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The Effect of Triphosphate on the Crystallization of Strontium Sulfate[*1]

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The inhibiting action of triphosphate on the crystallization of strontium sulfate has been investigated conductometrically. The crystallization of strontium sulfate is remarkably inhibited by a minute amount of triphosphate. A supersaturated solution of 0.02 M strontium sulfate is, in practice, completely stabilized in the presence of 3×10^{-5} M triphosphate. In this stabilized solution, the growth of the seed crystal of strontium sulfate has been examined. The growth of the seed suggests that, in the stabilized solution, the formation of the critical nucleus of strontium sulfate is inhibited by the action of triphosphate. By utilizing the relation between the nucleation rate of strontium sulfate and the concentration of triphosophate, it has been shown that triphosphate increases the energy of formation of the critical nucleus. On the other hand, the adsorption of triphosphate on the crystal surface of strontium sulfate is endothermic; the heat of adsorption is estimated to be $3\boldsymbol{k}T$ per triphosphate from the temperature dependence on the adsorption isotherm. The heat of adsorption of triphosphate increases the energy of formation of the critical nucleus of strontium sulfate. It may, therefore, be concluded that the nucleation of strontium sulfate is inhibited by the adsorption of triphosphate. From the calculation of the collision between triphosphate and the embryo of strontium sulfate, it may be deduced that the adsorption of triphosphate is predominant in the initial stage of the formation of the embryo of strontium sulfate.

As has been reported previously, polyphosphates remarkably retard the crystallization of such

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sparingly-soluble inorganic salts as calcium carbonate,[1] calcium sulfate,[2] and strontium sulfate.[3-7] For example, in the presence of triphophate with a molar concentration even several hundred times less than that of strontium sulfate, the crystallization of strontium sulfate from a 0.02 M aqueous solution is completely inhibited, and its supersaturated solution remains perfectly clear for a long time.[3] Such an inhibiting action of triphosphate is very important not only from the viewpoint of industrial application, but also from that of fundamental aspect of crystallization.

So far, the mechanism for the inhibiting action of polyphosphates has been examined by various workers,[8-12] but no satisfactory explanation has yet been proposed. In the past investigations, it has been assumed that polyphosphates are adsorbed on the surface of crystal nuclei which are born in the supersaturated solution, thereby preventing the further growth of the nuclei. However, in spite of much effort, no direct evidence has yet been found to show the existence of such nuclei. Some investigators,[10,11] have therefore, thrown doubt on the existence of these nuclei.

In order to clarify such a characteristic action of polyphosphates on the crystallization, the present paper will deal with: I) the growth of the seed crystals of strontium sulfate in its supersaturated solution stabilized by triphosphate; II) the formation energy of the nucleus of strontium sulfate as a function of the concentration of triphosphate, and III) the adsorption energy of the triphosphate on the surface of strontium sulfate. From these results, the mechanism of the inhibiting action of triphosphate in the crystallization of strontium sulfate will be discussed.

Experimental

Materials. Special-grade reagents of strontium chloride and potassium sulfate (Wako Pure Chemical Co., Ltd.) were purified by recrystallizing them three times from their aqueous solutions. Sodium triphosphate labeled with ^{32}P was synthesized by calcinating an orthophosphate mixture containing ^{32}P; it was then recrystallized five times from the aqueous solution by adding ethyl alcohol.

Crystallization. The inhibiting action of triphosphate on the crystallization of strontium sulfate was investigated conductometrically at 25°C. The supersaturated solution of stronitum sulfate was prepared by mixing equal volumes of 0.04 M solutions of strontium chloride and potassium sulfate, the latter containing various amounts of triphosphate. By using an elaborate alternate-current bridge, the specific conductance of the supersaturated solution was measured at regular intervals. In this way, the effect of triphosphate on the crystallization of strontium sulfate was examined accurately.

