3. Electrodes reproducible to within ± 1 millivolt can be secured by making the dilute solutions with water recently boiled and cooled in hydrogen, the dilution taking place in an atmosphere of hydrogen, with the measurements being made while hydrogen is bubbling through the electrode vessel.

4. Using the precautions just described, the electrode potential of zinc in 0.5, 0.1, 0.01 and 0.002 $N$ concentration of zinc sulfate have been measured at room temperature. Calculated values based on the electrolytic dissociation of the zinc salt and these measurements are in good agreement with each other.

5. The Nernst electromotive formula is applicable within the range quoted.

6. In order to measure very small changes in zinc-ion concentration, the zinc electrode even with the precautions described, is not satisfactory. Possibly dilute zinc amalgam electrodes, with extreme precautions for the avoidance of oxygen, would serve the purpose.

---

# THE CRYSTAL STRUCTURES OF THE AMMONIUM HALIDES ABOVE AND BELOW THE TRANSITION TEMPERATURES.

BY GUY BARTLETT AND IRVING LANGMUIR.

Knowledge of the geometrical arrangement of atoms in crystals, which is now available as a result of X-ray crystal analysis, should lead to more definite conceptions of the shapes of atoms and the forces around them. In a recent paper[1] it was pointed out from considerations of atomic structure, that the ions of sodium, potassium, fluorine and chlorine should have cubic symmetry while the ammonium ion, like methane, should have tetrahedral symmetry. This conclusion was thought to receive support from the difference in the crystal structures of potassium and ammonium chlorides. The halides of sodium and potassium have simple cubic lattices such as would be expected if the crystals were built up of alternate cubical ions of alkali and halogen with their faces in contact. Each ion is surrounded by 6 equidistant ions of the opposite polarity. Bragg[2] found that the ions in ammonium chloride are arranged in a centered cubic lattice so that each ion is surrounded by 8 equidistant ions of the opposite polarity. It was suggested that the "tetrahedral ammonium ions force the chlorine ions to arrange themselves symmetrically with respect to faces or corners of the tetrahedrons." It was pointed out that the

---

[1] Langmuir, THIS JOURNAL, **41**, 1547 (1919).

[2] W. H. Bragg and W. L. Bragg, "X-Rays and Crystal Structure," *London*, 1916, p. 158.

apparently complete isomorphism betweem ammonium and potassium sulfates is probably to be ascribed to the relatively large volumes of the sulfate ion.

Groth[1] gives potassium and ammonium chlorides as belonging to the same sub-group of the cubic system, the pentagon-icositetrahedric. Yet from evidence on the formation of mixed crystals it is concluded that these salts are not strictly isomorphous. However, a second form of ammonium chloride, stable only at high temperatures, is probably to be regarded as isomorphous with potassium chloride. Ammonium bromide was found to be isomorphous with ammonium chloride while the iodode is isomorphous with potassium chloride.

These relationships have been studied in detail by P. W. Bridgman,[2] who used pressures up to several hundred atmospheres and temperatures up to 200°. In this way he was able to discover a second modification of ammonium iodide analogous to those of the chloride and bromide. The transition temperatures at ordinary pressures are 184.3° for the chloride, 137.8° for the bromide and —17.6° for the iodide. Bridgman suggested that this new low temperature form of the iodide would be found to be isomorphous with the ordinary (low temperature) forms of the chloride and bromide.

These conclusions seem to be in accord with the conception of a tetrahedral symmetry for the ammonium ion. Thus at low temperatures, where the ions are packed more closely, the shape of the ammonium ion exerts a predominating influence and causes the lattice to assume the centered cubic form. At higher temperature, as the distances between the ions increase, the shape of the ammonium ions becomes of relatively less importance, and the lattice changes to the more common (for salts at least) simple cubic form.

Just as in the case of the sulfates of potassium and ammonium, the shape of the ammonium ion plays a smaller part when the anion is of large volume. Thus the greater the atomic volume of the halogen ion the lower the temperature at which the transformation takes place.

