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# The Observation of the Precipitation Process by Electronmicroscope. I. Barium Sulfate.

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## Introduction

Production of powdery substance by the precipitation reaction is an important unit process in the chemical industry. It is not seldom that a chemical industry depends upon the inherent character of the powder. The preparation of barium sulfate in various conditions were observed and the precipitation process was considered phenomenologically. The object of this research is to set up a working hypothesis in the precipitation reaction of the chemical industry. Regarding the precipitation process of barium sulfate, many observations have been conducted by many chemists<sup>1)</sup>, and their results have been explained in various ways. Their bases of speculation however consist in the presumption in the smaller world than the resolving power of the optical microscope, although their discussions much helped us in our observation and consideration.

## The way of Observation

The electronmicroscope used in this research is of a magnetic field type made by Hitachi Co., Ltd., in Japan, of which the resolving power is 3 millimicrons in the best condition. Barium sulfate was made from the chemically pure sulfuric acid and barium chloride. Five or six microscopic specimens were prepared for each precipitation, but observations were made at points where the particles completely dispersed on the collodion membrane. As a matter of fact, such a way of observation is unavoidable in the electronmicroscopic observation, although this is not natural in the statistical view point. We obtained two hundreds and fifty electron micrographs. The conditions of experiments are summarized in Table I.

## Shapes of Particles and Pseudostructures

The shapes of particles which were observed in all electronmicrographs are classified into ten types. Figs. 1 and 2, and Table II show them.

Table I.

Exp. No.	Photo. No.	I Conditions of Observations	II Type of Particle (size $\mu$ )
1	B 46-51	A <sub>1</sub> B <sub>1</sub> H <sub>0</sub> D <sub>24</sub> b f d <sub>1</sub>	7(2-3)
2	B 52-55	" " " " " " " M	7(3-4)
3	B 56-57	" " " " " " " " Ig	7(4)
4	B 58-70	" " " D <sub>0</sub> " " " "	7(5-8)
5	B 77-82	" " " D <sub>48</sub> " " "	6(6), 7(6), 8(12), 4(0.25)
"	B 86-88	" " " " " " "	6(5), 7(6), 8(7)
6	B 83-85	" " " " " " " M	7(8)
7	B96-100	" " " D <sub>24</sub> " " " "	8(8-9)
"	C 1-9	" " " " " " " "	8(6-15)
8	C 10-15	" " " D <sub>0</sub> " " "	2, 3, 4, 7(3-6), 8(4), 9(1)
9	C 16-20	" " " D <sub>24</sub> " " "	6(2), 7(3), 8(2-6)
10	C 21	" " " " " " " Ig (1hr)	7
11	C 22-27	" " " " " " " " (3hr)	7(4), 8(5)
12	C 28-33	A <sub>4</sub> B <sub>2</sub> " D <sub>0</sub> t f <sub>0</sub> "	4(0.3-1.2), 5(0.3-0.4)
13	C 34-37	A <sub>1</sub> " " " b f "	8(7-12)
14	C 38-45	A <sub>5</sub> " " " t f <sub>0</sub> "	2, 3, 4(0.4-0.8), 5(1.0), 6(2-0.3), 8(3)
15	C 46-51	A <sub>4</sub> " " " " " "	3, 5(0.5), 9(2), 4(1), 4'(2), 6(3-5), 8(2-4)
16	C 66-67	A <sub>3</sub> " " " b " d <sub>2</sub>	5(0.5), 4(1)
17	C 68-70	" " " D <sub>24</sub> " " "	3, 4, 5(0.5), 9(2-3.5)
18	C 83-93	" " " D <sub>0</sub> " " "	1, 3, 5(0.8-1), 9(2)
19	C 71-82	A <sub>2</sub> " " " " " "	1, 3, 4(0.1-0.3), 5(0.5-6), 7(0.5-4), 8(3-18)
"	D 24-26	" " " " " " "	3, 4(0.1-0.2), 5(1-2), 8(2), 9(1)
20	D 27-29	A <sub>3</sub> " " " " " "	1, 4(1), 5(1-2)
21	D 30-42	A <sub>1</sub> " " " " " " u	1, 2, 3, 4(0.4-1), 5(0.4-1), 6(3), 8(2-10), 9(0.5-0.8)
22	D 43-44	A <sub>1</sub> B <sub>2</sub> H <sub>0</sub> D <sub>48</sub> b f <sub>0</sub> d <sub>2</sub>	3, 6(6), 7(10), 8(3)
23	D 45-50	" " " " " " " u	3, 6(2-3), 7(4-5), 9(0.9)
24	D 70	" " " D <sub>0</sub> " " " (1:1.5)	4(0.8), 5(1), 6(2)
"	D 71-72	" " " " " " " (1:3)	1, 3, 5(0.8-1), 9(2)
"	D 73-75	" " " " " " " (1:6)	1, 5(3), 6(2.5), 9(2)
25	D 76-77	" " " D <sub>24</sub> " " " (1;1.5)	4(0.8), 5(1), 6(2)
26	D 83	" " " " " " " (1:1.3)	4(1)
27	D 84	" " " " " " " ( " )	3, 6(1), 7(2)
"	D 90	" " " " " " " ( " )	7(4)
28	E 55-60	" B <sub>1</sub> H D <sub>0</sub> " f "	10
29	E 61-67	" " " D <sub>24</sub> " " "	10
30	E 69-79	" B <sub>2</sub> " " " f <sub>0</sub> " (1:1.5)	3, 4(0.5), 7(7), 9(1), 10
31	E 83-90	" " " D <sub>48</sub> " " "	3, 4(0.5), 6(3)
32	E91-100	" " " D <sub>0</sub> " " "	8(2-4), 10(6), 10

