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Effects of Pressure on the Chemical Properties of Solid Surface. VIII. The Surface Acidity of the Compressed Magnesium Sulfate

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In order to clarify the mechanism of the acidity change due to compression, magnesium sulfate was compressed under various pressures ranging from 0 to 12000 kg/cm^2, the surface acidities, the powder X-ray diffraction patterns, the DTA data, and infrared spectra of the compressed samples were thus obtained. According to the experimental results, the surface acidity of the sample did not vary upon the compression of low pressures (0—6000 kg/cm^2), and a further increase in the compacting pressure resulted in an increase in the surface acidity. From the results of the X-ray diffraction studies, infrared, and far infrared absorption studies and the DTA studies, the relations between the acidity change and the structural changes of the samples were discussed. As a result of this work, the observed acidity change was explained in terms of the distortion of the structural unit of magnesium sulfate.

In our previous studies[1-5] of the effects of pressure on the surface acidity of aluminum sulfate and zinc sulfate, explanations were given for the acidity change due to compression.

The present work has been undertaken to examine whether or not the same explanations are applicable to the acidity change of magnesium sulfate hydrate. The purpose of the present paper is to describe the details of the experimental results and to discuss the mechanism of the acidity change.

Experimental

Materials. Commercial magnesium sulfate heptahydrate was purified by means of recrystallization,[6] and the resulting sulfate was used as the raw material of the sample.

Preparation of the Compressed Sample. The raw sulfate was compressed by the procedures described in the previous papers.[1-5] The compression was carried out under various pressures ranging from 0 to 12000 kg/cm^2 and at a temperature of 20°C. Pressure was applied over a 10 min period. The resulting cylindrical pellet, 6 mm in diameter and 2 mm in height, was pulverized in an agate mortar, and the powdered material was subjected to drying in a vacuum over a 60 min period at a temperature of 18°C. Then, the powder served as a sample for the desired measurment. In order to minimize the effects from the change in ambient conditions, all the operations were carried out in an air-conditioned room.

For the sake of convenience, the respective samples which were compressed under 0, 2000, 4000, 6000, 8000, 10000, and 12000 kg/cm^2 were defined as P_0, P_{2000}, P_{4000}, P_{6000}, P_{8000}, P_{10000}, and P_{12000}.

Surface Acidity. The surface acidity was determined by Benesi's method[7] with the following two indicators: *p*-diphenylaminobenzene (pK_a=3.3) and phenylazonaphthylamine (pK_a=4.0). The acidity measurements were also carried out in an air-conditioned room.

Qualitative Tests for Lewis Acid. The Lewis-acid center on the sample surface was identified by the procedures used in a previous work[4] (color tests with phenolphthalein or trithylchloride).

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[1] Y. Ogino and T. Kawakami, This Bulletin, **38**, 972 (1965).

[2] Y. Ogino, T. Kawakami, and K. Tsurumi, *ibid.*, **39**, 639 (1966).

[3] Y. Ogino, T. Kawakami, and T. Matsuoka, *ibid.*, **39**, 859 (1966).

[4] T. Kawakami, A. Konno, and Y. Ogino, *ibid.*, **44**, 1772 (1971).

[5] T. Kawakami, A. Usui, and Y. Ogino, This Bulletin, to be published.

[6] J. W. Mellor, "A Comprehensive Treaties on Inorganic and Theoretical Chemistry," IV, Longmans, Green and Co., 1923.

[7] H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

Surface Areas. The specific surface area of the sapmle was evaluated by applying the BET theory to the adsorption data of nitrogen at −195°C.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA). The DTA and TGA runs were carried out on a Rigaku Denki unit. The DTA curves and the TGA curves were obtained at a temperature-programming rate of 2°C/min.

X-Ray Diffraction. The powder X-ray diffraction patterns[8] of the sample were obtained with a Shimadzu GX-1 X-ray Diffractometer. The Cu-$K\alpha$ radiation (Ni filter) at 30 KV and 15 mA was used.

Infrared Spectroscopy. The infrared spectra (IR) for a 400—4000 cm^{-1} wave number range were obtained by means of Perkin-Elmer Model 125 Infrared Spectrophotometer. In these works, a Nujol technique was employed. To minimize the interferences from the air moisture, a sample which had been compressed and evacuated was kept in the vessel containing dry nitrogen. Then, immediately before the IR experiment, the sample was withdrawn from vessel and mixed with nujol as quickly as possible.

Results

Surface Acidity. The surface acidities (H_0=3.3—4.0) of samples compressed under various pressures are given in Fig. 1. The acidity values in this figure are given by *n*-butylamine titers per unit of the surface area. As can be seen in Fig. 1, the acidity did not vary of compressions of 2000—6000 kg/cm^2, but a further increase in the compacting pressure resulted in an increase in the surface acidity.