Growth of Seed Crystals. Two kinds of samples were prepared as the seed crystals of strontium sulfate; a single crystal and a spherulite. The method of preparing the single crystal was the same as that reported previously.[7] The BET surface area of the single crystals was found to be 0.83 m^2/g by the adsorption of nitrogen gas at the temperature of liquid nitrogen. The spherulites were obtained by crystallizing them from a 0.02 M solution of strontium sulfate containing 1.5×10^{-5} M triphosphate. On the basis of the average size of the spherulites, their specific surface area was estimated to be approximately 10^{-2} m^2/g; this value may be underestimated, however, because the roughness factor of their surface is taken to be one.

The growth of the seed crystals was also examined conductometrically in the supersaturated solution of stronitum sulfate stabilized by triphosphate. The growth medium consisted of 0.02 M stronitum sulfate and 3×10^{-5} M triphosphate. In this medium, the crystallization of strontium sulfate is completely inhibited, as is shown by the curve C of Fig. 1, but the seed crystals added grow appreciably.

Adsorption. The adsorption of triphosphate on strontium sulfate was measured by the radio-tracer method at 6°C and 45°C with the aid of triphosphate labelled with ^{32}P, as has been described in a previous paper.[1] The crystal of strontium sulfate used as an adsorbent was the same as the single crystal used in the growth of the seed crystals.

Results

In Fig. 1, the crystallization of strontium sulfate from a 0.02 M aqueous solution is presented as a decrease in the specific conductance at the concentrations of 0, 10^{-5} M, and 3×10^{-5} M triphosphate.

Figure 2 shows the growth of the single crystals and the spherulites when a 20 mg portion of the seed crystals is put into 30 m*l* of the growth medium described in the experimental section.

The adsorption isotherms at 6°C and 45°C are shown in Fig. 3.

Discussion

(I) The Inhibiting Action of Triphosphate.

As may be seen in Fig. 1, the crystallization of

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[1] M. Miura, H. Naono and S. Otani, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 596 (1963).

[2] M. Miura, unpublished data.

[3] S. Otani, This Bulletin, **33**, 1544, 1549 (1960).

[4] M. Miura, S. Otani, M. Kodama and K. Shinagawa, *J. Phys. Chem.*, **66**, 252 (1962).

[5] M. Miura, S. Otani, Y. Abe and C. Fukumura, This Bulletin, **36**, 1096 (1963).

[6] H. Naono and M. Miura, *ibid.*, **38**, 80 (1965).

[7] M. Miura, H. Naono and M. Hara, *ibid.*, **39**, 344 (1966).

[8] G. B. Hatch and O. Rice, *Ind. Eng. Chem.*, **31**, 51 (1939).

[9] R. F. Reitemeier and T. B. Buehrer, *J. Phys. Chem.*, **44**, 535, 552 (1940).

[10] R. F. Reitemeire and A. D. Ayers, *J. Am. Chem. Soc.*, **69**, 2759 (1947).

[11] B. Raistrick, *Discussions Faraday Soc.*, **5**, 234 (1949).

[12] E. J. Burcik, *Producers Monthly*, **19**, No. 1, 42 (1954).

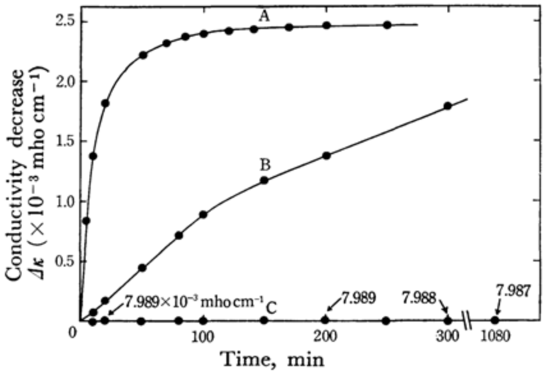

Fig. 1. Inhibiting action of triphosphate on the crystallization of strontium sulfate: A=0, B=1.5×10^{-5} M, C=3.0×10^{-5} M triphosphate.