## Key to Table I.

Combinations of Reagents:—

	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>
H <sub>2</sub> SO <sub>4</sub>	0.1N	0.01N	0.001N	0.01N	0.1N
BaCl <sub>2</sub>	0.1N	0.01N	0.001N	0.001N	0.05N

B<sub>1</sub>: BaCl<sub>2</sub> excess, (1:1.5 in volume), B<sub>2</sub>: H<sub>2</sub>SO<sub>4</sub> excess.D<sub>0</sub>: Sampling immediately after reaction, D<sub>24</sub>: Sampling after 24 hours, D<sub>48</sub>: Sampling after 48 hours.H<sub>1</sub>: Reaction at room temperature, H: Reaction at boiling state.

t: Reaction on the collodion membrane.

b: Reaction in the beaker.

f: Sample filtrated, f<sub>0</sub>: Sample not filtrated.d<sub>1</sub>: Drying in open air (no dust), d<sub>2</sub>: Drying in a heated dryer.

Ig: Ignition.

M: Balarew's treatment of precipitation by KMnO<sub>4</sub> solution<sup>1)</sup>. (There were no effects.)

u: Treatment by ultrasonic wave.

Column I: Methods of preparation of sample and of observation.

Column II: Type of particle observed, and size of particle is shown in the parentheses in micron.