Further, additions of phenolphthalein or trithylchloride to the sample showed no sign positive to the existence of Lewis acid on the sample surface. Thus, the acid appearing on the sample could be identified as protonic acid.

Water Content. The water contents of the samples compressed under various pressures are given in Fig. 2. From this figure, it can be understood that the samples compressed at pressures higher than 6000 kg/cm^2 contain 6 mol of water per mole of $MgSO_4$.

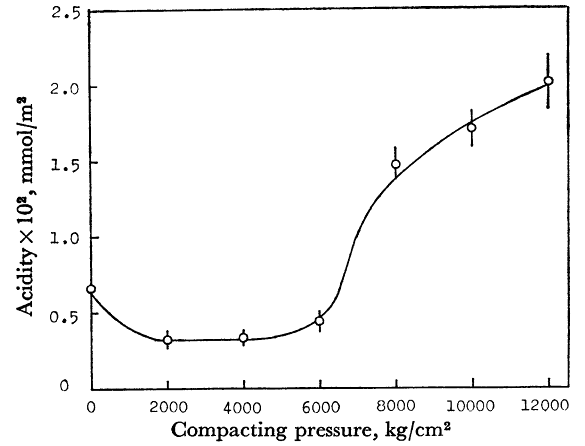

Fig. 1. Relations between the compacting pressure and the surface acidity (H_0=3.3—4.0).

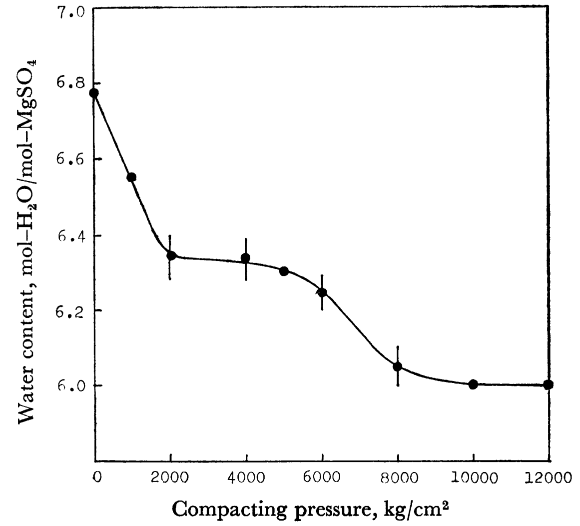

Fig. 2. Relations between the compacting pressure and the water contents.

X-Ray Diffraction. The powder X-ray diffraction patterns of the samples compressed under various pressures are given in Fig. 3. From these patterns, it can be understood that the sample consists of crystallites of magnesium heptahydrate[9] and hexahydrate.[10]

The half-widths of the diffraction peak for the heptahydrate (2θ=21.0°) and that of the hexahydrate

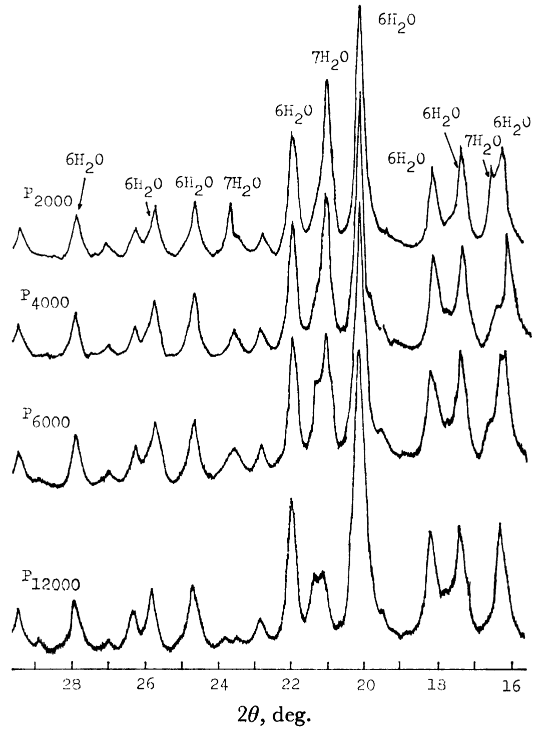

Fig. 3. X-ray diffraction patterns for various samples.

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[8] In the X-ray diffraction studies for some metal sulfates, e.g. $Al_2(SO_4)_3\cdot 18H_2O$, it was found that the diffraction pattern varics from time to time. This phenomenon is due to the interference of air moisture, it was avoided by covering the compressed and evacuated sample with collodion. However, in the case of the samples used in the present study, the X-ray diffraction pattern did not vary with the time. Therefore, the collodion treatment was not carried out.

