

scopic examination of specimens. Its relations indicated that in the long series of paragenetic transformations of these minerals it was one of the first to be formed, but was later replaced by others. It was thought not improbable that a large amount of albite might have appeared among the first products, but that little of it survived. In more recent years the finding of occasional specimens of albite has been reported by collectors, but no description appears to have been given in the literature. The discovery of such specimens seems to support the view expressed in the earlier article.

## SOME FACTORS INFLUENCING CRYSTAL HABIT

(Concluded)

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### B. CRYSTALS FORMED IN AQUEOUS SOLUTIONS CONTAINING ONE FOREIGN SUBSTANCE

(Continued from page 239)

To determine the effect of foreign substances, or impurities, on crystal habit a series of experiments was carried out testing the influence of a number of inorganic salts which differ somewhat in solubility. Also, some organic substances were used as impurities. Some insoluble substances reduced to a very fine powder were likewise used as suspensions. The experiments in which inorganic salts were used as impurities will be described first.

Experiments were conducted with the same three salts listed under A, viz: lead nitrate, barium nitrate, and strontium nitrate. Four different conditions for crystal growth were employed:

1. Evaporation "medium"; temperature 20°C to 24°C.
2. Evaporation "medium"; temperature 25°C to 30°C.
3. Evaporation "slow"; temperature 20°C to 24°C.
4. Evaporation "slow"; temperature 25°C to 30°C.

Observations for record were made after 12 hours, 36 hours, and 60 hours of crystal growth. Experiments were conducted in the same manner as under A. The results obtained from a few experiments will be briefly described in the following pages. Other results from a number of these experiments using inorganic salts as impurities will be tabulated in table No. III.

It was found that within certain limits, the result obtained was influenced by the amount of impurity added. In order, therefore,

to make comparisons more valuable, equivalent amounts of the impurities were used.

Barium nitrate was added as an impurity to a solution of lead nitrate. Because of its low solubility the amount employed was not equivalent to that of the other salts used. The amount of barium nitrate added was the amount necessary to make a 1/7 normal solution. For all other salts, unless otherwise indicated, an amount sufficient for a 2/5 normal solution was used. For the sake of making comparisons it was found that results were more consistent and more pronounced by using that amount or more. Appreciable results were obtained by adding the amounts required for a 1/10 normal solution.

LEAD NITRATE + SILVER NITRATE

Evaporation "medium"

Temperature 25°C to 30°C

All the crystals that were first formed under these conditions were combinations of  $\pm$  tetrahedrons, about equally developed. After 12 hours of crystal growth some of the crystals began to show a small pyritohedron in combination with the  $\pm$  tetrahedrons and as crystal growth was allowed to continue the pyritohedrons steadily increased in number and also became relatively larger. The tetrahedrons, however, remained the dominant forms.

If this experiment is performed at temperatures of 20°C to 24°C it will be found that for the first 12 hours the same results are obtained as with temperatures of 25°C to 30°C. As crystal growth is allowed to continue under temperature conditions of 20°C to 30°C the form to appear first in combination with the  $\pm$  tetrahedrons is the cube. If the process of crystal growth continues for 10 or 15 hours, after the cube has entered into combination with the majority of the crystals, the pyritohedron may develop on a small percent of crystals as a very subordinate form.

LEAD NITRATE + SILVER NITRATE

Evaporation "slow"

Temperature 25°C to 30°C.

Crystals first started under conditions of "medium" evaporation are transferred to conditions of "slow" evaporation. The crystals first formed are combinations of  $\pm$  tetrahedrons. In a few hours after changing from "medium" conditions to "slow" conditions of

evaporation, the crystals become more complex and after 36 hours of crystal growth the pyritohedron is relatively larger than for the same period of time under conditions of "medium" evaporation. The cube is present as a subordinate form on a small percent of crystals. After 60 hours of crystal growth the pyritohedron has increased in relative size.

By comparing these results with those obtained when lead nitrate crystals are grown in pure aqueous solutions a pronounced contrast may readily be noted. For the same conditions of evaporation and temperature there is a decided tendency for the crystals, of the experiment just described, to be more simple in habit than crystals from pure aqueous solutions. The tendency for crystals of simple habit to form is stronger during the first 12 hours of crystal growth than for a longer period of growth. After 60 hours, the crystals from aqueous solutions, with silver nitrate as an impurity, become as complex as those from pure aqueous solutions. The complex forms from pure aqueous solutions, however, occur in relatively higher percent.

The presence of silver nitrate in solutions of barium nitrate or strontium nitrate has qualitatively the same effect on the habit of the crystals obtained as in the case of lead nitrate.

If crystal growth is allowed to continue for 60 hours or more, the crystals in the liquor gradually become more complex in habit. The crystals finally obtained under conditions of "slow" evaporation and at temperatures between 25°C and 30°C are as complex as those obtained from pure aqueous solutions under the same conditions and for the same period of crystal growth.