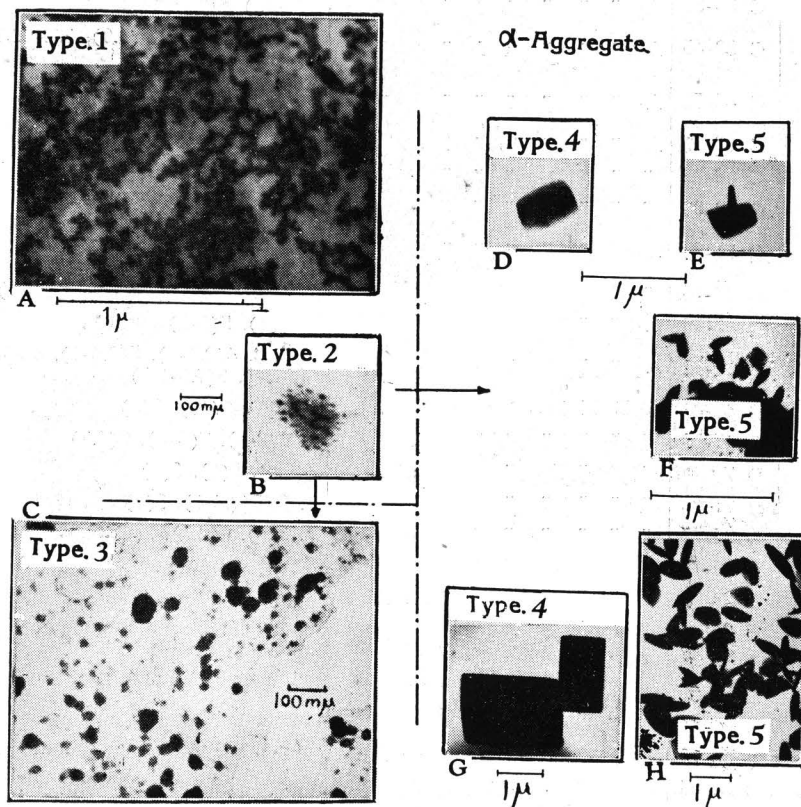


Fig 1.

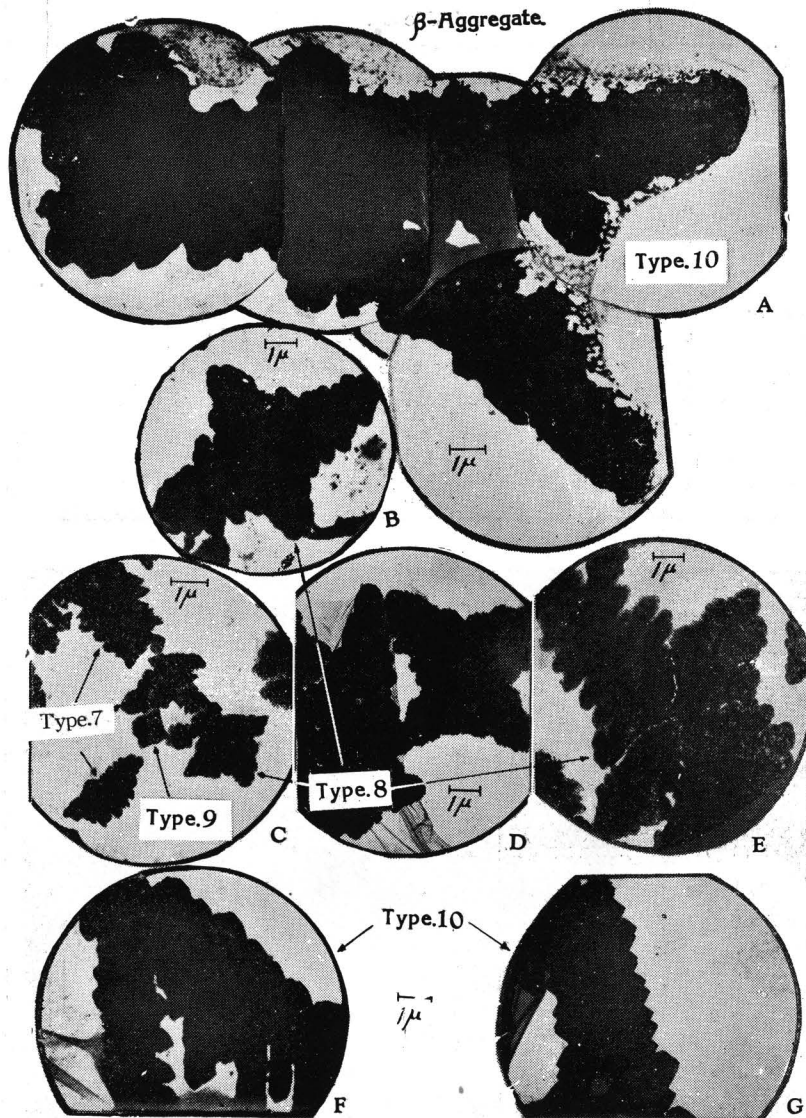


Fig. 2.

Particles on the collodion membrane were stable against the electron bombardment, but the naked particles to the beam were effected by the electron beam. Some pseudostructures were observed.

