Effects of Pressure on the Chemical Properties of the Solid Surface. I. Surface Acidities of Some Compressed Sulfates and Bisulfate

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The effects of pressure on the chemical properties of gases and liquids have been thoroughly investigated. Furthermore, recent advances in high pressure chemistry have revealed an enhanced reactivity of solid substances at high pressures. However, except for some contributions from the Russian researchers,[1] no systematic investigations concerning the effect of pressure on the surface properties of solids have been reported. These circumstances have prompted the authors to investigate the chemical properties of the surface of a compressed solid. In the present paper, which is the first of a series, the effect of pressure on the surface acidity of some sulfates and a bisulfate is investigated.

Some solids have characteristic surface acidities, and it is believed that this acidity plays an important role in some surface catalyses where hydrocarbons or their derivatives are the reactants and products. Thus, it becomes important to increase the acidity to improve the catalytic activity. Attempts have been made to achieve this,[2,3] but application of high pressure to the solid has not yet been tested.

A well known fact[4] that the application of high pressure to an acidic solution makes the solution more acidic suggests that the surface acidity of solids might also be increased by compression. Of course, the detailed mechanism of the compression of solids should be different from that of liquids, and knowledge about a liquid system under high pressure can not always be extended to a solid system under high pressure. Nevertheless, the suggestion seems worth testing experimentally.

In the experimental work in this research, several metal sulfates and potassium bisulfate served as samples. The sample material was pulverized and the powder was compressed in a piston-cylinder apparatus at a pressure of 0—3000 kg./cm^2. The surface acidity, the water content, and the X-ray diffraction pattern were obtained for both the compressed sample and the uncompressed one. With some samples, the acidity was increased by the compression, whereas with other samples the acidity remained unchanged. In this paper, details of the experimental results are described and some possible explanations are discussed.

Experimental

Apparatus. — The apparatus used for this study was essentially a piston-cylinder device employing a hardened chromium steel piston and a cylinder assembly of stainless steel. A cross section of the apparatus is given in Fig. 1. The piston consists of a head (20 mm. diam.) and a stem (8 mm. diam.). The cylinder is assembled from a body, a bottom cover, and four sets of nuts and bolts. The body cavity, in which the piston is to be inserted, consists essentially of two concentric vertical holes; the larger hole (20.1 mm. diam.) accomodates the piston head, and the smaller hole (8.1 mm. diam.) houses the piston stem, thus permitting vertical motion of the piston head.

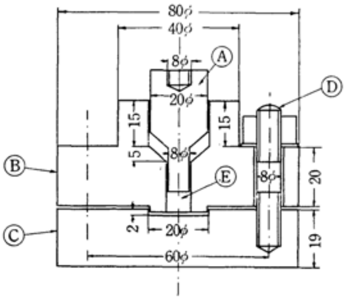

Fig. 1. A cross section of apparatus.
A: Piston B: Body
C: Bottom cover D: Bolt and nut
E: Sample room

The sample is compressed in the space bounded by the upper surface of the bottom cover, the wall of the smaller hole, and the face of the piston stem.

Pressure was applied to the piston by means of a commercial 4 ton scale oil press having two parallel beds, viz. a stationary bed and a moving bed. The load was measured by a Bourdon-gauge which is connected to the oil chamber of the press.

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[1] M. G. Gonikberg, "Chemical Equilibria and Reaction Rates at High Pressures," Israel Program for Scientific Translations, Jerusalem (1963), p. 92.

[2] T. Shiba and E. Echigoya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1046 (1955).

[3] K. Tanabe and R. Ohnishi, *J. Research Inst. Catalysis, Hokkaido University*, **X**, 229 (1962).

[4] S. D. Hamann, "High Pressure Physics and Chemistry," Vol. 2, Ed. by R. S. Bradley, Academic Press, London and New York (1963), p. 148.

The pressure generated at the sample was estimated by dividing the load by the piston area (0.503 cm^2).

Sapmle. — The samples used in this study were colorless, commercial, metal sulfates (reagent grade) and potassium bisulfate (reagent grade). The material was gently pulverized in an agate mortar, and about 1 g. of the powder was packed into the sample room of the apparatus. Then, the apparatus was sandwiched between the two beds of the press, and the desired load was applied to the piston during 10 min., at room temperature. After compression, the sample was taken out from the apparatus, pulverized again, weighed and dried in a desiccator for 6 hr. Immediately after the drying,* the sample was submitted to the tests described below.