TABLE NO. III  
LEAD NITRATE; EVAPORATION "MEDIUM"; TEMPERATURE 20°C to 24°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
AgNO <sub>3</sub>	12	± (111) . . . . . 100%	Equally developed
AgNO <sub>3</sub>	36	± (111) . . . . . 75% ± (111), (100) . . . . . 25%	± (111) . . . . . 100%
AgNO <sub>3</sub>	60	± (111) . . . . . 60% ± (111), (100) . . . . . 40%	± (111) . . . . . 75% (100) . . . . . 25%
NH <sub>4</sub> NO <sub>3</sub>	12	± (111) . . . . . 100%	Equally developed
NH <sub>4</sub> NO <sub>3</sub>	36	± (111) . . . . . 63% ± (111), (100) . . . . . 37%	± (111) . . . . . 100%
NH <sub>4</sub> NO <sub>3</sub>	60	± (111) . . . . . 60% ± (111), (100) . . . . . 40%	± (111) . . . . . 80% (100) . . . . . 20%
Ca(NO <sub>3</sub> ) <sub>2</sub>	12	± (111) . . . . . 100%	Equally developed
Ca(NO <sub>3</sub> ) <sub>2</sub>	36	± (111) . . . . . 60% ± (111), (100) . . . . . 40%	± (111) . . . . . 100%
Ca(NO <sub>3</sub> ) <sub>2</sub>	60	± (111) . . . . . 55% ± (111), (100) . . . . . 45%	± (111) . . . . . 67% (100) . . . . . 33%
Cu(NO <sub>3</sub> ) <sub>2</sub>	12	± (111) . . . . . 95% ± (111), (100) . . . . . 5%	± (111) . . . . . 100%
Cu(NO <sub>3</sub> ) <sub>2</sub>	36	± (111) . . . . . 50% ± (111), (100) . . . . . 50%	± (111) . . . . . 100%
Cu(NO <sub>3</sub> ) <sub>2</sub>	60	± (111) . . . . . 48% ± (111), (100) . . . . . 52%	± (111) . . . . . 60% (100) . . . . . 40%

LEAD NITRATE; EVAPORATION "MEDIUM"; TEMPERATURE 20°C TO 24°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
NaNO <sub>3</sub>	12	±(111) . . . . . 100%	Equally developed
NaNO <sub>3</sub>	36	±(111) . . . . . 75% ±(111), (100) . . . . . 25%	±(111) . . . . . 100%
NaNO <sub>3</sub>	60	±(111) . . . . . 68% ±(111), (100) . . . . . 32%	±(111) . . . . . 90% (100) . . . . . 10%
Mg(NO <sub>3</sub> ) <sub>2</sub>	12	±(111) . . . . . 85% ±(111), (100) . . . . . 15%	±(111) . . . . . 100%
Mg(NO <sub>3</sub> ) <sub>2</sub>	36	±(111) . . . . . 80% ±(111), (100) . . . . . 20%	±(111) . . . . . 93% (100) . . . . . 7%
Mg(NO <sub>3</sub> ) <sub>2</sub>	60	±(111) . . . . . 75% ±(111), (100) . . . . . 25%	±(111) . . . . . 88% (100) . . . . . 12%
LiNO <sub>3</sub>	12	±(111) . . . . . 100%	Equally developed
LiNO <sub>3</sub>	36	±(111) . . . . . 82% ±(111), (100) . . . . . 18%	±(111) . . . . . 100%
LiNO <sub>3</sub>	60	±(111) . . . . . 30% ±(111), (100) . . . . . 70%	±(111) . . . . . 80% (100) . . . . . 20%
KNO <sub>3</sub>	12	±(111) . . . . . 80% ±(111), (100) . . . . . 20%	±(111) . . . . . 100%
KNO <sub>3</sub>	36	±(111) . . . . . 65% ±(111), (100) . . . . . 35%	±(111) . . . . . 100%
KNO <sub>3</sub>	60	±(111) . . . . . 35% ±(111), (100) . . . . . 65%	±(111) . . . . . 78% (100) . . . . . 22%
Ba(NO <sub>3</sub> ) <sub>2</sub>	12	±(111) . . . . . 30% ±(111), (100) . . . . . 70%	±(111) . . . . . 85% (100) . . . . . 15%
Ba(NO <sub>3</sub> ) <sub>2</sub>	36	±(111) . . . . . 28% ±(111), (100) . . . . . 72%	±(111) . . . . . 83% (100) . . . . . 17%
Ba(NO <sub>3</sub> ) <sub>2</sub>	60	±(111) . . . . . 20% ±(111), (100) . . . . . 80%	±(111) . . . . . 80% (100) . . . . . 20%

LEAD NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
AgNO <sub>3</sub>	12	±(111)..... 80% ±(111), (100)..... 8% ±(111), (hko)..... 12%	±(111).....100%
AgNO <sub>3</sub>	36	±(111)..... 30% ±(111), (100)..... 30% ±(111), (hko)..... 40%	±(111).....100%
AgNO <sub>3</sub>	60	±(111)..... 18% ±(111), (100), (hko). 50% ±(111), (hko)..... 32%	±(111)..... 80% (100)..... 12% ±(111), (hko)..... 8%
NH <sub>4</sub> NO <sub>3</sub>	12	±(111)..... 83% ±(111), (100)..... 12% ±(111), (100), (hko). 5%	±(111).....100%
NH <sub>4</sub> NO <sub>3</sub>	36	±(111)..... 13% ±(111), (100)..... 28% ±(111), (100), (hko). 59%	±(111)..... 90% (100)..... 3% ±(111), (hko)..... 7%
NH <sub>4</sub> NO <sub>3</sub>	60	±(111)..... 3% ±(111), (100)..... 35% ±(111), (hko)..... 12% ±(111), (100), (hko). 50%	±(111)..... 85% (100)..... 8% ±(111), (hko)..... 7%
Ca(NO <sub>3</sub> ) <sub>2</sub>	12	±(111)..... 70% ±(111), (100)..... 12% ±(111), (100), (hko). 18%	±(111).....100%
Ca(NO <sub>3</sub> ) <sub>2</sub>	36	±(111)..... 7% ±(111), (100)..... 35% ±(111), (hko)..... 15% ±(111), (100), (hko). 43%	±(111)..... 87% (100)..... 5% ±(111), (hko)..... 8%
Ca(NO <sub>3</sub> ) <sub>2</sub>	60	±(111)..... 5% ±(111), (100)..... 35% ±(111), (hko)..... 20% ±(111), (100), (hko). 40%	±(111)..... 75% (100)..... 10% ±(111), (hko)..... 15%