[9] "Index to the Powder Diffraction File," ed. by J. V. Smith, ASTM Publication (1965), 8-467.

[10] *Ibid.*, 1-0356.

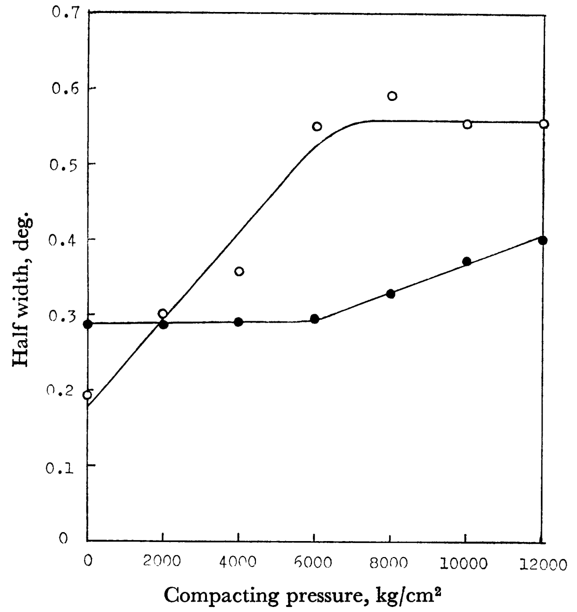

Fig. 4. Relations between the compacting pressure and the half widths of the X-ray diffraction peaks for magnesium sulfate heptahydrate (-○-, $2\theta=21.0°$) and for magnesium sulfate hexahydrate (-●-, $2\theta=20.2°$).

($2\theta=20.2°$) were found to vary on compression (Fig. 4). From this figure, it may be considered that the crystallites of heptahydrate were destroyed by the compression at pressures lower than 6000 kg/cm², while the crystallites of hexahydrate were little affected in this pressure range. The change in the half-width of the diffraction peak of hexahydrate was observed only at compacting pressures higher than 6000 kg/cm².

The relation between the compacting pressure and the relative intensity of the diffraction peak of heptahydrate ($2\theta=21.0°$) against the peak of hexahydrate ($2\theta=20.2°$) is given in Fig. 5. This seems to show that the relative content of heptahydrate to hexahydrate in the sample remained constant in the range of 2000—6000 kg/cm² and that the transition from heptahydrate to hexahydrate occurred somewhat above 6000 kg/cm². Such a discontinuous transition may be suggested by a rather discontinuous change in the water content in the sample (Fig. 2).

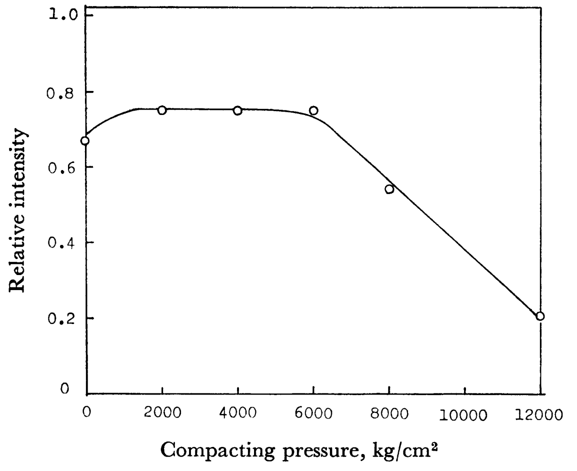

Fig. 5. Relations between the compacting pressure and the relative intensity of the X-ray diffraction peak of heptahydrate against the peak of hexahydrate.