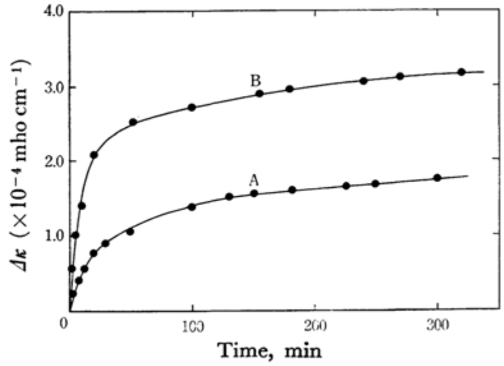

Fig. 2. Growth of the seed crystals of strontium sulfate in the stabilized supersaturated solution of strontium sulfate. A, single crystals and B, spherulites.

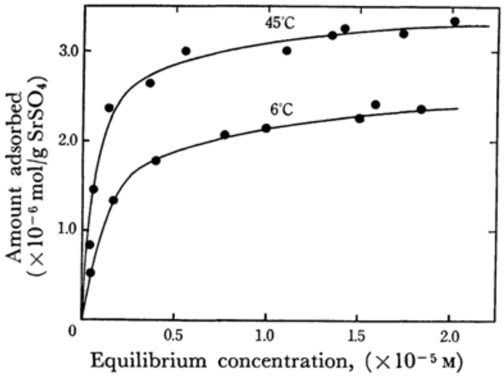

Fig. 3. Adsorption isotherms of sodium triphosphate on the crystal surface of strontium sulfate.

strontium sulfate is remarkably retarded, and finally comes to be completely inhibited, when 3×10^{-5} M triphosphate is also present in the system. In the inhibited system (curve C in Fig. 1), the decrease in the conductance could not be detected within 1000 min. Our alternate-current bridge is so sensitive that a change of 0.01% in conductance can easily be detected. Therefore, it may be concluded that the crystallization of strontium sulfate is, in practice, completely inhibited in the stabilized system.

The inhibiting action of polyphosphates on the crystallization of calcium carbonate[8-11] and calcium sulfate[12] has also been observed previously. Since Rosenstein[13] discovered the above phenomenon, it has mainly been utilized in such fields as the prevention of a calcium carbonate deposit in process water[8] and of a gypsum deposit in producing wells.[12]

On the other hand, this phenomenon has been discussed from the fundamental point of view. According to the first explanation proposed by Hatch and Rice[8], the growth of any calcium carbonate nuclei formed is inhibited by the adsorption of polyphosphate on them, and their size does not exceed the colloidal dimensions. On the basis of their precise measurements of clacium ion activity, however, Reitemeier and Ayers[10] refuted the existence of the nuclei in the supersaturated solution of calcium carbonate stabilized by polyphosphate. Further, in order to explain the fact that the stabilized solution of calcium carbonate remains perfectly clear for weeks, Raistrick[11] stated that "the embryos do not become big enough to be incapable of dissociating completely once more into disordered ions." However, the inhibiting action of polyphosphate on the crystallization has not yet been clarified.

(II) Growth of the Seed Crystals. In order to get a clue as to whether or not the formation of the nuclei is inhibited in the stabilized supersaturated solution, the growth of the seed crystals was examined. Figure 2 shows that the growth of the single crystals and the spherulites can be detected as the conductance decreases.

In order to examine the crystal growth in more detail, it is necessary to estimate the growth per unit of area, since crystal growth is a surface phenomenon. Thus, the growth of the single crystals and the spherulites per cm^2 is estimated.

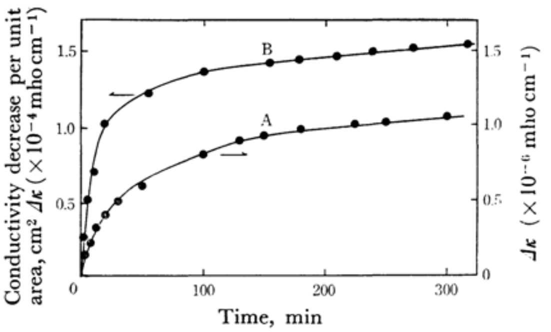

Fig. 4. Growth of the seed crystals per unit area, cm^2. A, single crystals and B, spherulites.