LEAD NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
Cu(NO <sub>3</sub> ) <sub>2</sub>	12	±(111) . . . . . 63% ±(111), (100) . . . . . 18% ±(111), (hko) . . . . . 7% ±(111), (100), (hko) . 12%	±(111) . . . . . 100%
Cu(NO <sub>3</sub> ) <sub>2</sub>	36	±(111) . . . . . 10% ±(111), (100) . . . . . 27% ±(111), (hko) . . . . . 13% ±(111), (100), (hko) . 50%	±(111) . . . . . 80% (100) . . . . . 8% ±(111), (hko) . . . . . 12%
Cu(NO <sub>3</sub> ) <sub>2</sub>	60	±(111) . . . . . 0% ±(111), (100) . . . . . 43% ±(111), (hko) . . . . . 15% ±(111), (100), (hko) . 42%	±(111) . . . . . 68% (100) . . . . . 18% ±(111), (hko) . . . . . 14%
NaNO <sub>3</sub>	12	±(111) . . . . . 55% ±(111), (100) . . . . . 30% ±(111), (hko) . . . . . 7% ±(111), (100), (hko) . 8%	±(111) . . . . . 100%
NaNO <sub>3</sub>	36	±(111) . . . . . 8% ±(111), (100) . . . . . 32% ±(111), (hko) . . . . . 8% ±(111), (100), (hko) . 52%	±(111) . . . . . 77% (100) . . . . . 5% ±(111), (hko) . . . . . 18%
NaNO <sub>3</sub>	60	±(111) . . . . . 5% ±(111), (100) . . . . . 50% ±(111), (hko) . . . . . 20% ±(111), (100), (hko) . 25%	±(111) . . . . . 65% ±(111), (hko) . . . . . 35%
Mg(NO <sub>3</sub> ) <sub>2</sub>	12	±(111) . . . . . 28% ±(111), (100) . . . . . 30% ±(111), (hko) . . . . . 22% ±(111), (100), (hko) . 20%	±(111) . . . . . 78% ±(111), (hko) . . . . . 20% ±(111), (100), (hko) . 2%
Mg(NO <sub>3</sub> ) <sub>2</sub>	36	±(111) . . . . . 12% ±(111), (100) . . . . . 32% ±(111), (hko) . . . . . 16% ±(111), (100), (hko) . 40%	±(111) . . . . . 48% ±(111), (100) . . . . . 10% ±(111), (100), (hko) . 12% ±(111), (hko) . . . . . 30%
Mg(NO <sub>3</sub> ) <sub>2</sub>	60	±(111) . . . . . 8% ±(111), (100) . . . . . 30% ±(111), (hko) . . . . . 32% ±(111), (100), (hko) . 30%	±(111) . . . . . 57% ±(111), (100) . . . . . 7% ±(111), (hko) . . . . . 30% ±(111), (100), (hko) . 6%

LEAD NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity ■■■	Hours of Crystal Growth	Percent predominance	Percent dominance
LiNO <sub>3</sub>	12	±(111)..... 32% ±(111), (100)..... 30% ±(111), (hko)..... 25% ±(111), (100), (hko). 23%	±(111)..... 85% ±(111), (hko)..... 8% ±(111), (100), (hko) 7%
LiNO <sub>3</sub>	36	±(111)..... 15% ±(111), (100)..... 28% ±(111), (hko)..... 17% ±(111), (100), (hko). 40%	±(111)..... 50% ±(111), (100)..... 15% ±(111), (hko)..... 35% ±(111), (100), (hko) 10%
LiNO <sub>3</sub>	60	±(111)..... 10% ±(111), (100)..... 35% ±(111), (hko)..... 32% ±(111), (100), (hko). 23%	±(111)..... 60% ±(111), (100)..... 10% ±(111), (hko)..... 25% ±(111), (100), (hko) 5%
KNO <sub>3</sub>	12	±(111)..... 23% ±(111), (100)..... 35% ±(111), (hko)..... 22% ±(111), (100), (hko). 20%	±(111)..... 70% ±(111), (100)..... 5% ±(111), (hko)..... 15% ±(111), (100), (hko) 10%
KNO <sub>3</sub>	36	±(111)..... 13% ±(111), (100)..... 32% ±(111), (hko)..... 20% ±(111), (100), (hko). 35%	±(111)..... 47% ±(111), (100)..... 20% ±(111), (hko)..... 30% ±(111), (100), (hko) 3%
KNO <sub>3</sub>	60	±(111)..... 5% ±(111), (100)..... 30% ±(111), (hko)..... 28% ±(111), (100), (hko). 37%	±(111)..... 35% ±(111), (100)..... 15% ±(111), (hko)..... 38% ±(111), (100), (hko) 12%
Ba(NO <sub>3</sub> ) <sub>2</sub>	12	±(111), (100)..... 42% ±(111), (hko)..... 30% ±(111), (100), (hko). 28%	±(111)..... 40% ±(111), (100)..... 15% ±(111), (hko)..... 40% ±(111), (100), (hko) 5%
Ba(NO <sub>3</sub> ) <sub>2</sub>	36	±(111), (100)..... 35% ±(111), (hko)..... 23% ±(111), (100), (hko). 42%	±(111)..... 30% ±(111), (100)..... 25% ±(111), (hko)..... 45%
Ba(NO <sub>3</sub> ) <sub>2</sub>	60	±(111), (100)..... 25% ±(111), (hko)..... 20% ±(111), (100), (hko). 55%	±(111)..... 22% ±(111), (100)..... 33% ±(111), (hko)..... 40% ±(111), (100), (hko) 5%