No data are available on polymorphism of ammonium fluoride but a consideration of Bridgman's data for the other ammonium halides suggests that the fluoride likewise may occur in 2 isometric forms, with a transition temperature higher than that of the chloride. Marignac[3] reported, however, ammonium fluoride as in the hexagonal system.

The following experiments were undertaken to determine definitely the relationships between the various ammonium halides, especially in regard to their crystal structure.

[1] "Chemische Kristallographie," Part I, Leipzig, 1906, p. 167.

[2] Bridgman, *Proc. Am. Acad. Arts Sci.*, **53**, 91 (1916); see especially pp. 133–139 and 151–152.

[3] Marignac, *Ann. mines*, [5] **15**, 221 (1859).

## Experimental Results.

By means of Hull's method[1] of X-ray crystal analysis the crystal structures of the following salts were determined: ammonium chloride at 20° and 250°, the bromide at the same temperatures, and the iodide at 20°. The calculations are based on the tables and formulas contained in Hull's article in the *Physical Review*.

Under ordinary temperature and pressure conditions the lattice of ammonium chloride crystals consists of 2 systems of intermeshed cubes of ammonium and chlorine ions. The corners of one of the series of cubes occupy the centers of the other series of cubes, giving a centered cubic arrangement of the ions ($NH_4^+$ and $Cl^-$), each being surrounded by 8 equidistant ions of the other kind. The length of the side of the elementary cube is 3.859 Å (one Ångstrom $= 10^{-8}$ cm.), and this is also the distance from any ion to the nearest ion of the same kind. The shortest distance between ions of opposite signs is 3.342 Å. The density calculated from this lattice is 1.536 in good agreement with the value usually given in tables, 1.520.

When the ammonium chloride is heated to 250° the structure changes, the lattice becoming simple cubic with alternate ammonium and chlorine ions, each ion being surrounded by 6 equidistant ions of the other kind. The unit spacing is 6.533 Å so that the nearest distance between ions of the same kind is 4.620 Å, while between ions of opposite kinds it is 3.266 Å. The calculated density is 1.265 at 250°, which is 15.7% less than the density at 20°. Bridgman observed a decrease of density of about 13% as the temperature was raised through the transition point.

Ammonium bromide is similarly affected by heat. At 20° the structure is centered cubic and the distance between like ions is 3.988 Å, while between unlike ions it is 3.453 Å. This gives a density of 2.548. Landolt-Börnstein gives 2.256 to 2.41. At 250° the structure is simple cubic, the distance between like ions being 6.90 Å, and between unlike ions 3.45 Å. The density is found to be 1.972 or 20.8% less than at 20°. Bridgman found a decrease of density of about 14% at the transition point.

The lattice of ammonium iodide at 20° is simple cubic like those of the high temperature forms of the chloride and bromide and like that o sodium chloride. The distance between like ions in ammonium iodide is 5.090 Å and between unlike ions 3.60 Å. The density is calculated to be 2.563 at 20°, while Landolt-Börnstein gives 2.443 to 2.501.

A photograph of the pattern given by ammonium chloride at 200° showed lines of both structures—the high and low temperature forms. This seems to be due to the slow rate of change when near the transition

[1] A. W. Hull, *Phys. Rev.*, **10**, 661 (1917); This Journal, **41**, 1168 (1919).

temperature. The rate of change was much increased by raising the temperature.

The results of the above X-ray analyses indicate that the structure of ammonium iodide at room temperature and of the chloride and bromide at high temperature are similar, simple cubic like the sodium and potassium halides; and that the crystal structure of ammonium chloride and bromide are alike at room temperature, centered cubic.

These results constitute very definite evidence in favor of the theory that the ammonium ion has tetrahedral symmetry while the alkali and halogen ions are cubic in shape.

Preparations are now being made for X-ray analyses of the structures of ammonium fluoride at room and high temperatures and of ammonium iodide at low temperature. It will probably be necessary to employ high pressures to obtain the low temperature form of ammonium iodide. It is probable that the structure of the fluoride at room temperature and of the iodide at low temperature will be like that of the chloride at room temperature, and that a high temperature form of the fluoride may exist corresponding to the high temperature form of the chloride.

