatinate was prepared by carefully neutralizing chloroplatinic acid with barium hydroxide solution and dehydrating the resulting solution in a vacuum desiccator over sulfuric acid.

Results of the Experiments

The reaction whose equilibrium constant is to be found is



The corresponding mass action expression is

$$\frac{(\text{I}_2)^{1/2} (\text{Cl}_2)^{1/2}}{(\text{ICl})} = K \quad (2)$$

The partial pressure of the chlorine at any given temperature is fixed and is calculated from the following formula, which was constructed from Gire's data

$$\log_{10} p_{\text{mm}} = -\frac{6171}{T} + 9.356 \quad (3)$$

Some pressure measurements, made at various temperatures before admitting iodine, confirmed Gire's results.

If p_1 is the partial pressure of chlorine, p_2 the calculated pressure of iodine for no reaction and p_3 the total pressure in the system, then

$$2(p_3 - p_1 - p_2) = \text{partial pressure of ICl} \quad (4)$$

$$2p_2 - p_3 + p_1 = \text{partial pressure of I}_2 \quad (5)$$

In Table I are presented the results of the experiments. Equilibrium was approached from both directions but the extreme slowness of the reaction made the exact attainment of equilibrium somewhat uncertain. Five or six days were usually required to reach a constant pressure in the system. The most accurate values of K are probably those for 681.7 Å. and 682.8 Å., not merely because of their good agreement but also because the rate of reaction is much greater than at the lower temperatures and because the magnitudes of the various partial pressures are less subject to errors than those at the higher temperatures. It is to be noted that the pressure of chlorine varied twenty-fold over the range

of temperatures investigated. Quantities of iodine differing by 20% were used in two different sets of experiments. All pressures are expressed in mm. of mercury.

TABLE I

Temperature, °K.	681.7	641.1	667.9	667.6	736.6	746.4	682.8
Pressure of Cl ₂ = <i>p</i> ₁	2.01	0.54	1.31	1.30	9.51	12.22	2.08
Pressure (initial) of I ₂ = <i>p</i> ₂	205.1	192.8	200.9	158.5	174.7	177.3	162.1
Total pressure (observed) = <i>p</i> ₃	350.8	280.9	352.6	239.5	342.3	356.6	281.6
Pressure of ICl	287.4	175.0	300.8	159.4	316.2	334.2	234.8
Pressure of I ₂ (final)	61.4	105.3	50.5	78.8	16.6	10.2	44.7
<i>K</i>	0.0386	0.0431	0.0270	0.0633	0.0398	0.0335	0.0411
log ₁₀ <i>K</i>	-1.41	-1.37	-1.57	-1.20	-1.40	-1.42	-1.39

Experimental Method II

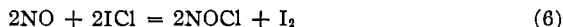
The reaction vessel of known volume consisted of a Pyrex bulb equipped with a click gage, a closed side arm, an open side arm and a tube by-passing the click gage. The closed side arm contained a capsule inclosing very pure nitrosyl chloride and a glass incased iron plunger. After introducing through the open side arm an evacuated glass capsule containing a known weight of iodine, the side arm was sealed off. The apparatus was then evacuated and baked out. The by-pass tube was sealed off and removed. The nitrosyl chloride in the side arm was then frozen with liquid air, the capsule broken, and the nitrosyl chloride allowed to evaporate. After coming to room temperature the pressure and temperature of the nitrosyl chloride were carefully determined. The iodine capsule was broken by shaking the reaction bulb. The apparatus was then connected to the manometer system and both the reaction bulb and gage were submerged in an electrically heated oil thermostat.

Experiments were made at various temperatures and with two separate loadings of the apparatus. The reaction was found to be rapid and readily reversible, less than an hour being required for constant pressure to be attained. Most of the final readings were made, however, after twenty-four hours with the given temperature held constant to $\pm 0.2^\circ$.