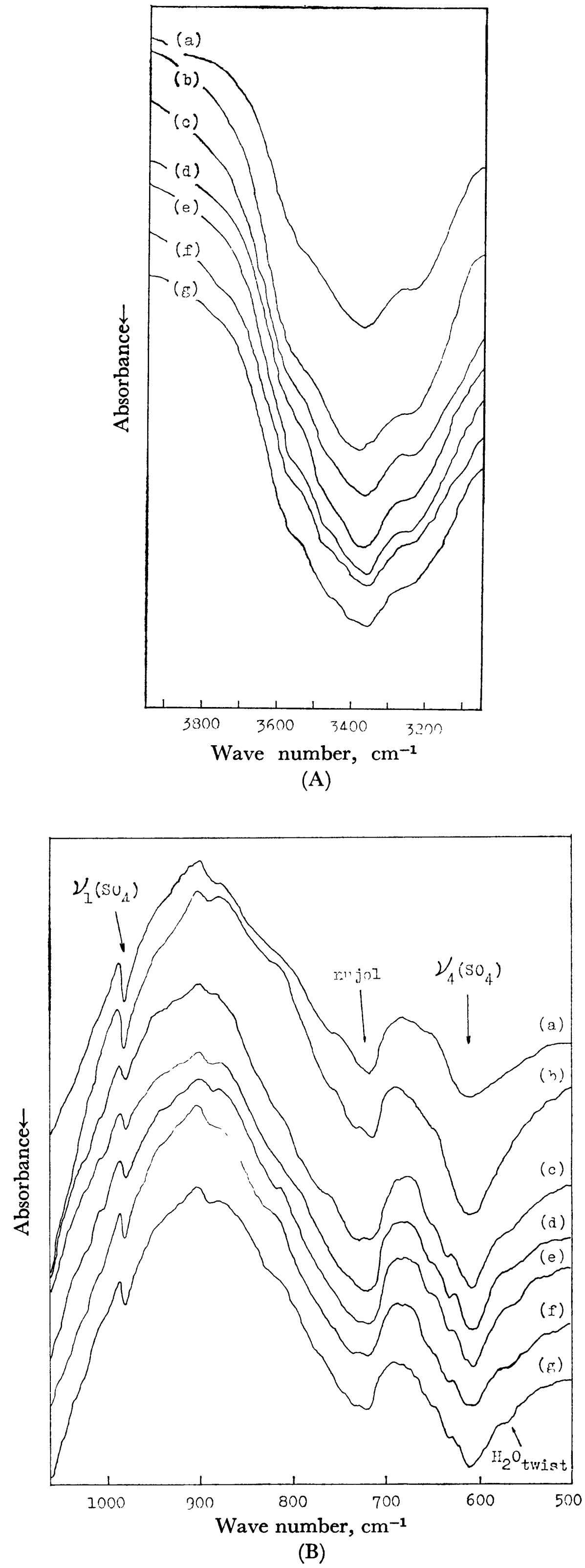

Fig. 6. Infrared spectra for the samples compressed at various pressures: (a) P_0; (b) P_{2000}; (c) P_{4000}; (d) P_{6000}; (e) P_{8000}; (f) P_{10000}; (g) P_{12000}.

Infrared Spectra. The infrared (IR) spectra of the samples compressed under various pressures are given in

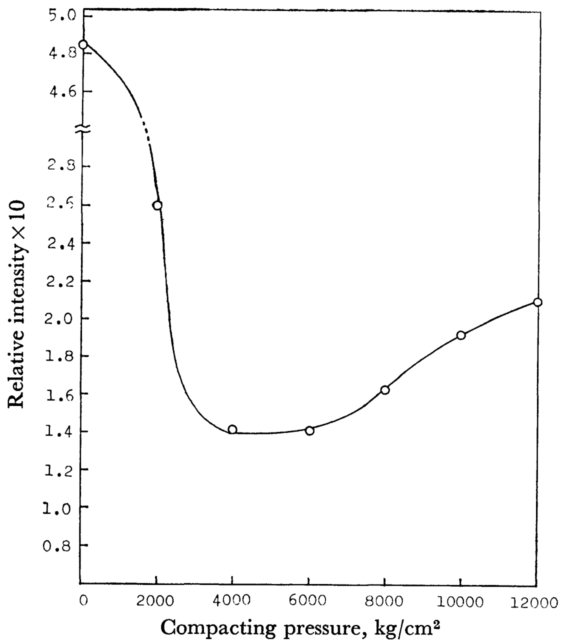

Fig. 7. Relations between the compacting pressure and the relative intensity of the ν_1 absorption against the ν_4 absorption for sulfate ion.

Fig. 6. The IR data may be summarized as follows;[11]

i) A broad band ranging from 3000 to 3600 cm^{-1} was assigned to the OH stretching vibration.[12] On compressing the sample at pressures higher than 6000 kg/cm^2, this band appeared to shift slightly toward lower wave numbers (Fig. 6-A). However, this is somewhat ambiguous because of the uncertainty of the exact peak position of the broad absorption band.

ii) An absorption band appearing at 985 cm^{-1} (Fig. 6-B) was assigned to the ν_1 vibration of the sulfate ion.[13] The relation between the compacting pressure and the relative intensity[14] of the ν_1 absorption against the ν_4 vibration for the sulfate ion (610 cm^{-1}) is given in Fig. 7. As can be seen in this figure, the relative intensity increased with an increase in the compacting pressure ranging from 6000—12000 kg/cm^2, while the relative intensity varied little at compacting pressures lower than 6000 kg/cm^2.