In Hull's method of crystal analysis all the metallic elements which crystallize in any one of the 3 types of cubic lattice (simple cubic, centered cubic or face centered cubic) produce similar patterns. This is because the atoms of the crystal are all alike. In the analysis of salts, however, different results are obtained because of differing atomic numbers of the 2 or more atoms. Thus potassium chloride, simple cubic in structure, consists of ions containing the same number of electrons so that the pattern produced corresponds to that of a simple cubic lattice built up of atoms of one kind only. In sodium chloride, however, also simple cubic in structure, where the atomic weights of the 2 atoms are different, the pattern produced is that of a face-centered lattice of twice the linear dimension. This is because a simple cubic structure with alternate corners of different atoms can be resolved into 2 intermeshed face-centered lattices of twice the size, a lattice of each kind of atom. A salt having a centered cubic structure, when the atomic weights of the 2 elements are different, produces a pattern like that of an element in simple cubic arrangement, (the same pattern as of potassium chloride), because a centered cubic arrangement is equivalent to 2 intermeshed simple cubic lattices, one lattice for each kind of atom.

The low temperature forms of the ammonium halides produce patterns of the potassium chloride type (simple cubic), although they are centered cubic in structure, because of the difference in atomic weights between the ammonium radical and the halogen atoms. The high temperature forms produce patterns of the sodium chloride type (face cen-

tered), although the ions are arranged in a simple cubic lattice having half the spacing of the face-centered lattice shown by the pattern.

In the case of ammonium fluoride it is expected that the patterns, because of the closeness of atomic numbers will be more nearly like those of elements having similar structure.

## Experimental Data.

The X-rays were obtained from a water-cooled Coolidge tube with molybdenum target. The rays, being filtered by a thin sheet of zirconium oxide and one of metallic molybdenum, had an effective wave length of 0.712 Å. The exposures were of 16 hours duration with 30,000 volts and 20 milliamperes. The radius of the film holder was 10.16 cm. and duplitized films and calcium tungstate intensifying screens were used. The samples examined were finely powdered chemically pure salts sealed in thin-walled glass capillary tubes. Heat was applied by a small electrically heated coil placed just below the sample and parallel to it. The temperatures were estimated by substituting liquids of known boiling points for the salts in the capillaries.

The following tables give the relative intensities of the lines found on the 5 films and the spacings of the planes calculated from the lines. In most cases more than one film was taken but as these were essentially

TABLE 1.

Ammonium Chloride at 20°.

Simple Cubic Lattice.                 Unit Spacing 3.860Å.

| Indices of plane. | Relative intensity estimated. | Spacing of planes. | |
|---|---|---|---|
| | | Observed. | Calculated. |
| 110 | 10 | 2.718 | 2.730 |
| 111 | 1 | 2.238 | 2.228 |
| 200 | 2 | 1.924 | 1.931 |
| 210 | 1.5 | 1.725 | 1.727 |
| 211 | 3 | 1.568 | 1.576 |
| 220 | 1.5 | 1.362 | 1.365 |
| 221–300 | 1 | 1.287 | 1.286 |
| 310 | 1.5 | 1.214 | 1.221 |
| 311 | 0.8 | 1.162 | 1.163 |
| 222 | 0.8 | 1.111 | 1.117 |
| 320 | 0.6 | 1.073 | 1.071 |
| 321 | 1.8 | 1.024 | 1.031 |
| 400 | 0.3 | 0.958 | 0.965 |
| 410–322 | 0.6 | 0.935 | 0.936 |
| 411–330 | 0.8 | 0.912 | 0.910 |
| 331 | 0.5 | 0.891 | 0.886 |
| 420 | 0.5 | 0.867 | 0.863 |
| 421 | 0.5 | 0.844 | 0.842 |
| 332 | 0.5 | 0.822 | 0.823 |
| 422 | 0.4 | 0.787 | 0.788 |
| 430–500 | 0.3 | 0.772 | 0.772 |
| 431–510 | 0.7 | 0.755 | 0.757 |

TABLE II.