The iodine used was of the same quality as that previously employed. The nitrosyl chloride was kindly furnished by Mr. J. Leermakers from the material prepared by him for the determination of its absorption spectrum.⁸

Results of the Experiments

From these experiments the equilibrium constant can be calculated for the reaction



and is given by the expression

$$\frac{(\text{NOCl})^2(\text{I}_2)}{(\text{NO})^2(\text{ICl})^2} = K_1 \quad (7)$$

Starting with NOCl and I₂, the total pressure measured will be greater by Δp than the sum of the NOCl and I₂ pressures calculated for no reaction. If *p*₁ and *p*₂ are the pressures of iodine and nitrosyl chloride, respectively, assuming no reaction, then 2 Δp is equal to the partial pressure of the iodine monochloride and also that of the nitric oxide while

⁸ Leermakers and Ramsperger, *THIS JOURNAL*, **54**, 1837 (1932).

$p_1 - \Delta p$ and $p_2 - 2\Delta p$ give the partial pressures of the iodine and nitrosyl chloride, respectively. All pressures are expressed in millimeters and the values of K_1 in atmospheres.

TABLE II
RESULTS OF THE EQUILIBRIUM MEASUREMENTS

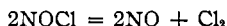
$T, ^\circ\text{C.}$	Initial pressure		Pressure increase, Δp	Equilibrium pressure of				$K_1, \text{atm.}$	$\log_{10} K_1$
	I_2	NOCl		NO	NOCl	I_2	NOCl		
136.4	162.2	320.8	588.8	105.8	211.6	56.4	109.2	0.255	-0.593
136.9	156.9	321.2	582.5	104.4	208.8	52.5	112.4	.265	- .577
145.5	160.2	328.0	598.1	109.9	219.8	50.3	108.2	.192	- .717
149.0	167.2	330.7	611.8	113.9	227.8	53.3	102.9	.159	- .799
153.6	169.0	334.3	620.4	117.1	234.2	51.9	100.1	.131	- .883
164.4	167.4	342.8	632.8	122.6	245.2	44.8	97.6	.0897	-1.047
178.8	172.9	354.0	658.3	131.4	262.8	41.5	91.2	.0550	-1.260

The equation relating the equilibrium constant K_1 in atmosphere units with temperature is

$$\log_{10} K_1 = \frac{2888}{T} - 7.638 \quad (8)$$

Thermodynamic Constants of Iodine Monochloride

J. K. Dixon⁸ recently has made a very careful study of the reversible reaction



and finds that the equilibrium constants $K_2 = (\text{NO})^2(\text{Cl}_2)/(\text{NOCl})^2$ in atmospheres may be represented as a function of the temperature by the equation

$$\log_{10} K_2 = -\frac{3860}{T} + 3.348 \log_{10} T - 0.002457T - 1.1275 \quad (9)$$

It follows at once that $(K_1 K_2)^{1/2} = K$ where K is the equilibrium constant for reaction (1).

In Table III are given the data leading to values of K at the various temperatures investigated by Method II.

TABLE III
EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF NITROSYL CHLORIDE AND IODINE MONOCHLORIDE

Temp., $^\circ\text{C.}$	$10K_1$	$\log_{10} K_1$	$10^4 K_2$	$\log_{10} K_2$	$10^3 K$	$\log_{10} K$
136.4	2.55	-0.593	3.09	-3.510	8.89	-2.051
136.9	2.65	- .576	3.16	-3.500	9.16	-2.038
145.5	1.91	- .718	5.04	-3.298	9.82	-2.008
149.0	1.60	- .796	6.08	-3.216	9.86	-2.006
153.6	1.31	- .882	7.66	-3.116	10.02	-1.999
164.4	0.898	-1.047	13.12	-2.882	10.84	-1.965
178.8	.552	-1.258	25.71	-2.590	11.91	-1.924

When the values of $\log_{10} K$ in the last column are plotted against the corresponding reciprocal temperatures, a straight line may be drawn through the points with an uncertainty of about 10% in the slope. The

points for the three highest temperatures fall very closely on a straight line from whose slope ΔH is found to be 2620 cal. However, the remaining four points fall somewhat to one side of this line so that the best linear representation of all the points is a line whose slope gives ΔH the value 2500 cal. Considering the fact that the whole temperature range is only 42° , not a great deal of reliance should be placed on any value of ΔH computed from the results of these experiments alone.

A value of ΔH obtained by combining the data from experiments using Method I with those using Method II is probably much more reliable, since the extreme temperature interval is then 337° and the constants for each set of experiments are probably reasonably good. The value of ΔH so derived is 3125 cal. The experimental error involved in this result is estimated to be between ± 5 and $\pm 10\%$, the value of ΔH given being probably low.