(1) The part near periphery of the  $\beta$ -aggregate(cf. the following discussion) has some times weak points to the electron beam, and there, rectangular windows were observed, but the periphery and central parts are stable under the beam. (Fig. 3. 1, (C-21)).

Table II.

No. of Type	Shape of Particle
1	Particles connected like rosaries (particle: 20 m $\mu$ )
2	Gel-like isolated aggregate ( " )
3	Spherical isolated aggregate (50-150 m $\mu$ )
4	Rectangular particle (50-700 m $\mu$ )
4'	" " (2 $\mu$ )
5	Particle like a grain of rice (50-1500 m $\mu$ )
5'	Twin crystal (400 m $\mu$ )
6	Spindle-shaped, not crystalline particle
7	Leaf-shaped particle (4-6 $\mu$ )
8	Cross-shaped particle (rhombic; 10-13 $\mu$ )
9	" " (square; 2 $\mu$ )
10	" " (x-shaped; 6 $\mu$ )
	" " ( " 20-40 $\mu$ )

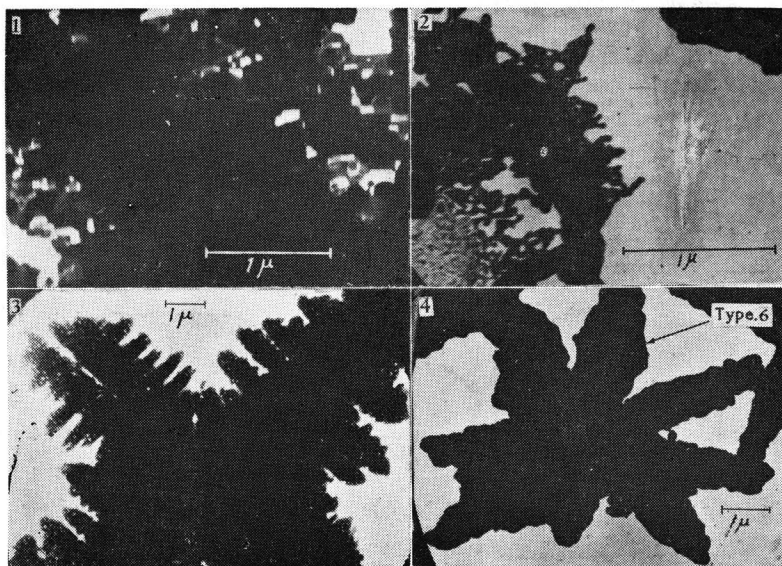


Fig. 3

(3) Along the X-axis or Y-axis of the  $\beta$ -aggregate, a deep crack caused by the electron beam was observed. (Fig. 3.3, (C-5)).

(4) When the electron beam was projected along the X-axis or Y-axis of the  $\beta$ -aggregate, the aggregate, was split into the Type-6 aggregates. (Fig. 3.4, (B-79)).

(2) when the above-mentioned effect of beam goes on violently, the periphery of the windows begin to melt, and the windows become rather round. (Fig. 3.2, (D-50)).

(5) It is interesting that pseudostructures were not observed in the very small particles, but observed in the  $\beta$ -aggregates.

### **On the Precipitation Process of Barium Sulfate**

Various types of precipitated particles are under the restriction that they belong to the same crystal system, and they are respectively steps of the systematic development of precipitation or crystal particles.

#### **(i) $\alpha$ -aggregates.**

The precipitate or crystal of barium sulfate is precipitated from its saturated or supersaturated solution through "cluster"<sup>3)</sup> and the nucleus of crystallization. Immediately upon the production of cluster or nucleus, a surrounding field of crystallization is induced in its circumference which consists of the gradient of the chemical potential, and the nucleus of crystal will grow at an irresistible rate, and the supersaturation cancels with its growth.<sup>2)</sup> As the concentration of the reactant is not uniform in the actual chemical reaction, the number of nuclei in the unit volume of solution will not be equal. At a point where the distance between the nuclei is not too long, a group of nuclei comes into being, and the field of crystallization around that group. The nuclei of crystals grow up rapidly at the bottom of the valley of the chemical potential, and come to the size of the resolving power of the electron microscope. At this stage, the particles should be observed as an isolated group or an aggregate of microcrystals. Type-2 corresponds to this aggregate and the size of the aggregate and that of the microcrystal are 50-150 millimicrons and 10-13 millimicrons, respectively.