Ammonium Chloride at 250°.

Face-centered Cubic Lattice.          Unit Spacing 6.533 Å.

| Indices of plane. | Relative intensity estimated. | Spacing of planes. | |
|---|---|---|---|
| | | Observed. | Calculated. |
| 200 | 10 | 3.295 | 3.267 |
| 220 | 10 | 2.308 | 2.310 |
| 311 | 5 | 1.962 | 1.970 |
| 222 | 5 | 1.888 | 1.886 |
| 400 | 2 | 1.629 | 1.633 |
| 331 | 4 | 1.494 | 1.498 |
| 420 | 4 | 1.454 | 1.428 |
| 422 | 3 | 1.334 | 1.334 |
| 511–333 | 1.5 | 1.253 | 1.286 |
| 440 | 1 | 1.165 | 1.154 |
| 531 | 1.5 | 1.105 | 1.104 |
| 600–442 | 1.5 | 1.089 | 1.088 |
| 620 | 1 | 1.034 | 1.033 |
| { 533 { 622 | 0.7 | 0.988 | { 0.996 { 0.985 |

TABLE III.

Ammonium Bromide at 20°.

Simple Cubic Lattice.          Unit Spacing at 3.988 Å.

| Indices of plane. | Relative intensity estimated. | Spacing of planes. | |
|---|---|---|---|
| | | Observed. | Calculated. |
| 110 | 10 | 2.832 | 2.820 |
| 111 | 2 | 2.303 | 2.303 |
| 200 | 2 | 1.991 | 1.995 |
| 210 | 4 | 1.785 | 1.783 |
| 211 | 4 | 1.639 | 1.629 |
| 220 | 2 | 1.413 | 1.410 |
| 221–300 | 2 | 1.327 | 1.329 |
| 310 | 2 | 1.261 | 1.261 |
| 311 | 1.5 | 1.191 | 1.202 |
| 222 | 1 | 1.164 | 1.152 |
| 320 | 1 | 1.105 | 1.106 |
| 321 | 1.5 | 1.059 | 1.066 |

TABLE IV.

Ammonium Bromide at 250°.

Face-centered Cubic Lattice.          Unit Spacing 6.90 Å.

| Indices of plane. | Relative intensity estimated. | Spacing of planes. | |
|---|---|---|---|
| | | Observed. | Calculated. |
| 200 | 10 | 3.440 | 3.449 |
| 220 | 10 | 2.439 | 2.439 |
| 311 | 8 | 2.082 | 2.080 |
| 222 | 4 | 1.990 | 1.992 |
| 400 | 2 | 1.750 | 1.725 |
| 331 | 6 | 1.585 | 1.582 |
| 420 | 6 | 1.543 | 1.543 |
| 422 | 4 | 1.420 | 1.408 |
| 511–333 | 4 | 1.330 | 1.327 |

TABLE V.

Ammonium Iodide at 20°.

Face-centered Cubic Lattice.    Unit Spacing 7.199 Å.

| Indices of plane. | Relative intensity estimated. | Spacing of planes. | |
|---|---|---|---|
| | | Observed. | Calculated. |
| 220 | 10 | 2.531 | 2.545 |
| 311 | 10 | 2.168 | 2.171 |
| 222 | 3 | 2.086 | 2.078 |
| 400 | 2 | 1.797 | 1.800 |
| 331 | 8 | 1.652 | 1.652 |
| 420 | 8 | 1.607 | 1.610 |
| 422 | 5 | 1.471 | 1.470 |
| 511-333 | 4 | 1.385 | 1.386 |
| 440 | 2 | 1.268 | 1.273 |
| 531 | 4 | 1.224 | 1.217 |
| 600-442 | 4 | 1.201 | 1.199 |
| 620 | 2 | 1.141 | 1.139 |
| 533 | 1.5 | 1.095 | 1.097 |
| 622 | 1.5 | 1.083 | 1.085 |
| 444 | 0.5 | 1.041 | 1.039 |
| 711-551 | 1.5 | 1.010 | 1.008 |
| 640 | .. | ... | 0.998 |
| 642 | 1 | 0.966 | 0.962 |
| 553-731 | 1 | 0.936 | 0.937 |