Uncompressed samples were also prepared by the above procedure but omitting the application of load.

Surface Acidity.—The qualitative effect of pressure on the surface acidity was observed by comparing the color of an indicator adsorbed on the sample compressed at 3000 kg./cm^2 with that of the same indicator adsorbed on the uncompressed sample. The comparison was carried out in the following way.

A given amount of sample powder was transferred to a 50 ml. conical flask containing 10 ml. of purified benzene. Then, several drops of an 0.1% indicator solution in benzene were added and the surface color of the sample was observed. At the same time, a similar observation was carried out with the uncompressed sample. The difference between the colors of the two samples was recorded. In this comparison, three indicators, i. e. *p*-dimethylaminoazobenzene (pK_a=3.3), benzeneazodiphenylamine (pK_a=1.5) and dicinnamalacetone (pK_a=−3.0) were used.

A quantitative determination of the surface acidity was carried out with four aluminum sulfate samples, compressed at 0, 1000, 2000 and 3000 kg./cm^2, respectively. For neutralization of the surface acid, a 1/100 or 1/1000 N solution of *n*-butylamine in benzene was used, and Benesi's method[5] was adopted to determine the quantity of *n*-butylamine required to neutralize the surface acid. In addition to the three indicators described above, phenylazonaphthylamine (pK_a=4.0) was also used in each of the determinations.

Water Content.—The content of the metal element in the desired sample was determined by a conventional chemical analysis, and on the basis of this result the water content in the sample was calculated. Six aluminum sulfate samples, compressed at 0, 1000, 2000, 3000, 4000 and 5000 kg./cm^2 respectively, were analyzed. Samples of magnesium sulfate, zinc sulfate, and potassium bisulfate, each compressed at 3000 kg./cm^2, as well as uncompressed samples of the above sulfates were similarly analyzed.

Identification by X-Rays.—The X-ray diffraction patterns of the powdered samples were determined with an X-ray diffractometer, employing Cu-*Kα* radiation at 30 kV. and 15 mamp.** All those samples analyzed as above were used in this study.

Results

Surface Acidity.—*Qualitative Results.*—Surface colors of the various samples are given in Table I; the samples are classified into three groups, i. e. I, II and III.

Potassium sulfate, barium sulfate, lead sulfate, and magnesium sulfate fall into group I. Both in the compressed and uncompressed

TABLE I.* SURFACE COLORS OF VARIOUS SAMPLES

Indicator	*p*-Dimethylaminoazobenzene		Benzeneazodiphenylamine		
Pressure kg./cm^2	0	3000	0	3000	
$BaSO_4$	No color	No color	No color	No color	I
$PbSO_4$	No color	No color	No color	No color	
K_2SO_4	No color	No color	No color	No color	
$MgSO_4\cdot7H_2O$	No color	No color	No color	No color	
$SrSO_4$	Pink	Pink ♯	Red	Red ♯	II
$CaSO_4\cdot2H_2O$	Pink	Pink ♯	Red	Red ♯	
$MnSO_4\cdot4H_2O$	Pink (faint)	Pink ♯ (faint)	No color	No color	
$ZnSO_4\cdot7H_2O$	Red	Red ♯	Red (faint)	Red ♯(faint)	
$CdSO_4\cdot8H_2O$	Red	Red +	Red	Red +	III
$Ce_2(SO_4)_3\cdot8H_2O$	Red	Red +	Red (faint)	Red +(deep)	
$Fe_2(SO_4)_3\cdot xH_2O$	Red	Red +	Red (faint)	Red +	
$Al_2(SO_4)_3\cdot18H_2O$	No color	Red +	No color	Red +	
$KHSO_4$	Red	Red +	Red (faint)	Red +	

* In this table, the mark ♯ indicates a case where the difference between the surface color of the uncompressed sample and the color of the compressed sample is uncertain, and the mark + indicates that the surface color was increased by compression.

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* By the use of such a procedure reproducible experimental results were obtained.

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

** The following experimental conditions were used in the X-ray diffraction study: count full scale 1000 c. p. s., time constant 2 sec., scanning speed 1° 2*θ*/min., chart speed 1.0 cm./min., divergence slit 0.2 mm., receiving slit 1.0 mm., room temperature 25°C.

states, these sulfates were nonacidic to all the indicators.