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13) L. Rosenstein, U. S. Pat. 2038316 (1936).

The results are shown in Fig. 4, from which it is obvious that the growth of the spherulites is remarkably rapid compared with that of the single crystals. Though this problem is of great interest with relation to the surface structure of the spherulites, it is not discussed in the present paper.

If the nuclei are formed in the growth medium, it is considered that their growth is similar to that of the spherulites, because the spherulites are deposited from the system in which triphosphate is present. Now, by assuming the growth of the nuclei to be the same as that of the spherulites, let us examine whether the growth of the nuclei can be detected conductometrically. As may be seen in the curve B of Fig. 4, the decreased amount of the specific conductance per cm^2 reaches 1.5×10^{-4} mho cm^{-1} after 300 min. On the other hand, the detection limit in conductance change is 2×10^{-6} mho cm^{-1} in the present experiment. The surface of 1.3×10^{-2} cm^2, therefore, brings about a detectable decrease in conductance after 300 min. Even if the surface area of the spherulites is underestimated to be one-tenth, the decrease in conductance can be detected by the existence of the surface of 1.3×10^{-1} cm^2.

As has been reported in a previous paper,⁶⁾ 8×10^6 of strontium sulfate nuclei are born in 1 m*l* of the 0.02 M solution per second. The critical nucleus of strontium sulfate contains thirty-two ions of strontium and sulfate, and it is claculated to be 17 Å in diameter by assuming the nucleus to be spherical, as will be shown in the later part of this paper. The surface area of a nucleus, therefore, is approximately 10^3 Å^2. The total surface of the nuclei formed per second in 30 m*l*. amounts to 2.4×10^{-5} cm^2. If the formation of the nuclei is not prevented by triphosphate, the nuclei surface reaches 1.3×10^{-1} cm^2 within 100 min. In addition, the formation of the nuclei itself results in a decrease in the conductance, but the contribution is so small that the amount decreased is far below the detection limit even after 1000 min. The above calculation shows that, after an extended period, the decrease in the conductance in the completely-stabilized supersaturated solution would be easily detected if the nuclei are born at the same rate as in the absence of triphosphate.

The conductance of the stabilized system (curve C in Fig. 1), however, is kept constant for 1000 min within the detection limit. Accordingly, it is concluded that triphosphate remarkably inhibits the formation of the nuclei of strontium sulfate. Further, this conclusion is strongly supported by a recent study on the light scattering of the supersaturated solution of strontium sulfate completely stabilized by triphosphate.⁶⁾

(III) Nucleation of Strontium Sulfate. In a previous work,⁶⁾ we examined the rate of the formation of the nuclei of strontium sulfate as a function of the concentration of triphosphate also present. The results are summarized in Table 2, which shows that even when such a minute amount of triphosphate as 1.5×10^{-5} M is present in the supersaturated solution, the rate is reduced to $1/10^9$. This result is consistent with the conclusion obtained from the discussion of the crystal growth.

TABLE 1. DIFFUSION COEFFICIENT AND IONS DIAMETER OF STRONTIUM SULFATE

Diffusion coefficient of strontium sulfate[a]		5×10^{-6} cm^2 sec^{-1}
Diameter of hydrated ions[b]	Strontium ion	4.2 Å
	Sulfate ion	4.0 Å
	Average size	4.1 Å

a) The value was deduced from the diffusion coefficient of $MgSO_4$, $CuSO_4$ and $ZnSO_4$.

b) R. A. Robinson and R. H. Stokes, " Electrolyte Solution," Butterworths Scientific Publications, London (1955).

TABLE 2. INFLUENCE OF TRIPHOSPHATE ON THE NUCLEATION RATE OF STRONTIUM SULFATE

Concentration of triphosphate, M	Rate of nuclei formation, J (nuclei cm^{-3} sec^{-1})
0	$(8\pm3)\times10^6$
2.0×10^{-6}	$(2.0\pm0.7)\times10^6$
5.0×10^{-6}	$(1.0\pm0.5)\times10^3$
1.0×10^{-5}	$(1.5\pm0.6)\times10^{-1}$
1.5×10^{-5}	$(5\pm1)\times10^{-3}$

Now, let us consider the formation of the nucleus of strontium sulfate in the light of the nucleation theory. In discussing the nucleation, it is necessary to know the formation energy of the nucleus of strontium sulfate, from which such important information as the size of the nucleus and the interfacial energy between the nucleus and the supersaturated solution can be obtained.