The growth of crystal goes on along the rate determining route where the free energy of the system decreases at the maximum rate, and as in the case of the snow crystal, the resulting crystal is not always in the state of the minimum free energy.

As the ions at the surface of the growing microcrystal are not stable, they migrate to the more stable position and in the course of the ion rearrangement the crystal becomes more stable within the restriction of the crystal system. In the crystallization of the substance, the ions of the substance itself are most strongly attracted to the lattice of the crystal, and the other kinds of ions and molecules absorbed are driven out from the surface of the crystal. Meanwhile, the autpurification goes on with the ion rearrangement. The driven out impurities diffuse out of the aggregate through the zig-zag canals formed by the walls of the microcrystals. As the growing and stabilizing particles orientate themselves and each other, making the contact point as a fulcrum, the canals among the particles become narrower, and the aggregates take more condensed forms and their volume

and surface area become smaller as a whole.

The impurities in the canals have to diffuse out of the aggregate, but this process goes well only when the rate of the rearrangement of ions and the orientation of the microcrystals are in harmony each other and the aggregate is not too large. When the process goes on favourably, the particles are strongly combined to each other by the force of short range and the resulting aggregates are very pure and isolated, and they as a whole present a definite crystal form. (Type-4, Type-5)

When the rate of the rearrangement of ions and the orientation lack harmony or when the aggregate is too large, the canals becomes too long and complex. Or when the impurities which are to be rejected remain in great quantity or do not easily diffuse, these impurities can not go out of the aggregate. In these cases, on the one hand, the rearrangement and the orientation become very difficult, and on the other the free energy of the aggregate will be fairly decreased, and thus the aggregate remains a relatively dense and not crystalline-formed one which occludes more impurities. (Type-3)

We consider this as the first process of the precipitation reaction, and for convenience's sake we call the resultant aggregate the  $\alpha$ -aggregate.

The dimension of the  $\alpha$ -aggregate is ascribed to the amount of barium sulfate in the composed field of crystallization. The microcrystals in the type-2 aggregate are stable in so far as they have once come into being, and we consider that they are not absorbed into a homogeneous particle in the first process of the precipitation. The largest type-2 aggregate is about 50 millimicrons and their shapes are cubic or rectangular in irregular ways and seldom like grains of rice.

When the concentration of the reaction system is low, the gradient of chemical potential becomes rapidly a gentle slope, and the route of the maximum rate of the free energy decrease nearly corresponds to the route which is statically stable.

Under such a condition, the number of nuclei of crystallization is small, and the shape of the  $\alpha$ -aggregate gets near its typical and essential crystal form, and at the low stage of growth, the growth in the  $c$ -axis is poor, and the side walls of the crystal are (102), (011) and (110) and the bottom is (001) on the collodion membrane, and they are like the grains of rice. (Type-5)

When the concentration in the field of crystallization is higher, the crystal grows along to the  $c$ -axis, and its bottom is (110); thus we can see the rectangular crystal. (Type-4)

When we see the twin crystals, the shape of the respective crystal is not typical Type-5 and Type-4, because its shape is projected obliquely. Especially, Type-5 are always found in the reaction between N/1000 solutions ( $A_3$ ,  $A_4$ ), and sometimes they are found in the other case, but they will be the last crystals in the precipi-



tation process or reaction. They seldom grow to larger crystal keeping their original shapes. (type-4')

(ii)  $\beta$ -aggregate.