DTA and TGA. The DTA curves for various samples are given in Fig. 8. As can be seen in this figure, endothermic peaks appeared at various temperatures, and Peak I[15] can be attributed to the dehydration:[6]

$$MgSO_4 \cdot 7H_2O \longrightarrow MgSO_4 \cdot 6H_2O + H_2O$$

On the other hand, Peak II was attributed to the dehydration:

$$MgSO_4 \cdot 6H_2O \longrightarrow MgSO_4 \cdot 5H_2O + H_2O$$

According to the results of the TGA experiment, the

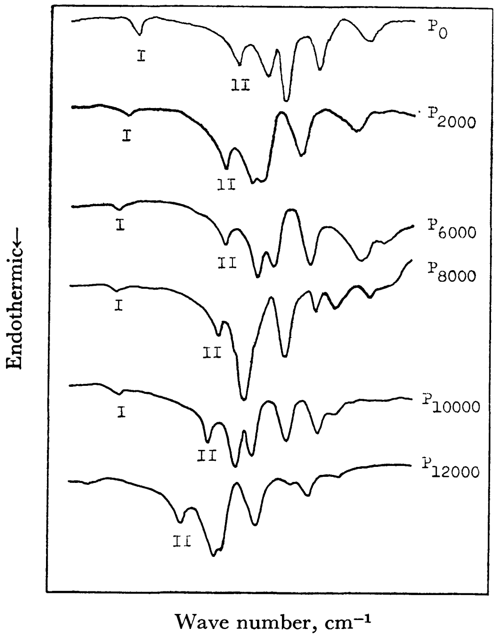

Fig. 8. DTA curves for the samples compressured at various pressures.

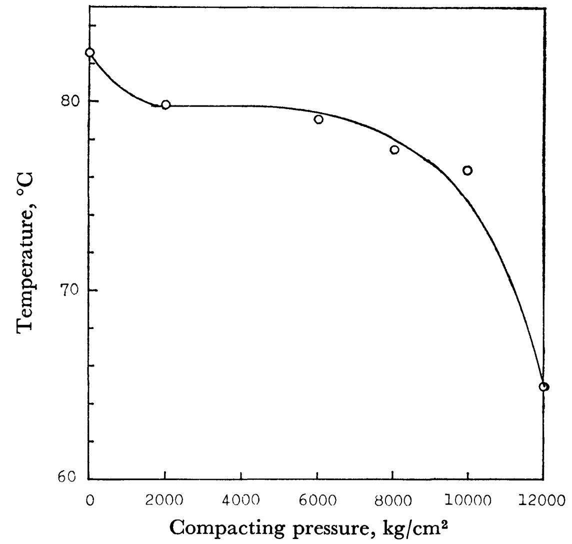

Fig. 9. Relations between the compacting pressure and the temperature of the DTA endothermic peak II.

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[11] The peak for H_2O_{rock} seemed to be overshadowed by a strong Nujol absorption and could not be detected on the IR chart. Further, the peak for H_2O_{twist} seemed to exist as a shoulder of the absorption peak of $\nu_4(SO_4)$. Since the shoulder peak was weak and broad, the existence of the peak is somewhat ambiguous and the effect of pressure on this peak could not be investigated. The peaks for ν(Mg-O) and for H_2O_{wag} could not be detected.

[12] I. Gamo, This Bulletin, **34**, 760 (1961).

[13] P. Krishnamurti, *Indian J. Phys.*, **5**, 183 (1930).

[14] Approximated by the ratio of the peak height for ν_1 to that for ν_4. A precise determination of the peak area for the ν_4 was difficult because of the existence of a shoulder peak. Therefore, the ratio of the peak heights was used as a measured of the intensity ratio.

[15] As can be seen in Fig. 8, the intensity of Peak I was very weak (especially for the compressed sample) compared with that of Peak II. This seems to mean that the phase change I requires far less energy than the phase change II. This view seems plausible because I is the dehydration of anion water and II is the dehydration of coordination water. Further, the compressed samples contain less anion water than 0.4 mol/mol-MgSO$_4$ (P=2000—12000 kg/cm^2). This would make the DTA peak I of the compressed sample smaller. Because of the instrumental limits, a quantitative comparison of the peak heights (I) of the different samples and the quantitative comparison of the peak height (I) with the water content (Fig. 2) were not possible.

amount of dehydration corresponding to the DTA endothermic peak II was found to be nearly one mole per unit mole of $MgSO_4$ for all of the samples.

Discussion

Acidity Change and X-Ray Diffraction Data. As can be seen in Fig. 1, the acidity values which varied upon compression were the values per unit of the surface area. Therefore, the acidity change can not be explained in terms of the change in the surface area. The acidity change due to compression must be attributed to structural changes other than that in the surface area.

A suggestion about the cause of the acidity change was derived from the information about the nature of the acid point. As was stated in the previous section, the acid point appearing on the surface of the compressed sample could be regarded as a protonic acid because the sample did not show any sign positive to the Lewis acid. Usually, the protonic-acid center and the water of crystallization are thought to be interrelated. Therefore, information about the change in the water of crystallization would be expected to throw some light on the cause of the acidity change.