Strontium sulfate, calcium sulfate, zinc sulfate and manganese sulfate form group II. Both in the compressed and uncompressed states, all these sulfates were acidic to all the indicators, except for dicinnamalacetone, but the difference in surface color between the two states was hardly recognizable.

The surface acidity of the group III samples, i. e. cadmium sulfate, cerous sulfate, ferric sulfate, aluminum sulfate, and potassium bisulfate, was significantly increased by compression of the samples at 3000 kg./cm². A typical example of this group is aluminum sulfate. This sulfate in the uncompressed state was nonacidic, whereas in the compressed state it was acidic to all indicators except for dicinnamalacetone.

Quantitative Results.—Acid strength distribution curves for the aluminum sulfate samples, compressed at 1000 and 2000 kg./cm² respectively, are given in Fig. 2. The abscissa is Hammett's H_0 function⁶⁾ and the ordinate is the *n*-butylamine titer. The figure shows that the acid, which has appeared on the compressed aluminum sulfate, has an H_0 value not less than −3.0. This means that the acid on the sample surface is moderately strong. In a separate experiment, it has been shown that even by the compression at 3000 kg./cm² the H_0 value can not be decreased to a value less than −3.0.

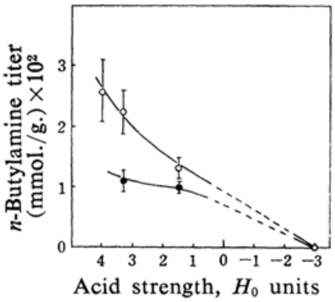

Fig. 2. *n*-Butylamine titers vs. acid strength for two aluminum sulfate samples compressed at 1000 kg./cm² (●) and 2000 kg./cm² (○), respectively.

The surface acidity of the aluminum sulfate sample at $H_0=3.3$ as a function of the compacting pressure is given in Fig. 3. The figure shows that the acidity is nearly proportional to the compacting pressure up to 2000 kg./cm², but beyond this pressure the increment of the acidity diminishes with increase of compacting pressure.

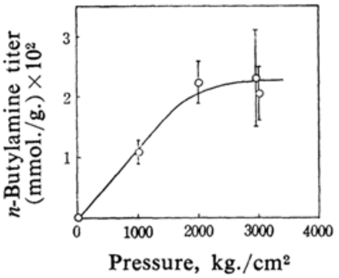

Fig. 3. *n*-Butylamine titers at $H_0=3.3$ vs. compacting pressure for aluminum sulfate.

Water Content.—*Aluminum Sulfate.*—The relation between the water content in the aluminum sulfate sample and the compacting pressure is given in Fig. 4 and Table II. In the figure, the water content is expressed as the number of moles of water per two gram atoms of aluminum. This figure shows a nearly proportional decrease of the water content with the compacting pressure in the range of 0—2000 kg./cm², but beyond 2000 kg./cm² the decrement of the content becomes smaller with increase of the compacting pressure, and at a pressure of 3000 kg./cm² or above, the content remains at a constant level.

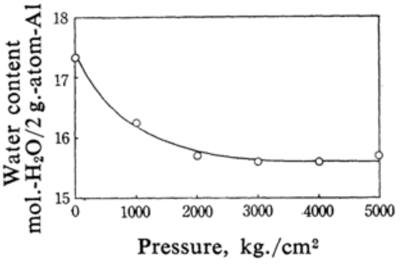

Fig. 4. Water contents of aluminum sulfate samples as a function of compacting pressure.

TABLE II. THE RATIO OF THE WATER CONTENT IN THE COMPRESSED SAMPLE TO THE WATER CONTENT IN THE UNCOMPRESSED SAMPLE

	Pressure, kg./cm²					
Sulfate	0	1000	2000	3000	4000	5000
Aluminum sulfate	1	0.94	0.91	0.90	0.90	0.91
Magnesium sulfate	1	—	—	0.98	—	—
Zinc sulfate	1	—	—	0.97	—	—

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6) C. Walling, *J. Am. Chem. Soc.*, **72**, 1164 (1950).

Potassium Bisulfate.—A potassium determination showed that the potassium content, K_0, in the uncompressed sample is less than the content, K, in the compressed sample. Namely, the ratio of K_0 to K was 0.96.

Magnesium Sulfate and Zinc Sulfate.—The results of the chemical analyses of a magnesium sulfate sample and a zinc sulfate sample given in Table II. For both sulfates, the water content in the compressed sample differed little from the content in the uncompressed sample.