alike only the data from the best films are recorded. The calculations were carried out in the way described by Hull. In every case the agreement between the observed and calculated spacings of the planes is very close and is sufficient to prove definitely the correctness of the assumed structure. The films obtained with ammonium chloride and iodide gave sharp and distinct lines so that a relatively large number of lines were observed. With ammonium bromide, however, the films were rather badly fogged by secondary radiation from the bromine excited by the rays from the molybdenum target. This might have been avoided by using an X-ray tube having a different target material. However, since the number of lines observed was sufficient to establish the structure of the crystals no effort was made to overcome this difficulty.

## Summary.

Ammonium chloride, bromide and iodide exhibit polymorphism and have well defined transition temperatures. X-ray crystal analysis by Hull's method shows that the high temperature form of each of these salts has a simple cubic structure like sodium chloride, each ion being surrounded by 6 equidistant ions of the opposite polarity. The ordinary or low temperature forms of the chloride and bromide show a centered cubic structure, each ion being surrounded by 8 equidistant ions of the opposite polarity, arranged as the corners of a cube about its center. These results furnish confirmatory evidence that the ammonium ion has

tetrahedral symmetry while the alkali and halogen ions are cubic in shape. Low temperatures, high pressures and anions of small atomic volume cause the shape of the ammonium ion to be a factor of predominating importance in determining the crystal structure. High temperatures, low pressures and anions of large volume make the shape of the ammonium ion of relatively less importance so that under these conditions ammonium salts tend to become isomorphous with the corresponding potassium salts.

The numerical data relating to the crystal structures of the ammonium halides are given in the following table.

TABLE VI.
Summary of Results.

| Salt. | Temp. ° C. | Arrangement of ions. | Distance between like ions. Å. | Distance between unlike ions. Å. | Density (calculated). | Molecular volume. |
|---|---|---|---|---|---|---|
| NH₄Cl | 20 | Centered cubic | 3.859 | 3.342 | 1.536 | 34.9 |
| NH₄Cl | 250 | Simple cubic | 4.620 | 3.266 | 1.265 | 42.3 |
| NH₄Br | 20 | Centered cubic | 3.988 | 3.453 | 2.548 | 38.4 |
| NH₄Br | 250 | Simple cubic | 4.88 | 3.45 | 1.972 | 49.7 |
| NH₄I | 20 | Simple cubic | 5.090 | 3.60 | 2.563 | 56.6 |

SCHENECTADY, N. Y.

# TRIVALENT TITANIUM. I. NOTES ON THE VOLUMETRIC DETERMINATION OF IRON BY MEANS OF TITANOUS SALTS.

BY WILLIAM M. THORNTON, JR., AND JAMES E. CHAPMAN.

## I. Introduction.

The use of titanous chloride for the estimation of iron was first suggested by Knecht.[1] A little later Knecht and Hibbert[2] supplied quantitative data, which seemed sufficient to prove that the method was accurate. Since then various analytical processes have been brought forward by Knecht and his co-workers[3] and others;[4] all of which depend, more or less directly, upon the great reducing power of the salts of trivalent titanium. Notwithstanding the many attractive features that these

[1] Knecht, *Ber.*, **36**, 166 (1903).

[2] Knecht and Hibbert, *ibid.*, **36**, 1549 (1903).

[3] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., **1918**.

[4] Rothmund, *Z. anorg. Chem.*, **62**, 108 (1909); Radlberger and Siegmund, *Oesterr. Ung. Z. Zuckerind.*, **42**, 34 (1913); Salvaterra, *Chem.-Ztg.*, **38**, 90 (1914); Monnier, *Ann. chim. anal.*, **20**, 1 (1915); **21**, 109 (1916); Mach and Lederle, *Landw. Versuchs.-Stat.*, **90**, 191 (1917); Hackl, *Chem.-Ztg.*, **43**, 9 (1919); Williams, *Chem. News*, **119**, 8 (1919).