X-Ray diffraction data revealed interesting aspects of the change in the crystallites of the sample hydrate. By a comparison of Fig. 4 with Fig. 1, it became evident that, in the pressure range of 2000—6000 kg/cm^2, where few changes in the surface acidity were observed, the half-width of the X-ray diffraction peak of hexahydrate was fairly constant, whereas the half-width of heptahydrate increased monotonously. Further, in the pressure range of 6000—12000 kg/cm^2, where the surface acidity was found to increase on compressing the sample, the half-width of the diffraction peak of hexahydrate increased, while that of the diffraction peak of heptahydrate varied little.[16] These facts strongly suggest that the disintegrations or distortions of hexahydrate crystallites play an important role in the acidity change, whereas the acidity change in the crystal of heptahydrate has little influence on the acidity change.

Probably, the change occurring in the hexahydrate crystallites is a distortion of the structural unit. Here, it must be pointed out that the X-ray diffraction data (Fig. 3) indicate the existence of heptahydrate even in the sample of P_{12000}, whereas the data on water content (Fig. 2) indicate 6 mol-H_2O/mol-$MgSO_4$ in this sample. Further, the DTA data (Fig. 8) indicate the existence of anion water in the P_{10000} sample, whose water content was also 6 mol-H_2O/mol-$MgSO_4$. A part of the cause of this discrepancy may be ascribed to the experimental error or to differences in the manner of sample handling in the different experiments. However, other factors must also be taken into consideration. For instance, the possibility that some lower hydrate may be contained in the sample could not be excluded. If the content of the lower hydrate is small or if the lower hydrate is in an amorphous state, its existence can not be detected by X-ray diffraction. Therefore, the water contents expected from the X-ray data would become larger than the true value. If the existence of the lower hydrate is true, posibilities that this hydrate may affect the acidity value arise. However, as can be seen in Fig. 2, the water content was fairly constant in the pressure range of 8000—12000 kg/cm^2. Therefore, it may be supposed that the content of the lower hydrate might also be constant in this pressure range. Thus, it is more plausible to consider that the acidity change in this pressure range is due to the distortion of the hexahydrate structure.

Structural Unit of Magnesium Sulfate Hydrate. As in the preceding works,[4,5] to serve for the discussion of the mechanism of the acidity change, models of the structural unit of magnesium sulfate hydrate[17] are given in Fig. 10. In this figure, A, B, and C are the models for heptahydrate, hexahydrate, and a distorted hexahydrate respectively. As can be seen in the figure, the central metal ion (Mg^{2+}) is coordinated by six water molecules, each of which is located on an apex of a hypothetical octahedron. In the structural unit of heptahydrate, one water molecule is located apart from the octahedron; this water may be regarded as anion water.

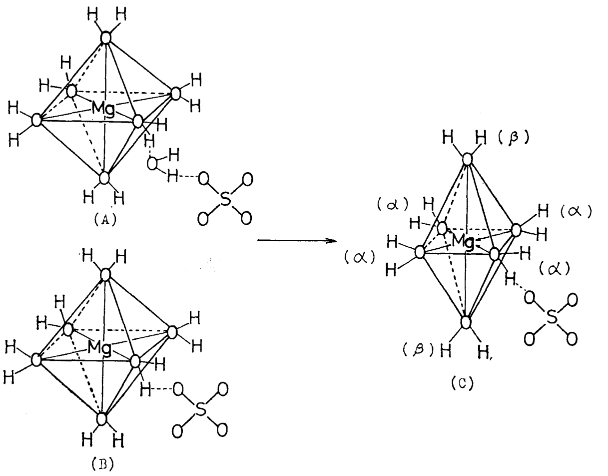

Fig. 10. Models of structural unit of magnesium sulfate:
(A) heptahydrate, (B) hexahydrate (not distorted),
(C) hexahydrate (distorted).

Changes in the Structural Unit of Heptahydrate. At pressures lower than 6000 kg/cm^2, only the changes in the structural unit of heptahydrate were taken into consideration, for the X-ray diffraction data (Fig. 4) indicated an invariance of hexahydrate structural unit in the samples compressed under low pressures.

Probably, the change occurring in the heptahydrate crystal is a liberation of the anion water (*cf.* Fig. 2). The coordinated water in heptahydrate would remain

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[16] At first sight, the X-ray data given in Fig. 3 (the decrease in the peak intensity and the splitting of the diffraction peak of heptahydrate at $2\theta=21°$) may give the impression that the distortion of the crystallites of heptahydrate occurred upon the compression of 6000—12000 kg/cm^2. However, this impression is erroneous; it is due to the abbreviation of the diffraction patterns of the P_{8000} and P_{10000} samples in the figure. It can be seen clearly in Fig. 4 that the half-width of the diffraction peak of heptahydrate is fairly constant in the pressure range of 6000—12000 kg/cm^2.