BARIUM NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
AgNO <sub>3</sub>	12	±(111) . . . . . 88% ±(111), (100) . . . . . 12%	±(111) . . . . . 100%
AgNO <sub>3</sub>	36	±(111) . . . . . 50% ±(111), (100) . . . . . 43% ±(111), (100), (hko) . 7%	±(111) . . . . . 45% ±(111), (100) . . . . . 20% ±(111), (hko) . . . . . 35%
AgNO <sub>3</sub>	60	±(111) . . . . . 20% ±(111), (100) . . . . . 45% ±(111), (100), (hko) . 35%	±(111) . . . . . 40% (100) . . . . . 5% ±(111), (100) . . . . . 12% ±(111), (hko) . . . . . 43%
NH <sub>4</sub> NO <sub>3</sub>	12	±(111) . . . . . 90% ±(111), (100) . . . . . 10%	±(111) . . . . . 100%
NH <sub>4</sub> NO <sub>3</sub>	36	±(111) . . . . . 48% ±(111), (100) . . . . . 50% ±(111), (100), (hko) . 2%	±(111) . . . . . 50% ±(111), (100) . . . . . 25% ±(111), (hko) . . . . . 25%
NH <sub>4</sub> NO <sub>3</sub>	60	±(111) . . . . . 25% ±(111), (100) . . . . . 43% ±(111), (100), (hko) . 32%	±(111) . . . . . 47% ±(111), (100) . . . . . 20% ±(111), (hko) . . . . . 33%
Ca(NO <sub>3</sub> ) <sub>2</sub>	12	±(111) . . . . . 80% ±(111), (100) . . . . . 20%	±(111) . . . . . 80% ±(111), (100) . . . . . 20%
Ca(NO <sub>3</sub> ) <sub>2</sub>	36	±(111) . . . . . 45% ±(111), (100) . . . . . 53% ±(111), (100), (hko) . 2%	±(111) . . . . . 43% ±(111), (100) . . . . . 20% ±(111), (hko) . . . . . 37%
Ca(NO <sub>3</sub> ) <sub>2</sub>	60	±(111) . . . . . 17% ±(111), (100) . . . . . 40% ±(111), (100), (hko) . 43%	±(111) . . . . . 50% ±(111), (100) . . . . . 25% ±(111), (hko) . . . . . 25%
Cu(NO <sub>3</sub> ) <sub>2</sub>	12	±(111) . . . . . 73% ±(111), (100) . . . . . 24% ±(111), (100), (hko) . 3%	±(111) . . . . . 100%
Cu(NO <sub>3</sub> ) <sub>2</sub>	36	±(111) . . . . . 45% ±(111), (100) . . . . . 47% ±(111), (100), (hko) . 8%	±(111) . . . . . 35% ±(111), (100) . . . . . 30% ±(111), (hko) . . . . . 35%