According to the nucleation theory, the rate of the nucleus formation, J (the number of nuclei formed from the supersaturated solution per unit of volume per second), is connected by the following relation with the free energy of the formation of a nucleus, ΔG^* ¹⁴⁾:

$$J=\frac{2D}{d^5}\exp\left(-\frac{\Delta G^*}{\boldsymbol{k}T}\right) \tag{1}$$

where D is the diffusion coefficient of the crystallizing ion; d, the ion diameter, $\boldsymbol{k}$, the Boltzmann constant, and T, the absolute temperature. By putting the value of the diffusion coefficient and the average value of the diameters of hydrated strontium and sulfate ions in Table 1 into the D and d of Eq. (1), the pre-exponential term of Eq.

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14) A. E. Nielsen, "Kinetics of Precipitation," Pergamon Press, Oxford, London (1964).

(1) is estimated to be $2\times10^{30}\ \mathrm{sec^{-1}\,cm^{-3}}$. Therefore:

$$J = 2\times10^{30}\exp\left(-\frac{\Delta G^*}{\boldsymbol{k}T}\right) \tag{2}$$

By using the data in Table 2, the values of ΔG^* are then calculated; the effect of triphosphate on the diffusion coefficient is neglected, because the amount of triphosphate is extremely small compared with that of strontium sulfate. In Fig. 5, the free energy of the formation of the strontium sulfate nucleus is plotted against the molar concentration of triphosphate. This figure shows that the energy of 54 $\boldsymbol{k}T$ is necessary to form a nucleus in the absence of triphosphate, and that the energy of the nucleus increases with the increase in the concentration of triphosphate. In other words, the energy barrier of the formation of the nucleus is increased by the action of triphosphate.

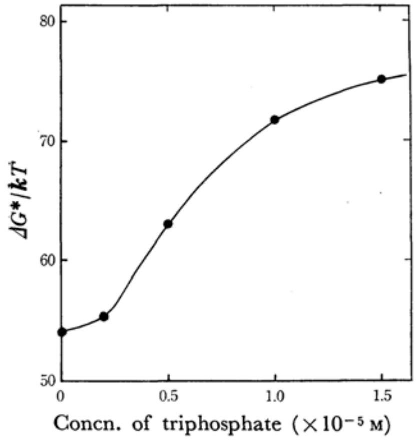

Fig. 5. Effect of triphosphate on the energy of the formation of strotium sulfate nucleus.

Next, let us examine the size of the nucleus and the interfacial energy of strontium sulfate. The number of strontium sulfate in a critical nucleus, n^*, and the interfacial energy, σ, are, respectively, connected by the following relations with the formation energy of the critical nucleus, ΔG^*⁽¹⁴⁾:

$$\Delta G^* = \frac{1}{2}\,\boldsymbol{k}T\,n^*\ln S \tag{3}$$

$$\Delta G^* = \beta\,\frac{\sigma^3 v^2}{(\boldsymbol{k}T\ln S)^2} \tag{4}$$

where S is the degree of supersaturation; β, a geometrical factor of the nucleus, and v, the molecular volume of a solute. Under the assumption that the nucleus is spherical, the value of β becomes 11.8. The value of v of strontium sulfate is 77 Å^3; this value is estimated from the density of the strontium sulfate crystal and its molecular weight. In the system examined, S is 32 and T is 298°K. By putting these values into Eqs. (3) and (4), the values of n^* and σ are calculated to be 32 and 80 ergs cm^{-2} respectively in the absence of triphosphate. From the value of n^*, the diameter of the nucleus is estimated to be 17 Å.