[17] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New Yrok, (1960).

unaffected by the compression because those two elements are thought to be coordinated in the same manner as in the hexahydrate structural unit, which is considered not to vary at low pressures. Since anion water is not directly coordinated to the central Mg^{2+} ion, its liberation might have little effect on the ionization states of Mg^{2+} or of the coordinated water. Therefore, the observed invariance of the acidity of the sample compressed under low pressures is acceptable.

Changes in the Structural Unit of Hexahydrate. As has been stated in the previous sections, evidence that the change in the structural unit of hexahydrate occurred only at pressures higher than 6000 kg/cm^2 is presented by the X-ray peak broadenings (Fig. 4). Since the water content did not vary at pressures higher than ~6000 kg/cm^2, one possible change in the structural unit may be a distortion of the octahedron.

In the present research, a distorted octahedron structural unit, as is shown in Fig. 10-C, was considered. In this model, the distances between Mg^{2+} and H_2O (α) are shortend and the distances between Mg^{2+} and H_2O (β) are stretched. In such a distorted structural unit, interactions between Mg^{2+} and the coordinated water should differ in character from those in the normal structural unit (Fig. 10-B).

The results of the DTA experiments also support the idea that the octahedron structural unit is distorted at high pressures. As can be seen in Fig. 9, the dehydration temperature of the coordinated water decreases with an increase in the compacting pressure. This fact supports the idea that a part of the coordinated water, presumably H_2O (β), becomes unstable. In the distorted octahedral coordination, H_2O (β) may be weakly bound by the central Mg^{2+} ion because the distance between H_2O (β) and Mg^{2+} is stretched.

In connection with the change in the structural unit, the behavior of the sulfate ion against the compression should be taken into consideration. The IR spectra gave interesting information about the behavior of the sulfate ion. As can be seen in Fig. 7, the relative intensity of the IR ν_1 absorption against ν_4 absorption for the sulfate ion varied on compression. This fact seems to indicate that interaction between the sulfate ion and its environment varies on compression.

The decrease in the relative intensity of the $\nu_1(SO_4)$ absorption at lower compacting pressures (0—2000 kg/cm^2) may be related to the dehydration of anion water from the heptahydrate crystal (*cf.* Figs. 2 and 4). Presumably, the symmetry of the crystal field around the sulfate ion would be reduced by the existence of anion water and the ν_1 vibration (which is originally inactive for the infrared absorption) becomes active for the infrared absorption. As the releasing of anion water proceeds, the symmetry of the crystal field may recover and the peak of the ν_1 vibration may become weaker.

On the contrary, the increase in the relative intensity of the $\nu_1(SO_4)$ absorption at compacting pressures higher than 6000 kg/cm^2 may be related to the increased interaction between oxygen in the sulfate ion and hydrogen in the OH group of the coordinated water (α). Approaches of the sulfate ion to the octahedral structural unit become easier at higher compacting pressures. Further, at higher compacting pressures, anion water, which may hinder the approach of the sulfate ion to the octahedron, no longer exists.

Mechanism of the Acidity Change. The small influence of the change in the heptahydrate structure on the surface acidity is made obvious by a comparison of Fig. 1 with Figs. 2, 4, 5, and 7. Therefore, the following discussions will be confined to the acidity change as well as to the structural change at pressures higher than 6000 kg/cm^2.

The observed acidity change of magnesium sulfate hydrate seems to be explainable in terms of the change in the structural unit of $MgSO_4\cdot 6H_2O$. That is, because of the distortion of the octahedral structure (Fig. 10-C), distances between the central Mg^{2+} ion and each coordinated water may vary; *i.e.*, the lengths of the four Mg^{2+}–H_2O (α) bonds are shortened and the lengths of the two Mg^{2+}–H_2O (β) bonds are stretched. Consequently, the degree of the interaction between Mg^{2+} and H_2O (α) may increase and the increased polarization of H_2O (α) may result. Thus, the polarized coordinated water can have a protonic acid property.

As has been discussed in the previous section, changes in the octahedral structural unit were considered to occur only at compacting pressures higher than 6000 kg/cm^2. Further, it was considered that the changes in the structural unit increase with an increase in the compacting pressure. Therefore, in the pressure range of 6000—12000 kg/cm^2, an increase in the compacting pressure may be considered to result in an increase in the content of polarized water (α). In other words, the compression at high pressures may result in an increase in the acidity of the sample.