BARIUM NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
Cu(NO <sub>3</sub> ) <sub>2</sub>	60	± (111) . . . . . 12% ± (111), (100) . . . . . 48% ± (111), (100), (hko) . 40%	± (111) . . . . . 25% ± (111), (100) . . . . . 37% ± (111), (hko) . . . . . 38%
NaNO <sub>3</sub>	12	± (111) . . . . . 70% ± (111), (100) . . . . . 25% ± (111), (100), (hko) . 5%	± (111) . . . . . 100%
NaNO <sub>3</sub>	36	± (111) . . . . . 35% ± (111), (100) . . . . . 47% ± (111), (100), (hko) . 18%	± (111) . . . . . 35% ± (111), (100) . . . . . 30% ± (111), (hko) . . . . . 35%
NaNO <sub>3</sub>	60	± (111) . . . . . 0% ± (111), (100) . . . . . 40% ± (111), (100), (hko) . 60%	± (111) . . . . . 7% ± (111), (100) . . . . . 38% ± (111), (hko) . . . . . 55%
Mg(NO <sub>3</sub> ) <sub>2</sub>	12	± (111) . . . . . 52% ± (111), (100) . . . . . 35% ± (111), (100), (hko) . 13%	± (111) . . . . . 92% ± (111), (100) . . . . . 8%
Mg(NO <sub>3</sub> ) <sub>2</sub>	36	± (111) . . . . . 22% ± (111), (100) . . . . . 55% ± (111), (100), (hko) . 23%	± (111) . . . . . 20% ± (111), (100) . . . . . 47% ± (111), (hko) . . . . . 33%
Mg(NO <sub>3</sub> ) <sub>2</sub>	60	± (111), (100) . . . . . 53% ± (111), (100), (hko) . 47%	± (111) . . . . . 3% ± (111), (100) . . . . . 45% ± (111), (hko) . . . . . 55%
LiNO <sub>3</sub>	12	± (111) . . . . . 60% ± (111), (100) . . . . . 32% ± (111), (100), (hko) . 8%	± (111) . . . . . 100%
LiNO <sub>3</sub>	36	± (111) . . . . . 28% ± (111), (100) . . . . . 60% ± (111), (100), (hko) . 12%	± (111) . . . . . 25% ± (111), (100) . . . . . 50% ± (111), (hko) . . . . . 25%
LiNO <sub>3</sub>	60	± (111), (100) . . . . . 48% ± (111), (100), (hko) . 52%	± (111) . . . . . 8% ± (111), (100) . . . . . 50% ± (111), (hko) . . . . . 42%

BARIUM NITRATE; EVAPORATION "SLOW"; TEMPERATURE 25°C TO 30°C.

Impurity	Hours of Crystal Growth	Percent predominance	Percent dominance
KNO <sub>3</sub>	12	±(111)..... 40%	±(111)..... 82%
		±(111), (100)..... 47%	±(111), (100)..... 18%
		±(111), (100), (hko). 13%	
KNO <sub>3</sub>	36	±(111)..... 17%	±(111)..... 30%
		±(111), (100)..... 53%	±(111), (100)..... 37%
		±(111), (100), (hko). 30%	±(111), (hko)..... 37%
KNO <sub>3</sub>	60	±(111), (100)..... 37%	±(111)..... 27%
		±(111), (100), (hko). 63%	±(111), (100)..... 33%
			±(111), (hko)..... 65%

EXPLANATION OF TABLE NO. III

An explanation of Table No. III can well be made by referring to a specific result indicated in the table. On page 262, the third horizontal column of data from the top indicates the results obtained by growing lead nitrate crystals from an aqueous solution to which some silver nitrate had been added as an impurity. Crystals were grown under conditions of "medium" rate of evaporation and at temperatures ranging from 20°C to 24°C. Observations were made after the crystals had been growing for 60 hours. The result was that 60% of the crystals were ± tetrahedrons in combination, and 40% of the crystals were ± tetrahedrons in combination with a cube. Of 75% of all the crystals the ± tetrahedrons were regarded as dominant and of 25% of all the crystals the cube was dominant. In determining the percent of dominance of ± tetrahedrons, it was considered that of crystals which were combinations of just the two tetrahedrons the tetrahedrons were dominant. These were counted in with the crystals which were combinations of ± tetrahedrons and a cube of which the tetrahedrons were dominant. The ± tetrahedrons are always considered to be equally developed. When they are not equally developed it will be indicated.

The table suggests rather strongly that the influence of the inorganic salts was determined to some extent by their relative solubility. When a salt present as an impurity is more soluble than the salt forming into crystals, the effect is to increase the tendency

to form crystals of simple habit. If the salt present as an impurity is less soluble than the one whose crystals are growing the effect is to cause a tendency to form crystals of a more complex habit. Sodium nitrate, lithium nitrate, and potassium nitrate indicate a stronger influence to produce crystals of simple habit than would be expected by comparing their respective solubilities with some of the other salts such as copper nitrate, zinc nitrate and nickel nitrate. This suggests that there is undoubtedly another property besides solubility which should be considered.

#### ORGANIC COMPOUNDS

In addition to the list of experiments showing the effect of inorganic salts on the habit of crystals of lead nitrate, barium nitrate, and strontium nitrate, a series of experiments was carried out in which the following organic compounds were used as impurities:

Methylene blue  
Urea  
Picric acid

#### METHYLENE BLUE

LEAD NITRATE + METHYLENE BLUE. Methylene blue was added to solutions of lead nitrate and crystals of lead nitrate were allowed to grow under the following conditions:

Evaporation "medium"  
Temperature 15° to 20°C.  
Temperature 20° to 24°C.  
Temperature 25° to 30°C.  
Evaporation "slow"  
Temperature 15° to 20°C.  
Temperature 20° to 25°C.  
Temperature 25° to 30°C.

Observations of results of each of the above experiments were made for record at the end of each of the following periods of time after crystals were first observed: 12 hours, 36 hours, 60 hours.

No. 1.—Evaporation "medium"; Temperature 15° to 20°C.

All lead nitrate crystals are cubes that are formed from a solution in which a small amount of methylene blue is present as an impurity if conditions are of "medium" evaporation, and temperatures between 15° and 20° C. The crystals appear as cubes from the time they can first be seen with a 20 power binocular micro-

scope. They continue to grow as cubes for periods of 36 and 60 hours.

No. 2.—Evaporation “medium”; Temperature 20° to 24°C.