Recently, the interfacial energy of strontium sulfate has been re-examined in detail by Enüstün and Turkevich,⁽¹⁵⁾ utilizing the dependence of the solubility on the particle size. They have given 84±8 ergs cm^{-2} as the mean interfacial energy between strontium sulfate and its saturated solution. This value is in good agreement with that mentioned above.

(IV) Adsorption Energy of Triphosphate on Strontium Sulfate. As has already been pointed out by the past investigators, the inhibiting action of polyphosphates on the crystallization of sparingly-soluble inorganic salts is closely correlated with their adsorption on these crystal surfaces. It was recently confirmed experimentally by Miura *et al.* that the adsorption of several completely-separated oligophosphates plays an important role in the inhibition of the crystallization of calcium carbonate⁽¹⁾ and strontium sulfate.⁽⁴,⁵⁾

Judging from the result that the formation energy of the strontium sulfate nucleus is increased by the action of triphosphate, the adsorption energy of triphosphate is considered to give a key to solving the mechanism of the inhibiting action. From this point of view, the adsorption energy of triphosphate on the crystal surface of strontium sulfate may be estimated from the dependence of the adsorption isotherm on the temperature.

The amount of triphosphate adsorbed is less at a lower temperature than that at a higher temperature, as may be seen in Fig. 3. This indicates that the adsorption of triphosphate is endothermic. The following relations are used to obtain the thermodynamic quantities.⁽¹⁶⁾ The changes in free energy, ΔF, enthalpy, ΔH, and entropy, ΔS, by adsorption are, respectively, given by:

$$\Delta F = -\boldsymbol{R}T\ln K \tag{5}$$

$$\Delta H = \boldsymbol{R}\left(\frac{T_1T_2}{T_1-T_2}\right)\ln\frac{K_1}{K_2} \tag{6}$$

$$\Delta S = \frac{\Delta H-\Delta F}{T} \tag{7}$$

where $\boldsymbol{R}$ is the gas constant and T, the absolute temperature, and where K is the equilibrium constant for the following process:

$$\mathit{Triphosphate}_{\text{in solution}} \rightleftarrows \mathit{Triphosphate}_{\text{adsorbed}}$$

and is defined by:

$$K = \frac{\Gamma}{t\,c_{\text{bulk}}} \tag{8}$$

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15) B. V. Enüstün and J. Turkevich, *J. Am. Chem. Soc.*, **82**, 4502 (1960).

16) F. E. Bartell, T. L. Thomas and Y. Fu, *J. Phys. Chem.*, **55**, 1456 (1951).

where Γ is the adsorbed amount of triphosphate expressed by moles per cm^2; c_{bulk}, the concentration of triphosphate in bulk at equilibrium (given in moles per cm^3), and t, the thickness of the adsorbed layer in cm.

The thickness of the adsorbed layer of triphosphate is taken as 5.8 Å; this value is deduced from the previous data and from the molecular model of triphosphate.4) The amount adsorbed per cm^2 is estimated from the specific surface area of an adsorbent; the results are presented in Fig. 3. By putting the values of Γ, t and c_{bulk} into Eq. (8), the values of the equilibrium constants at 6°C and 45°C are estimated. By using the K values, the values of ΔF, ΔH and ΔS are calculated from Eqs. (5), (6) and (7); the results are summarized in Table 3.

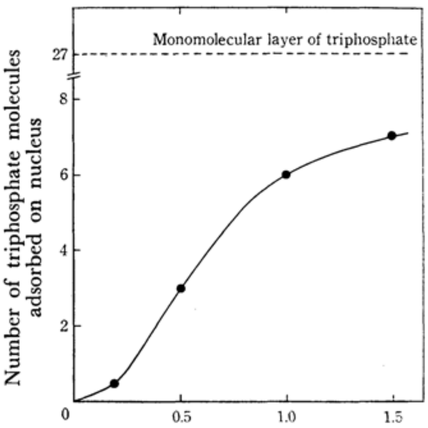

Fig. 6. Relation between the concentration of triphosphate in bulk and the number of triphosphate molecules adsorbed on an nucleus.