The interaction between the sulfate ion and coordinated water (α) seems to contribute also to the acidity change. When the hydrogen-bridge donor property of the coordinated water (α) in the distorted structural unit increases, the hydrogen bond between the sulfate ion and the coordinated water (α) may be strengthened. Then, the distorted octahedral structural unit may be brought to a quasi-stable state by the aid of this strengthened hydrogen bond. Thus, the presence of the sulfate ion, which may be displaced nearer to the octahedron by the compression, seems to contribute to the acidity change. As has been discussed in the previous section, approaches of the sulfate ion to the octahedron were considered to be possible only at pressures higher than 6000 kg/cm^2, above which point the acidity change was observed.

The above-mentioned mechanism of the acidity change seems to be supported also by the linear relationship between the acidity change and the relative intensity of the IR ν_1 absorption for sulfate (Fig. 11).

Comparisons to the Acidity of Other Sulfates. The present mechanism for the acidity change in the compressed magnesium sulfate hydrate is almost identical with those proposed for the acidity changes in aluminum sulfate hydrate[4)] and zinc sulfate hydrate.[5)] In the acidity changes in these metal sulfates, including magnesium sulfate, interactions between the central cation and the octahedrally-coordinated water were thought

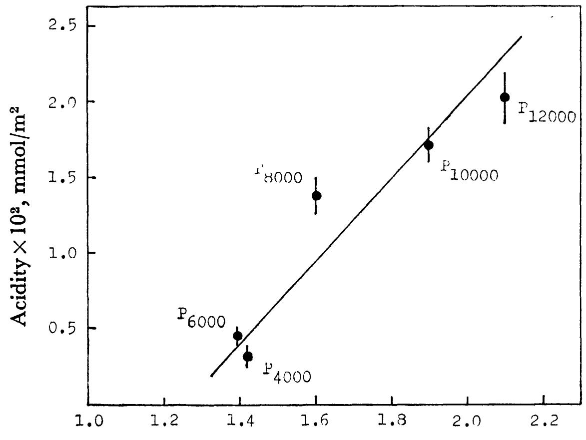

Fig. 11. Relations between surface acidity and the relative intensity of ν_1 absorption against ν_4 absorption for sulfate ion.

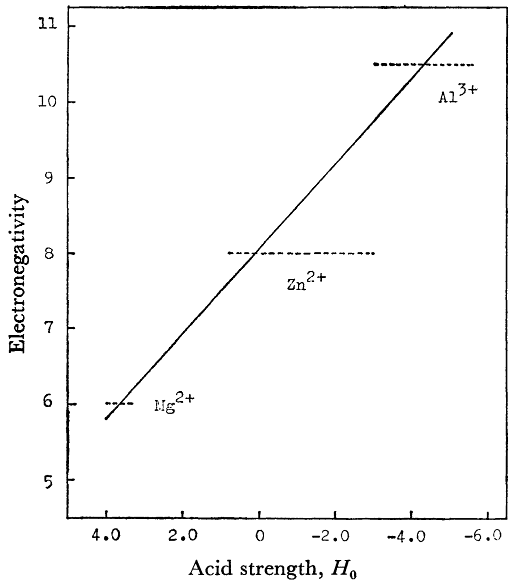

Fig. 12. Relations between electronegativities of some cations and the acid strength of the compressed sulfates containing the corresponding cations.

to play the most important roles. A question arises, therefore, if any differences among the acidic properties of these sulfates exist, for different cations (Al^{3+}, Zn^{2+}, Mg^{2+}) would yield differences in the strength of the cation field, which affects the degree of polarization in H_2O (α). Thus, the electronegativities of these cations[18] were compared with the observed values of the acid strength (H_0 values) of the corresponding sulfates (Fig. 12). As can be seen in this figure, an approximate linear relationship was obtained. The existence of such a simple relationship as above seems to support the validity of the common mechanism of the acidity changes for various metal sulfates.

In summarizing the published works of this series, the following point should be emphasized. The samples treated in these works were subjected to compression and evacuation. Further, it must be taken into consideration that the compacting pressure was released after the compression of the sample during a given period. Therefore, the observed pressure effects should be regarded as indirect ones. Some pressure effects might be relaxed by the release of the compacting pressure, and some other effects might be amplified or modified by the evacuation-dehydration. It must be remembered that the term "pressure effects" which is used in the works of this series means that the differences in the degree of compression induce diffrences in the effects of the other operations which follow the compression.

It seems to be important to study the details of the effects of evacuation as well as the effects of the pressure releasing. Measurements under pressure are also necessary in order to ascertain the direct effect of pressure. All of these works require special techniques and include many experimental difficulties, however, and so they were not included in the works of this series.

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[18] K. Tanaka, A. Ozaki, and K. Tamaru, *Shokubai*, **6**, 262 (1964).