While the first process goes on and the  $\alpha$ -aggregates are coming into being, at the points of rather higher concentration, surrounding the  $\alpha$ -aggregates, the other  $\alpha$ -aggregates are born. There also the first process of crystallization goes on. The group of adjacent  $\alpha$ -aggregates induces the composed field of crystallization and a larger field of crystallization is born. These groups of  $\alpha$ -aggregates decrease their free energies as a whole and orientate themselves and aggregates, absorbing new nuclei and Type-2 aggregates in each group. In this process, it is the Type-2 aggregate and the  $\alpha$ -aggregate which is in the stage of crystallization and is near the Type-2 aggregate, that makes an active rearrangement of surface ion. These active  $\alpha$ -aggregates reject impurities, being in contact with the  $\alpha$ -aggregates which are at higher stage of the first process than the Type-2 aggregates, and become the binder between the other  $\alpha$ -aggregates. Each  $\alpha$ -aggregate orientates itself in its group, driving out the purged impurities through the canals to the outside of its group.

The aggregates composed of  $\alpha$ -aggregates is generally much larger than  $\alpha$ -aggregates and the size is between about 2 microns and 15 or 16 microns. The above stated process becomes characteristic in the latter stage of the first process, and the purge of impurities is more difficult than in the first process, and then the aggregates as the results of this second process occlude more impurities. We call this particle the  $\beta$ -aggregate, and it generally is this aggregate that we observe by the optical microscope as the barium sulfate particles, and we call this latter process the second process of crystallization.

These two processes go in parallel, but the latter consists in orientation and coagulation, and the autopurification does not go on as in the first process. Then we consider that the most part of impurities of precipitation are ascribed to the state of the second process.

Fig. 4 (1) is a part of the typical  $\beta$ -aggregate, and show the columnar  $\alpha$ -aggregates which orientate themselves in parallel with each other, being in contact side by side with their crystal faces (110). In the latter stage of the second process, we may expect that the Type-4, Type-5 aggregates, younger type aggregates or their group will be found on and near the  $\beta$ -aggregate. Fig. 4 (2) shows the case, and we can see the Type-3  $\alpha$ -aggregates which perhaps remained free from aggregate since the beginning of the first process. As a result of the above mentioned view, we may expect the Type-4 and Type-5  $\alpha$ -aggregates on the periphery of the  $\beta$ -aggregate. A pseudostructure (Fig. 3(1)) suggests the internal structure: many