The lead nitrate crystals formed under conditions of No. 2 begin as cubes and continue as such for a period of 12 hours. After 36 hours of crystal growth some of the crystals of the original crop are combinations of a cube and  $\pm$  tetrahedrons. The cube in all cases is the dominant form. After 60 hours the pyritohedron is in combination as a decidedly subordinate form on some crystals.

No. 3.—Evaporation “medium”; Temperature 25° to 30°C.

Crystals of lead nitrate formed under conditions represented under No. 3 after the first 12 hours are a mixture of cubes and cubes in combination with  $\pm$  tetrahedrons. The cube is the dominant form. Crystals of single cubes predominate in number. After 48 hours some crystals are combinations of a cube,  $\pm$  tetrahedrons and a pyritohedron. The cube is still the dominant form. The pyritohedron has increased relatively in number after 60 hours of crystal growth, and is as abundant in the combination as the  $\pm$  tetrahedrons.

If the above experiments are repeated by allowing “slow” evaporation in each case instead of “medium” there is no difference to be noticed in No. 1. In No. 2 there is an increase in the percent of crystals having  $\pm$  tetrahedrons in combination and in No. 3 there is an increase in the percent of crystals having the pyritohedron in combination. The pyritohedron form is also relatively larger. In over 50% of the crystals it is relatively larger than the tetrahedrons.

BARIUM NITRATE + METHYLENE BLUE. STRONTIUM NITRATE + METHYLENE BLUE. The results obtained with barium nitrate and methylene blue and with strontium nitrate and methylene blue are qualitatively the same as with lead nitrate under the same conditions. In each case satisfactory results are more difficult to obtain than with lead nitrate.

Gaubert<sup>11</sup> has reported results with lead nitrate and methylene blue and also with strontium nitrate and methylene blue. He reports that the influence of methylene blue on crystals of these salts is to produce cubes. The results reported by him may be obtained under conditions of “fast” or “medium” rates of evaporation and temperatures of 15° to 22°C and for a period of 10 or 12 hours

<sup>11</sup>Paul Gaubert: *Revue Scientifique*, Paris, No. 3. Jan. 15, 1910.

of crystal growth. These results are obtained with a very small amount of methylene blue in solution.

Modifications in crystal habit are produced more easily with weak solutions of methylene blue than with concentrated solutions. Crystals in general are colored blue due to inclusions of the dye. The depth of color depends somewhat upon the concentration of methylene blue, and also somewhat on the rate of crystal growth. Crystals grown in a rapidly cooling solution are quite generally colorless and transparent.

Gaubert considers the cube habit to be due to the fact that the included methylene blue is arranged parallel to the cube faces. ✓ Crystals have been obtained, however, in the form of cubes that were colorless and transparent. Many crystals have also been obtained with small patches of blue scattered irregularly throughout the crystals. There seemed to be no orderly manner of arrangement. Microscopic examinations of crushed crystals show that some of the included methylene blue is faintly doubly refracting. The largest amount appears to be amorphous and with no special order of arrangement.

**STRIATIONS.** Crystals of lead nitrate and of barium nitrate grown from aqueous solutions containing methylene blue may show striations on the cube faces. These striations are of interest because they may occur arranged parallel to the cube edges, as in the case of pyrite, or they may occur diagonally arranged on the cube faces as in the case of sphalerite. When arranged in a diagonal manner they are parallel to the edges between faces of a tetrahedron and the cube. The striations parallel to the cube edges are, obviously, parallel to the edges between the faces of a pyritohedron and the cube.

It is of interest to note that crystals do not always show striations. When they are to be found on any of the crystals resulting from an experiment they usually occur on the majority or all of the crystals of that same experiment. Several experiments have been conducted to determine the cause of these striations and also a reason for their being arranged parallel to the edges between the cube and a pyritohedron for one set of crystals and in a diagonal manner for another set of crystals. The results obtained suggest very strongly that striations parallel to the edges between the cube and a pyritohedron are formed under conditions which would be more favorable to the pyritohedron than the cube in a pure aqueous

solution. The conditions, however, are not the most favorable that are possible for the development of the pyritohedron. Three or four degrees higher temperature would be more favorable. Because of a condition in the solution produced by the presence of methylene blue the cube develops instead of the pyritohedron. There is, however, a constant tendency for the pyritohedron to form. The striations indicate the places where it existed in each case for a comparatively short time.

When crystals are allowed to develop at temperatures three or four degrees higher, in other words, at 28° to 30°C instead of 24° to 26°C, the cube faces will not be found to show striations. If crystals are allowed to grow for two or three weeks at temperatures of 28° to 30°C under conditions of "slow" evaporation, the pyritohedron will become decidedly dominant. After the first few hours of crystal growth the pyritohedron continues to grow without being interrupted.

The diagonal striations form to the best advantage at temperatures below 21°C. These temperatures are more favorable to the development of the tetrahedron than the cube in a pure aqueous solution. The conditions imposed on the solution by the presence of methylene blue, however, cause the cube constantly to interrupt the growth of the tetrahedron. The striations mark the places at which the tetrahedron had a temporary existence.

A close examination of these striations reveals the fact that they are not at all uniform in dimension. In many cases a sufficient amount of the pyritohedron faces or tetrahedron faces is present to be readily recognized.