X-Ray Diffraction Studies.—*Aluminum Sulfate.*—The X-ray diffraction pattern for an uncompressed aluminum sulfate sample is given in Fig. 5a. A sharp peak at $2\theta=20.1°$ was identified as the most characteristic peak of aluminum sulfate octadecahydrate. Further, each of the other main peaks, except for the peaks at $2\theta=24.8°$, 25.9°, 29°, and 36.8°, had a diffraction angle which corresponds well to the angle of the octadecahydrate, though its relative intensity against the peak height at $2\theta=20.1°$ did not strictly agree with that of the standard value.[7]

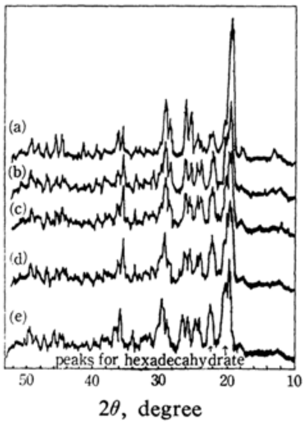

Fig. 5. X-Ray diffraction patterns for aluminum sulfate samples compressed at various pressures.
(a) Uncompressed sample
(b) 1000 kg./cm² (c) 2000 kg./cm²
(d) 3000 kg./cm² (e) 4000 kg./cm²

X-Ray diffraction patterns for aluminum sulfate samples compressed at various pressures are given in Figs. 5b—5e. Almost all the peaks which appear in Fig. 5a are also present in these patterns, though the peak at $2\theta=20.1°$ in Figs. 5b—5e has a low peak height in comparison with the corresponding peak height in Fig. 5a. Further, some peaks, especially peaks at $2\theta=20.3°$ and 22.7°, are more evident in the patterns for the compressed samples than in the pattern for the uncompressed sample. These two peaks were identified as the peaks which belong to the aluminum sulfate hexadecahydrate crystal.[8]

Potassium Bisulfate. — The X-ray diffraction pattern for uncompressed potassium bisulfate is given in Fig. 6a. A sharp peak at $2\theta=23°$ was identified as the most characteristic peak of potassium bisulfate. Except for some trivial peaks, e. g. peaks at $2\theta=20.2°$, 20.7°, 21.4°, 25°, and 25.6°, all of the other peaks were identified as the peaks of potassium bisulfate, though the observed diffraction angles and relative intensities against the peak at $2\theta=23°$ were somewhat irregular in comparison with the standard values.[9]

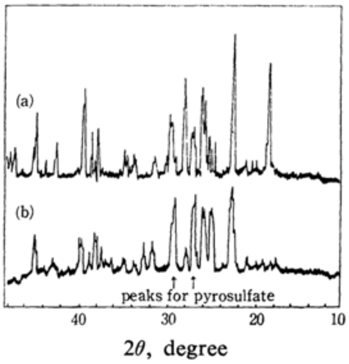

Fig. 6. X-Ray diffraction patterns for potassium bisulfate samples.
(a) Uncompressed sample
(b) Compressed sample (3000 kg./cm²)

The X-ray diffraction pattern for a compressed potassium bisulfate sample is given in Fig. 6b. In comparison with Fig. 6a, a general broadening in peak widths and reductions in peak heights for almost all peaks are seen in this figure. The most remarkable reduction in peak height is seen at $2\theta=23°$. Only a few peaks, e. g. peaks at $2\theta=25.3°$, 27.4° and 29.5°, are more evident in Fig. 6b than the corresponding peaks in Fig. 6a.

Magnesium Sulfate and Zinc Sulfate.—X-Ray diffraction patterns for an uncompressed magnesium sulfate sample and a compressed magnesium sulfate sample are given in Figs. 7a and 7b, respectively. In both figures sharp peaks due to magnesium sulfate heptahydrate are present, and small differences in the diffraction angle, in the relative intensity, and in Fig. 7b can be recognized.

X-Ray diffraction patterns of an uncompressed zinc sulfate sample and a compressed zinc sulfate sample are given in Figs. 8a and

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[7] "Index to the Powder Diffraction File," Ed. by J. V. Smith, ASTM Special Technical Publication 48-M2, Philadelphia (1963), No. 13.

[8] H. Basset and T. H. Coodwin, *J. Chem. Soc.*, **1949**, 2239.

[9] Ref. 7, No. 132.