TABLE 3. THERMODYNAMIC QUANTITIES ON THE ADSORPTION OF TRIPHOSPHATE ON STRONTIUM SULFATE

Temp. °C	Thermodynamic quantities		
	ΔF kcal mol^{-1}	ΔH kcal mol^{-1}	ΔS cal deg^{-1} mol^{-1}
6	−8.5	1.8 (3 $\boldsymbol{k}T$ molecule^{-1})	37
45	−9.9		

In spite of the fact that the adsorption of triphosphate becomes saturated at an extremely low concentration, the enthalpy change is positive. The entropy change, therefore, is sufficiently large and positive to allow the free energy change to have a negative value. Triphosphate is adsorbed from its aqueous solution, where it is hydrated. The increase in entropy by the adsorption is considered to be related to the hydration waters around triphosphate. When hydrated triphosphate is adsorbed on the solid surface, some of the hydration waters are released and made free. The increase in entropy due to the release of waters may exceed the decrease in entropy due to the triphosphate fixed on the solid surface, and the net change of the entropy may become positive.

The phenomenon mentioned above is unique and in contrast with the adsorption of gas onto the solid surface, where the entropy change is always negative and where the process of the adsorption of gas is essentially exothermic. When the heat of adsorption is exothermic, the solid surface becomes more stable than before adsorption because of the release of the heat of adsorption. On the other hand, when it is endothermic the solid surface becomes less stable than before, although the system, as a whole, becomes stable by adsorption.

Now, let us consider the stability of the nucleus of strontium sulfate before and after the adsorption of triphosphate. It is shown in Table 3 that the enthalpy change of the adsorption of triphosphate is 3 $\boldsymbol{k}T$ per molecule. It may, therefore, be concluded from the above discussion that the surface of the nucleus of strontium sulfate becomes less stable upon the adsorption of triphosphate. By assuming that the enthalpy change causes the formation energy of the nucleus to increase, the number of triphosphate adsorbed on the nucleus may be estimated from Fig. 5; the results are shown in Fig. 6 as a function of the concentration of triphosphate. Since the cross-sectional area of triphosphate is 37 Å^2 4) and the surface area of the nucleus is *ca.* 10^3 Å^2, the number of the triphosphate adsorbed on the nucleus may be far below those of the monolayer coverage, even in a remarkably stabilized solution.

(V) Collision between Triphosphate and Embryo. The fact that the formation of the nucleus is inhibited by the adsorption of triphosphate suggests that triphosphates are adsorbed during the growth of the embryo of strontium sulfate. In this section, the collision between the embryo and triphosphate will be examined and the adsorption of triphosphate during the growth of the embryo will be discussed. Since this problem is extremely complex, a rather rough approach will be attempted.

When an embryo containing n molecules of strontium sulfate, $(\mathrm{SrSO_4})_n$, is formed in the supersaturated solution, the free energy of its formation, ΔG_n, is given by14):

$$\Delta G_n = -\boldsymbol{k}Tn \ln S + 4\pi \beta^{2/3} v^{2/3} \sigma n^{2/3} \qquad (9)$$

where S, β, v, σ, $\boldsymbol{k}$, and T are the same as before. In Fig. 7, the ΔG_n of strontium sulfate is plotted against n in the absence of triphosphate. By using the values of ΔG_n, we can estimate the concentration of the embryo, $(\mathrm{SrSO_4})_n$. Under the assumption that the supersaturation is kept constant, the concentration of the embryo, c_n, is

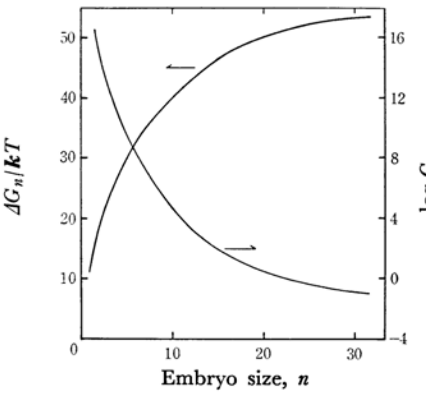

Fig. 7. Energy of the formation of embryo and the concentration of embryo as a function of embryo size.