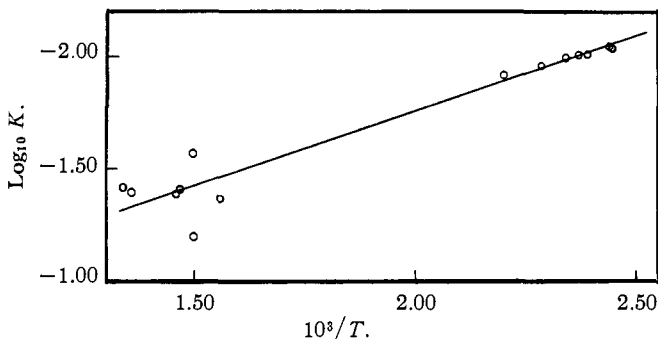
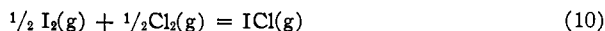


Fig. 1.—Equilibrium constants for the dissociation of gaseous iodine monochloride.

A graph of $\log_{10} K$ against $1/T$ for all experiments by both methods is shown in Fig. 1.

The free energy equation which best represents the experimental data for the reaction



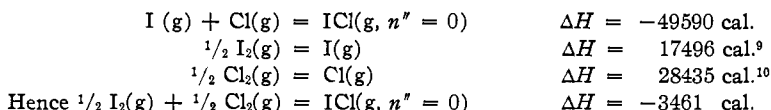
is

$$\Delta F^\circ = -3125 - 1.77T \quad (11)$$

Since for a reaction of this type ΔC_p is certainly small, the absence of non-linear terms does not affect the validity of the equation even over a fairly large temperature range.

The spectroscopical investigations of iodine monochloride make it possible to derive, quite independently, a free energy equation for reaction (11). Gibson and Ramsperger¹ and Wilson² have determined the absorption limit corresponding to the dissociation of the monochloride. If we take their value and assume that the dissociation results in normal atoms and if, in accordance with the extensive work of Patkowski

and Curtis,⁴ the absorption is due to molecules in their lowest vibrational state, then the following thermochemical equations may be written.



This value of -3461 cal. refers to the absolute zero of temperature and must be corrected to ordinary temperatures before a comparison with the thermochemical value may be made. It may be shown, however, that the heat of the reaction depends but little on the temperature and the correction is therefore very small. The agreement between the spectroscopic and thermochemical values of ΔH is quite satisfactory.

If the dissociation of the iodine monochloride by radiation were to result in an activated chlorine atom, the value of ΔH would be -2041 cal. or -951 cal. depending on whether the absorbing molecule were in the first or in the lowest vibrational state. If, on the other hand, the dissociation products are normal atoms, then ΔH has the value -4551 cal. if the absorbing molecule is in the first vibrational state and -3461 cal. if in the lowest state. All of these values except the last differ from that obtained from the equilibrium measurements by an amount considerably greater than corresponds to the experimental error. The present results show, therefore, that the absorption limit results from a molecule in its lowest vibrational state being dissociated into normal atoms of iodine and chlorine.¹¹ It may also be added that Thomsen's calorimetric result combined with accurately known heat data gives $\Delta H = -3748$ cal., which gives added support to this conclusion.

It is also possible to compare the present value of 1.77 cal./deg. for ΔS of reaction 10 with that derived spectroscopically. Using Giauque's¹² values of 62.29 cal./deg. and 53.31 cal./deg. for the entropies of iodine and chlorine vapors, respectively, and the value 59.2 cal./deg. for iodine monochloride vapor which we have calculated from spectroscopic data,¹¹ a value of $\Delta S = 1.40$ cal./deg. is found. This is in satisfactory agreement with the thermochemical value.

The two standard free energy equations obtained from entirely independent types of experiments are then

$$\begin{aligned} \frac{1}{2} \text{I}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) &= \text{ICl(g)} & (10) \\ \Delta F^\circ &= -3125 - 1.77T \text{ (thermochemical measurements)} & (12) \\ \Delta F^\circ &= -3461 - 1.40T \text{ (spectroscopic measurements)} & (13) \end{aligned}$$

⁹ Brown, *Phys. Rev.*, **38**, 709 (1931).