These results corroborate the idea advanced by Wherry<sup>12</sup> that surface phenomena do not always indicate the symmetry or internal structure of crystals. If the symmetry of lead nitrate and of barium nitrate, as suggested by their crystal forms, is correct, there are no planes of symmetry. The striations formed on the surface of the cube faces would indicate that some crystals possess axial planes of symmetry and other crystals diagonal planes of symmetry. From this it seems that it is not safe to infer the symmetry of a crystalline substance from one type of striations. Having obtained both types, as in this case, even though they do not occur on the same set of crystals, it is evident that the true symmetry is indicated.

<sup>12</sup>Edgar T. Wherry: *Am. Mineral.*, 9, pp. 53-54.

The above results suggest further that the striations found on crystals occurring in nature such as are characteristic of pyrite and topaz, may be there because the temperature condition favorable to one crystal form was counteracted by the presence of impurities. Due to the presence of impurities a form developed which would not have developed ordinarily under the prevailing temperature condition. There resulted a constant struggle for existence between two forms and the striations indicate the places where one form was temporarily in existence.

#### UREA

The effect of urea on the crystal habit of lead nitrate, barium nitrate and strontium nitrate is to produce simple forms. During the first 36 hours after crystals have formed at temperatures of 20° to 24°C and at a "slow" rate of evaporation, the forms are more predominantly the  $\pm$  tetrahedrons than would be the case in a pure aqueous solution. At the higher temperatures of 25° to 30°C and especially after 60 hours of crystal growth the crystals are of a highly complex character, with combinations of the cube, pyritohedron and  $\pm$  tetrahedrons.

#### VISCOSITY

LEAD NITRATE + GLYCERINE. In order to determine the effect of the viscosity or of thickening of the liquid on the habit of the crystals of lead nitrate, barium nitrate and strontium nitrate, 15cc. of glycerine were added to a 25cc. solution of a salt. In each case, under conditions of "medium" evaporation and at temperatures of 20° to 25°C, at the end of 48 hours all of the crystals were combinations of a cube,  $\pm$  tetrahedrons and a pyritohedron.

With lead nitrate under conditions of "medium" evaporation and temperatures above 25°C, a striking result was obtained that was not obtained with any other set of experiments. The plus and minus forms of the pyritohedron developed in combination with a cube and two tetrahedrons upon a number of crystals. These results indicate very strongly that in a liquid of high viscosity there is a strong tendency for crystals to be represented by the most complex forms possible on the substance so crystallizing, if temperature conditions are proper.

<sup>18</sup>J. W. Retgers: Über den Einfluss fremder Substanzen in der Lösung auf die Form, die Reinheit und die Grösse der ausgeschieden Krystalle. *Zeit. Phy. Chem.*, 9, 267, (1892).



J. W. Retgers<sup>13</sup> reports that by thickening the solution through the addition of gelatine, dextrine, or glycerine, there is a tendency for the promotion of skeletal growth and satisfactory results are not obtained. The results with dextrine or sugar obtained in this work confirm Retgers' results; however, those obtained with glycerine were very satisfactory.

Allowing the solution to cool suddenly from a temperature above 25°C to a temperature below 20°C had the result of changing the habit of all the crystals (75 in number) from the complex habit to a simple habit of  $\pm$  tetrahedrons. The complex forms were enclosed as phantom crystals.

**BARIUM NITRATE IN AGAR-AGAR.** Barium nitrate crystals were produced in agar-agar by mixing a solution of barium chloride with agar-agar and then, after the agar-agar had set as a thick gel, a solution of sodium nitrate was poured over the top. The two solutions mixed by slow diffusion. The experiment was conducted under temperature conditions above 25°C. Crystals were grouped throughout the gel in arborescent fashion and the crystals in general were considerably distorted. The forms in combination on practically all of the crystals after crystal growth had been going on for a period of five weeks were  $\pm$  tetrahedrons as the dominant forms, and a pyritohedron. On some crystals the cube had also developed. The crystals in general were tabular in development.

**LEAD NITRATE + SUSPENSIONS.** The effect of a fine suspension on crystal habit was determined by using magnesium oxide, powdered alundum, powdered kaolinite, and powdered barite. These experiments did not give the results expected. From the results obtained with glycerine it was predicted that a suspension of a fine powder in a solution of either of the nitrates used would have the effect of causing the crystals to become more complex. This, however, was not the case. The crystals produced with lead nitrate at temperatures up to 24°C even at a slow rate of evaporation were all  $\pm$  tetrahedrons in combination, equally developed. The tendency is for a smaller number of crystals to form and therefore the crystals produced are larger. The powdered substance was included in all the crystals but was not arranged in any orderly fashion. The distribution was in patches arranged in an irregular manner. No explanation is offered for the results obtained.

## DISCUSSION

By way of review it may be mentioned that in general in the study of crystal habit by far the greatest amount of effort seems to have been directed to determine the influence of foreign substances. There seems to have been very little consideration given to control conditions for crystal growth, even to considering the possible influence of such conditions. Very little consideration seems to have been given to the nature of the impurity, to the temperature at which crystal growth takes place and not a great deal to the rate of crystal growth.

The explanations advanced to account for the influence of foreign substances, are based on (1) adsorption, (2) capillarity, and (3) inclusion of the foreign substance into the crystal in a definite manner.