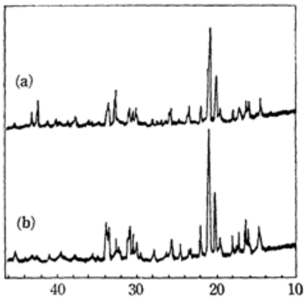

Fig. 7. X-Ray diffraction patterns for magnesium sulfate samples.
(a) Uncompressed sample
(b) Compressed sample (3000 kg./cm²)

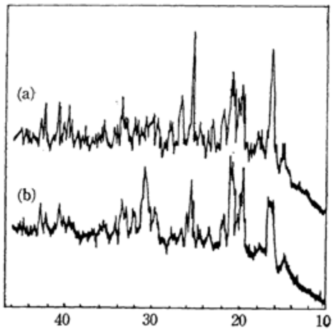

Fig. 8. X-Ray diffraction patterns for zinc sulfate samples.
(a) Uncompressed sample
(b) Compressed sample (3000 kg./cm²)

8b, respectively. There are some differences between these two figures. However, no evidence for the appearance of a new substance in the compressed sample can be seen from an inspection of Fig. 8b.

Discussion

A brief survey of the experimental results presented in Table I might give the impression that the presence of a large quantity of crystallization water in the original material is the cause of the increase in acidity on compression. However, this impression is incorrect since the surface acidity of potassium bisulfate, which has no crystallization water in its original state, was increased markedly by compression.

Dehydration of the sample on compression seems to correlate with the acidity change on compression. For example, as can be seen from Table II, analysis of the aluminum sulfate samples, which showed a typical increase in acidity on compression, indicates that a considerable amount of water has disappeared from the compressed sample. Further, as is seen in Fig. 3 and Fig. 4, the relation between the water content of the aluminum sulfate sample and the compacting pressure parallels the relation between the acidity at $H_0=3.3$ and the compacting pressure.

The dehydration from the compressed aluminum sulfate samples might also be proved by the results of X-ray diffraction studies. Namely, X-ray diffraction patterns in Figs. 5b—5e show that the compressed aluminum sulfate sample is composed of aluminum sulfate octadecahydrate and aluminum sulfate hexadecahydrate, whereas Fig. 5a shows that the uncompressed aluminum sulfate sample may be regarded as a single phase which is composed of aluminum sulfate octadecahydrate. Irregularities* recognized in Fig. 5a are trivial, and they may be ignored in this discussion. Thus, it seems to be plausible to consider that the hexadecahydrate was formed through compression of the original octadecahydrate by the reaction

$$\mathrm{Al_2(SO_4)_3\cdot 18H_2O} \rightarrow \mathrm{Al_2(SO_4)_3\cdot 16H_2O} + \mathrm{2H_2O} \qquad (1)$$

It is well known that this sort of reaction can occur under a high pressure.[10)]

With the aluminum sulfate sample, an interesting fact was deduced from a comparison of the results of the X-ray diffraction study and chemical analysis. Namely, as is seen in Fig. 4, at about 1300 kg./cm² or above, the water content in the compressed aluminum sulfate sample is less than 16, which corresponds to the number of moles of water in one mole of pure hexadecahydrate, whereas the X-ray diffraction pattern indicated that crystallites of the octadecahydrate and the hexadecahydrate coexist in the compressed sample. This leads to a contradiction, if the compressed sample is regarded as a mixture of these two hydrates with their pure forms. Therefore, a nonstoichiometric water content in either the octadecahydrate or the hexadecahydrate, or in both hydrates, must be assumed in order that the result of the X-ray diffraction study be compatible with the result of the chemical analysis. The surface property of a solid is often attributed to its nonstoichiometric composition, or a defective structure of the surface. Similarly, the deficiency of water in the compressed

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10) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworths Scientific Publications, London (1957), p. 208.

* Preferred orientations of cleavage planes by compression or structural changes of sample materials by air moisture etc. might be considered as the cause of irregularities of X-ray diffraction patterns of aluminum sulfate sample or other samples.

aluminum sulfate sample is suspected to play an important role in the appearance of acid centers on the surface of this sulfate.

A dehydration from the compressed potassium bisulfate sample is also possible, though this sample has no crystallization water in its original state. For instance, a dehydration through the reaction

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \qquad (2)$$

might occur, because the equivalent volume* of potassium bisulfate is 121.6, and the values for potassium pyrosulfate and water are 112 and 18 respectively, hence, according to Le Chatelier's principle, in a system where liberated water can escape out of the system, a shift of the equilibrium of the reaction 2 towards the right may be expected.