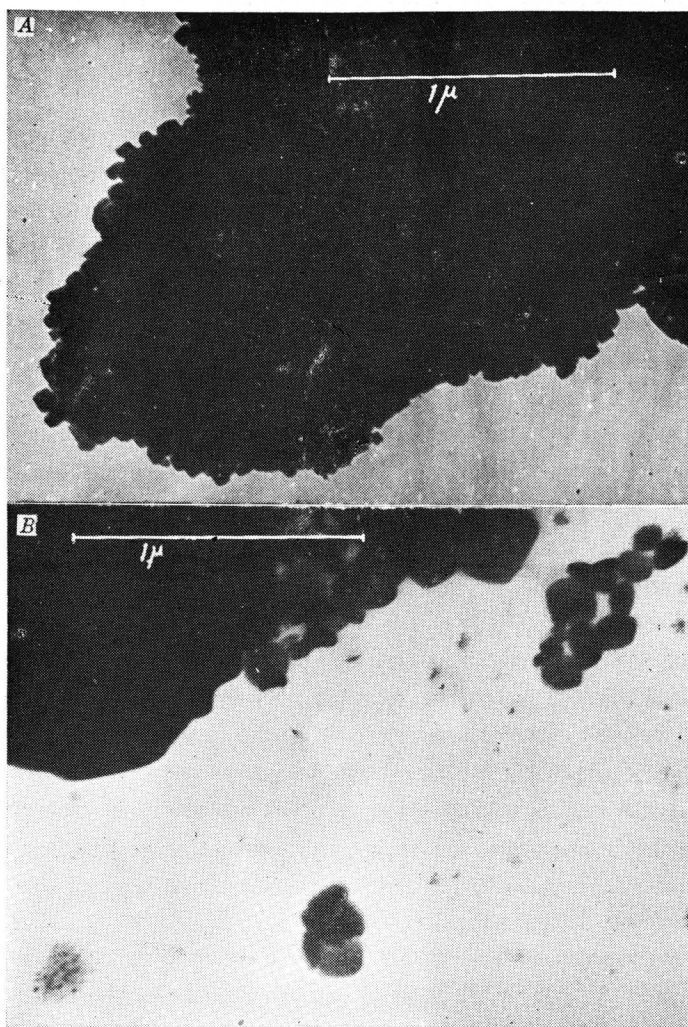


Fig. 4

rectangular windows which were made by electron bombardment open nearly in parallel, and this fact shows that the typical  $\beta$ -aggregate is constructed by the columnar  $\alpha$ -aggregate. The fact that the periphery of the  $\beta$ -aggregate is stable to the electron beam suggests that the periphery is constructed by the dense  $\alpha$ -aggregates (Type-4, Type-5) which have come into being in the latter stage of the process. Our view coincides with the view of Balarew's school in many points.

When the  $\beta$ -aggregates were subjected to ignition, water in the interior canal is driven out and orientation goes on, and the microcrystals on the surface are

extinguished as a result of sublimation or surface migration. Then the surface of the  $\beta$ -aggregate becomes very smooth.

**(iii) The Shapes of the  $\beta$ -Aggregates.**

The  $\beta$ -aggregates of barium sulfate are classified into certain types by their shapes. (Fig. 2) But the relation between shapes and precipitation process is very complex. Generally all types of the  $\alpha$ -aggregates may take part in the second process, and the shapes of the  $\beta$ -aggregates depend upon these  $\alpha$ -aggregates and the conditions of the field of crystallization.

Generally the cross type (Fig. 2 (E), C-34) prevails, and we observe the existence of the centre in them, and they are all nearly symmetrical (Fig. 2B(B-78), C(C-12), D(B-87)). This fact shows that the  $\beta$ -aggregates grow along the X-axis and the Y-axis and not the Z-axis; they are two dimensional aggregates.

The pseudostructure (Fig. 3, 4) suggests that the  $\beta$ -aggregate such as Fig. 2 B is the aggregate of the Type-6  $\beta$ -aggregates, and these aggregates are not broken by the ultrasonic wave.

The rugged surface has more free energy, and for elements on the surface it becomes possible to migrate to the lower energy level by the electron bombardment, but the  $\beta$ -aggregates are the solid body as a whole, and the contraction of surface provokes the crack of the  $\beta$ -aggregate. (Fig. 3.3)

Generally, the number of types of precipitated particles increases with the advance of concentration of reaction system. As the column II of Table I shows, the reaction  $A_1$  has all types, the reaction  $A_3$  Type-4 and Type-5, and when the concentration is moderate, the number of types is in the middle of the cases  $A_1$  and  $A_3$ .

**(iv) Effect of Temperature.**

Main factors of the above mentioned process are the number of nuclei, the distribution of nuclei, the rearrangement rate, and the orientation rate. And the effect of temperature rise on the last factor is not so great as on the other three factors, because the orientation is a movement of relatively large particles and the fluidity and flexibility of  $\beta$ -aggregate are little.

When the reaction goes on at the boiling point, each process of crystallization is accelerated, but each process goes on very smoothly. And in this case, each aggregate becomes larger, because the field of the crystallization becomes extensive by the effective diffusion and agitation. The  $\beta$ -aggregates precipitated at the boiling temperature are very large and their surfaces are very smooth.

Generally, the cross type becomes very rare, and  $x$ -Type  $\beta$ -aggregate (Fig. 2 A(E-85)) prevails. Fig. 2 F(E-92) and Fig. 2 G(E-60) show a part of these  $\beta$ -

aggregates. We did not observe the isolated  $\alpha$ -aggregates.

We know that the amount of impurities in these aggregates are very small.

#### Summary.

We observed phenomenologically the precipitations of barium sulfate which were made under various conditions, and we may conclude as follows:

(1) The precipitation reaction of barium sulfate is divided into two processes:

(2) Both processes go in parallel, and the main part of the first process is autopurification and orientation, and the process of the second consists in orientation and coagulation of  $\alpha$ -aggregates.

We may call the product of the first process the  $\alpha$ -aggregate, and that of the second the  $\beta$ -aggregate.

(3) The particle of barium sulfate which has been observed by the optical microscope is  $\beta$ -aggregate.

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