¹⁰ Sponer, Landolt-Börnstein-Roth, "Phys. Chem. Tab.," Julius Springer, Berlin, 1931, Part 2, second Ergänzungsband, p. 1615.

¹¹ This same behavior is also observed in the case of iodine monobromide. Cf. Badger and Yost, *Phys. Rev.*, **37**, 1548 (1931).

¹² Giauque, *THIS JOURNAL*, **53**, 507 (1931); **54**, 1731 (1932).

The thermodynamic constants of iodine monochloride may be calculated from the present results by combining them with the following thermal data. For iodine the values given in a previous paper¹³ will be used and for the entropy of chlorine we use the value 53.31 cal./deg. employed above. The vapor pressure of liquid iodine monochloride has been accurately measured by one of us (D. M. Y.)¹⁴ and is given by the empirical equation

$$\log_{10} p_{\text{mm}} = -\frac{2079.7}{T} + 8.5038 \quad (14)$$

from which the free energy change attending vaporization at 25° has been calculated. Thomsen's¹⁵ value for the heat of formation of the monochloride is also presented but not used in any of the calculations. We use 2668 cal.¹⁶ for the heat of fusion of the solid monochloride at the melting point, 27.2°.

Table IV contains the so-calculated thermodynamic constants at 25° (expressed in calories) for one mole of the substance given in the first column. The reference states are indicated in each case. In the case of entropy values the state referred to is that indicated in the first row, the gases being present at a pressure of one atmosphere. The values for the heat contents given in parentheses are based on Thomsen's determination of the heat of formation of the liquid monochloride and are not employed elsewhere in the table.

TABLE IV
THERMODYNAMIC CONSTANTS OF IODINE MONOCHLORIDE AT 25°

Substance	ICl(g)	ICl(g)	ICl(l)	ICl(s)
Reference substances	I ₂ (g)	I ₂ (s)	I ₂ (s)	I ₂ (s)
	Cl ₂ (g)	Cl ₂ (g)	Cl ₂ (g)	Cl ₂ (g)
Free energy (thermochemical)	-3653	977	- 867	- 887
Free energy (spectroscopical)	-3879	751	-1093	-1113
Heat content (thermochemical)	-3125	4313	-5207	-7875
	(-3748)	(3690)	(-5830)	(-8498)
Heat content (spectroscopical)	-3461	3977	-5543	-8211
Entropy (thermochemical)	59.6	59.6	57.0	48.1
Entropy (spectroscopical)	59.2	59.2	56.6	47.7
Heat of vaporization			9520	12,188

Discussion

As pointed out in a former paper,¹³ the entropies of the diatomic interhalogen compounds in the gaseous state appear to lie between those of the diatomic elements from which they are formed, and the data for iodine

¹³ McMorris and Yost, *THIS JOURNAL*, **53**, 2625 (1931).

¹⁴ The experiments were carried out with the assistance of Mr. John B. Hatcher and the results have not been published. The values calculated from the equation agree with the observations to within the limits of experimental error ≈ 0.2 mm. The equation is valid over the temperature range 0 to 70°, the liquid being supercooled below 27.2°, the melting point.

¹⁵ Thomsen, *Ber.*, **15**, 3021 (1882).

¹⁶ "International Critical Tables," 1929, Vol. V, p. 131.

monobromide and bromine monochloride were adduced in support of this statement. The value obtained for iodine monochloride is also in complete accord with this ordering of the entropies. The values of the entropy changes attending the formation of iodine monobromide and monochloride from the gaseous diatomic elements do not differ greatly (1.74, 1.77 (1.40)) and this fact might indicate that the same would be true for bromine monochloride and chlorine monofluoride, but the value calculated for bromine monochloride is less numerically than those just given and of opposite sign. However, the data available¹⁷ are stated to be in error by an amount that could give a positive value for ΔS of the order of magnitude found for iodine monobromide and chloride.

In Table V are given the entropy values for the halogens and diatomic interhalogen compounds at 25° and one atmosphere.