The experiments presented in this paper have been conducted under conditions controlled to a certain extent. The conditions under which the crystals developed were very carefully noted and recorded. The nature of the impurity has been taken into consideration and considerable attention has been given to temperature conditions. An effort has also been made to determine by means of X-ray study, if impurities actually enter into the crystal structure.

There may be cases where adsorption has in some way, not yet fully understood, influenced crystal habit. The results obtained in a large number of experiments point very strongly to the conclusion that this is not always the case. If adsorption were regarded as the cause for the formation of the cube in connection with certain dyes present in a solution of lead nitrate, barium nitrate or strontium nitrate, one would meet with difficulties in explaining results that may be obtained at a temperature of 30°C. If crystals are allowed to grow rapidly at that temperature as has been pointed out, the combination of  $\pm$  tetrahedrons results. If the solution while remaining at this same temperature is suddenly transferred to conditions where "slow" crystal growth takes place, pyritohedrons will develop, instead of a cube, in combination with the two tetrahedrons. Furthermore, perfect cubes of each of the three salts studied have been obtained from solutions in which some methylene blue was present, which were entirely free from color.

Also, allowing crystals to grow in the presence of methylene blue at 20°C and then slowly increasing the temperature and finally changing to "slow" rate of evaporation, the crystals will change in

habit from cubes to combinations of cubes and pyritohedrons and also cube, pyritohedrons and  $\pm$  tetrahedrons. The fact that crystals may be brought to change in habit in a pure aqueous solution by changing the temperature of crystal growth suggests that the nature of the solvent may have some relation to crystal habit.

Water in an aqueous solution is considered to have different properties than water alone. This has been suggested by the fact that there is a difference in transparency of water in a solution and water in which no substance is dissolved. The modification in crystal habit may possibly be due, in at least some cases, to the nature of the solvent instead of to a peculiar condition existing at the surface of some of the crystal faces by virtue of adsorption of the foreign material. The effect of the nature of the solvent has been clearly demonstrated in some organic compounds, where substances may be produced as needle-like crystals from one solvent and as flaky or tabular crystals from another solvent.

In reviewing further the results obtained with inorganic salts as impurities, it is quite striking that the effect of a foreign substance is intimately related to its solubility. There is sufficient evidence by way of variation in results to suggest that other properties besides the solubility enter into the action to influence crystal habit. The results obtained with ammonium nitrate for instance suggest that viscosity is a property which should be considered.

Also, the salts of elements entering into alkaline and basic compounds (K, Na, Ca, Mg) show a stronger tendency to produce crystals of a simple habit than would naturally be expected by considering their solubilities. Jenkins<sup>14</sup> in considering the velocity of crystallization of urea, acetanilide and ammonium nitrate in various solvents reports that the viscosity of the solution is an important factor.

In considering the effect of inorganic impurities it seems evident that impurities of greater solubility than the salt crystallizing out, increase the rate of crystal growth especially during the first twenty-four hours of crystal development. Ammonium nitrate is known to produce the effect of lowering the viscosity of solutions and the effect of the presence of ammonium nitrate as an impurity to produce simple forms is most marked. In the light of the results reported by Jenkins, it may be concluded that the effect of ammonium nitrate is actually to increase the rate of crystal growth. Hence allowing some for effect of viscosity, it may be regarded, in general,

<sup>14</sup>John D. Jenkins: *J. Am. Chem. Soc.*, 47, No. 4, April, 1925.

that the effect of inorganic salts is to increase or decrease the rate of crystal growth, depending upon the relative solubility.

The outstanding factors influencing crystal habit seem to be temperature and rate of crystal growth. Of the two, temperature decidedly seems to be the controlling condition. In the light of the theories of Federov, Schönflies and Barlow, partitioning space into space unites or space lattices, or elementary cells which have been substantiated by X-ray studies of crystal structure, it seems quite reasonable to assume that crystal habit is intimately related in some way to crystal structure.

**X-RAY PHOTOGRAPHS.** It seems reasonable to assume that if foreign substances enter into intimate relation with the atoms or molecules as has been suggested there might be a change in the size of the unit cells, and consequently a change in the space relations of the structure planes. However, a comparison of powder photographs, made by Dr. L. S. Ramsdell of the University of Michigan, showing on the same film diffraction patterns of crystals from pure aqueous solutions and of crystals of the same salt obtained from aqueous solutions containing impurities revealed no difference in structure or in dimensions of the unit cell.

#### CONCLUSIONS

For every crystalline substance there are possible certain crystal forms. The forms possible may be considered to be determined by the crystal structure. Considering, then, that there is a constant tendency of a crystal surrounded by a liquid medium containing its own substance to reach a state of equilibrium with respect to its immediate surroundings, one particular form may approach a state of equilibrium for a specific condition or set of conditions, more easily than any other form. Several important factors which make up the conditions to which the crystal reacts are: (1) temperature; (2) nature of solvent; (3) presence of foreign particles; (4) viscosity; (5) rate of crystal growth.

When forms are in combination it means the conditions have successively changed, or that the conditions prevailing during the time of crystal growth were not exactly the most favorable for either but a fairly close approach and the forms developed simultaneously, each struggling for existence. If we understood solutions more completely and had a more definite knowledge of the shape of the structural units a more satisfactory explanation of crystal habit might possibly be formulated.