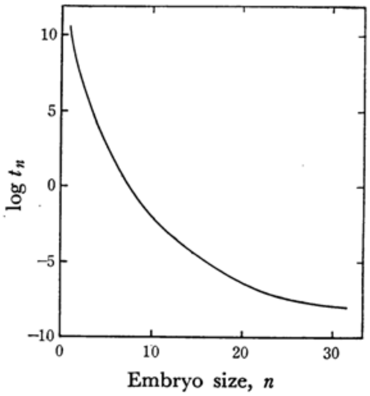

Fig. 9. Average life time of embryo as a function of its size.

given approximately by[14]:

$$c_n = v_0^{-1} \exp\left(-\frac{\Delta G_n}{kT}\right) \tag{10}$$

where v_0 is the molecular volume of a solvent. By putting the volume of a water molecule and ΔG_n into Eq. (10), the embryo concentration in a 0.02 M solution of strontium sulfate can be estimated; the results also are shown in Fig. 7.

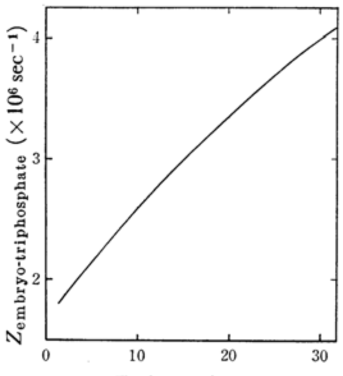

Fig. 8. Frequency of collision between an embryo and triphosphate in 10^{-5} M solution of triphosphate, $Z_{\text{embryo-triphosphate}}$.

Now, let us consider the collision between the embryo and triphosphate in a supersaturated solution of 0.02 M strontium sulfate stabilized by 10^{-5} M triphosphate. By using the concentration of the embryos, the frequency of collision between an embryo and triphosphate can be calculated; the results are shown in Fig. 8 as a function of the size of the embryo. The average time of one collision, t_c, is found to be 2—3$\times 10^{-7}$ sec.

As may be seen from Fig. 7, the number of the embryo extremely increases with a decrease in the size of the embryo. When the degree of supersaturation is kept constant, the rate of the nuclei formation is constant. Therefore, the velocity of the growth of the embryo decreases with a decrease in the size of the embryo. As a measure of the velocity of the growth of the embryo, we use the average life time, t_n, which is given by dividing the number of the embryo of $(SrSO_4)_n$ in cm^3 by the rate of the nuclei formation, that is, c_n/J. In Fig. 9, t_n is plotted against the size of the embryo, n. This figure shows that t_n is *ca.* 10^{-8} sec for the embryos near the critical nucleus. This time is about one-thirtieth of t_c; this shows that, among thirty embryos, only one embryo collides with triphosphate. In the vicinity of the size of $(SrSO_4)_{20}$, t_n is nearly equal to t_c, while below the size of $(SrSO_4)_{20}$, t_n is longer than t_c. Accordingly, the collision of triphosphate with the embryo may be predominat in the initial stage of embryo formation.

In conclusion, the inhibiting action of triphosphate on the crystallization of strontium sulfate may be attributed to the endothermic adsorption of triphosphate on the embryos which are formed in the supersaturated solution of strontium sulfate. When triphosphate is adsorbed endothermically on the embryo of strontium sulfate, the energy barrier of the formation of the critical nucleus increases; as a result the rate of the nucleation of strontium sulfate remarkably decreases and the crystallization is strikingly retarded.

The author wishes to express his sincere gratitude to Professor Masaji Miura of Hiroshima University for his guidance and valuable advice, given throughout the course of this work, and to Dr. Sadaichi Otani for his many helpful discussions. He is indebted to Miss Junko Miyahara for her skilled technical assistance in a part of experimental work. He also wishes to express his thanks to Professor Tetsuo Morimoto of Okayama University for his encouragement.