TABLE V
ENTROPIES OF THE HALOGENS AND DIATOMIC INTERHALOGEN COMPOUNDS AT 25° AND ONE ATMOSPHERE

Substance	I ₂	IBr	ICl	Br ₂	BrCl	Cl ₂	ClF	F ₂
Entropy	62.29	62.2	59.15	58.63	56.9	53.31	?	48.0

It is to be noted that the order of the substances is that which would obtain if the chemical and physical properties were used instead of the entropies.

Summary

The equilibrium between barium platinic chloride, barium chloride, platinum, gaseous iodine and iodine monochloride, and that between nitrosyl chloride, nitric oxide, iodine and iodine monochloride have been measured. From the results the free energy equation for the reaction $\frac{1}{2} \text{I}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) = \text{ICl}(\text{g})$ has been found to be $\Delta F^\circ = -3125 - 1.77T$.

This resulting value of ΔH (-3125 cal.) was used to interpret existing spectroscopical data. A free energy equation, $\Delta F^\circ = -3461 - 1.40T$, was then derived using spectral data alone.¹⁸ The agreement between the two equations is satisfactory.

¹⁷ Jost, *Z. physik. Chem.*, [A] **153**, 143 (1931).

¹⁸ W. G. Brown, in a recently received private communication, has kindly given us the results of his recent spectroscopic investigation of iodine monochloride, bromine and chlorine. He finds the entropies of these substances to be 59.15, 58.63 and 53.29 cal./deg., respectively. Using his newly determined values for the entropies and heats of dissociation of iodine monochloride and chlorine, the standard free energy equation for reaction (10) becomes $\Delta F^\circ = -3280 - 1.36T$. The value $\Delta H = -3280$ cal. is in excellent agreement with the one derived from the results of the equilibrium experiments, -3125 cal. The new data have been used in reconstructing Table V but are not employed elsewhere. The new entropy value for bromine has changed those for iodine monobromide and bromine monochloride, but this does not, of course, affect the free energy equations for the latter substances.

With iodine and chlorine in their standard states of solid and gas, the free energies of formation of the various forms of iodine monochloride as determined by physical chemical methods are as follows: ICl(g) , 977 cal.; ICl(l) , -867 cal.; ICl(s) , -887 cal.

The degree of dissociation of iodine monochloride gas into gaseous iodine and chlorine has the value 0.42% at 25° and 1.58% at 100°.

The entropy of ICl(g) at 25° and one atmosphere is 59.6 cal./deg. (59.2 cal./deg. spectroscopical).

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE CRYSTAL STRUCTURE OF RHOMBIC AMMONIUM NITRATE

By C. D. WEST

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No x-ray measurements on the rhombic form (IV) of ammonium nitrate have been published other than the three axial lengths. In addition to rounding out the univalent nitrate group, a complete structure is desirable for the interpretation of some of the unusual properties of this compound, such as birefringence, polymorphism and plastic deformation.

Crystallographic.—According to Groth the crystals are of the rhombic bipyramidal class, axial ratios 0.9092 : 1 : 1.0553, density 1.725, optic axial plane (100), acute bisectrix b . Bowen¹ found $2V = 35^\circ$ and the refractive indices: electric vector parallel to b , $\alpha = 1.41$; parallel to a , $\beta = 1.61$; parallel to c , $\gamma = 1.64$. This form is stable only in the interval -16 to +32°.

Methods.—Recrystallization from water at room temperature gave suitable (110) prisms. Molybdenum radiation was employed exclusively; it was filtered in taking powder photographs and a set of 30° oscillation diagrams about the three axes. In a set of Laue patterns with the primary beam nearly parallel to the three axes, the minimum wave length was 0.30 Å. Intensities of reflections were estimated visually. All Miller indices refer to the above axes.

Lattice Constants.—The constants determined from zero lines of accurate rotation photographs are: $a = 4.92_3$, $b = 5.43_4$, $c = 5.73_2$, ratios 0.9069 : 1 : 1.0548, $Z = 2$, $V = 76.7$, density = 1.720. The former are identical with Bragg's values to three figures.²

Choice of Structure.—The only systematic extinctions noted were for $(0kl)$ when $k + l$ is odd; assuming holohedral symmetry this indicates V_h^{13} . In disposing the atoms in this space-group primary consideration was

¹ N. L. Bowen, *J. Phys. Chem.*, **30**, 722 (1926).

² W. H. Bragg, *Trans. Faraday Soc.*, **20**, 59 (1924).