Indirect evidence for the occurrence of reaction 2 can be seen in the results of chemical analysis. Namely, the potassium content of the compressed potassium bisulfate sample is larger than that of the uncompressed sample, indicating that some of the original constituents, presumably water, have disappeared during compression.

The results of the X-ray diffraction study give additional evidence for the dehydration from the compressed potassium bisulfate sample. As is seen in Fig. 6b, the peak at $2\theta=23°$ is broad and low in comparison with the corresponding peak in Fig. 6a. This shows that compression has caused partial destruction of the original crystal structure. Further, the peaks at $2\theta=27.4°$ and 29.5° in Fig. 6b are more evident than the corresponding peaks in Fig. 6a. These two peaks were identified as the peaks of potassium pyrosulfate, though a minor deviation of the diffraction angle from the standard value11) exists for each peak.

In contrast to the cases where the surface acidity was increased by compression, in cases where the acidity was not altered by compression, only minor dehydration of the compressed sample had occurred and changes in the crystal structure were trivial.

For instance, as is seen in Table II, the difference between the water contents of the compressed and the uncompressed samples of magnesium sulfate is slight. Further, the X-ray diffraction patterns in Figs. 7a and 7b show that little change in the crystal structure has resulted from compression of the magnesium sulfate. These results correspond well with the fact that the surface acidity of this sulfate was not increased by compression. In addition, Figs. 7a and 7b show that well developed crystallites of magnesium sulfate heptahydrate exist in both the compressed and the uncompressed samples, from which it can be concluded that surface defects would be sparse in both samples. This supposition is consistent with the result of the previous discussion in which the surface acidity of the compressed sample was interpreted in terms of a surface defect.

As is seen in Table II, the water content in the compressed zinc sulfate sample is only slightly different from that in the uncompressed sample. Thus, the small effect of pressure on the surface acidity of this sulfate may be attributed to the small extent of dehydration in the compressed sample.

On the other hand, as is seen in Figs. 8a and 8b, there are small differences in the X-ray diffraction patterns of the uncompressed and the compressed zinc sulfate samples; the former pattern has two sharp peaks at $2\theta=16.7°$ and 25.8°, while in the latter pattern these two peaks are broad and low. From this result, some differences in the surface acidities of the two samples might be expected. However, the expected increase in surface acidity could hardly be recognized from a color comparison. This apparent discrepancy may be partly ascribed to the existence of a considerable amount of surface acidity in the original sample, and partly to the small extent of dehydration in the compressed sample. Namely, any small increase in the surface acidity would be insignificant compared to the original high surface acidity of the sample and would not be detected simply by an indicator color change.

The surface acidity of the original zinc sulfate sample may be explained in terms of the X-ray diffraction data. As is seen in Fig. 8a, the peak at $2\theta=21.1°$ is low. If the uncompressed zinc sulfate has a perfect crystal structure, this peak should be the highest.12) Therefore, it appears that the crystal structure of the uncompressed zinc sulfate is imperfect. As noted previously, imperfect crystal structures may be a cause of surface acidity.

Previously, Kiyama and Yanagimoto13) reported that neither the chemical composition nor the crystal structure of calcium sulfate dihydrate was altered by compression. As might have been predicted from their results, compression of calcium sulfate dihydrate did not cause any change in its surface acidity (see Table I).

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* The equivalent volume is defined by the following formula (Molec. wt./Specific wt.)×(No. of mol. of a reactant or a product in the stoichiometric eq.). (cf. Ref. 10).

11) Ref. 7, No. 134.

12) Ref. 7, No. 190.

13) R. Kiyama and T. Yanagimoto, *Rev. Phys. Chem. Japan*, **22**, 34 (1952).

Summary

Compression of potassium bisulfate and certain other metal sulfate has been shown to cause an increase in their surface acidities. This increase in surface acidity has been correlated with dehydration of the compressed sample, and X-ray diffraction studies have revealed that dehydration is accompanied by minor structural changes involving the formation of a less hydrated substance.

In those sulfates where compression produced little or no change in the surface acidity, the extent of the dehydration from the compressed sample was meager, and X-ray diffraction studies proved that neither the formation of a new substance nor a great change in the crystal structure resulted from the compression.

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