tained, but immediately after it has occurred only the rapid reaction and no explosions are observed.

Three other types of surfaces were investigated, namely, (1) a silver mirror deposited on the inside of the quartz vessel; (2) the quartz surface rinsed with 1 *M* potassium chloride; (3) the quartz surface rinsed with 1 *M* aluminum nitrate.

In the temperature range 602–642°, and at pressures from 25 to 60 mm. of $1CH_4 + 2.4O_2$, the silver surface did not induce any explosions and the reaction rate was considerably slower than with hydrofluoric acid treated quartz. Under the same conditions of temperature and O_2/CH_4 ratio, the potassium chloride treated surface did not induce any explosions up to 110 mm. pressure, the reaction rate being greater than, but of the same order as, that in hydrofluoric acid-treated quartz. The alumina surface induced explosions in about the same pressure and temperature ranges as the hydrofluoric acid-treated quartz, but the surface aged very much more rapidly so that after twenty-four hours no explosions could be obtained.

It is perhaps of interest to note that with untreated quartz, Neumann and Serbinov[3] could obtain no explosions at temperatures below about 630°, whereas in the above experiments with hydrofluoric acid-treated quartz explosions were readily obtained at 602°. Another interesting fact is that neither the author nor Neumann and Serbinov[3] could obtain any explosions for O_2/CH_4 ratios appreciably less than 2.0.

It is apparent from the above experiments that any attempt to quantitatively check the diffusion theory[4] of low-pressure explosions of methane–oxygen mixtures must be preceded by the discovery of a surface which is accurately reproducible, and which does not age too rapidly.

The author has appreciated many helpful discussions with Dr. L. S. Kassel.

Summary

Experiments on the low-pressure explosion limits of methane–oxygen mixtures using various surfaces of reaction vessel show that these limiting pressures vary widely with the type of surface employed.

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(4) Kassel and Storch, THIS JOURNAL, **57**, 672 (1935).

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[CONTRIBUTION FROM THE NONMETALLIC MINERALS EXPERIMENT STATION OF THE U. S. BUREAU OF MINES, DEPARTMENT OF THE INTERIOR, RUTGERS UNIVERSITY]

The Optical Properties of Certain Salts in the System $(NH_4)_2SO_4$–$CaSO_4$–H_2O[1]

BY ALTON GABRIEL[2]

During investigations of the system $(NH_4)_2SO_4$–$CaSO_4$–H_2O, D'Ans and Schreiner[3] and Bell and Taber[4] obtained certain double salts of ammonium sulfate and calcium sulfate. The optical properties of two of them, ammonium pentacalcium sulfate and ammonium dicalcium sulfate, apparently have never been determined, while Merz, Hardesty and Hendricks[5] have published some optical data on the third salt, ammonium calcium sulfate.

In a more recent investigation of this system Hill and Yanick[6] prepared the three salts mentioned above and kindly permitted the writer to make an optical examination of them. The results are recorded in the following section.

Optical Properties

The colorless monoclinic crystals of the double salt ammonium pentacalcium sulfate monohydrate ($(NH_4)_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) correspond in habit to those of the potassium pentacalcium sulfate monohydrate described by Krüll and Vetter.[7] They are rather long unit prisms with base pinacoids. Pyramidal faces usually are developed. The crystals habitually lie on a prism face (110). (Fig. 1.)

As observed perpendicular to the plane 100, the prism shows a medium birefringence and parallel extinction. This view yields a nearly symmetrical interference figure of the obtuse bisectrix type. The plane of the optic axes lies

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(3) D'Ans and Schreiner, *Z. anorg. Chem.*, **62**, 139–144 (1909).

(4) Bell and Taber, *J. Phys. Chem.*, 11, 492 (1907).

(5) Merz, Hardesty and Hendricks, THIS JOURNAL, **55**, 3571 (1933).

(6) Hill and Yanick, *ibid.*, **57**, 645 (1935).

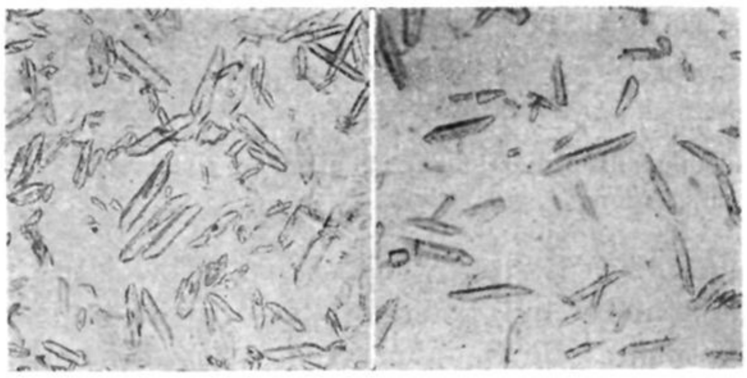
(7) Krüll and Vetter, *Z. Krist.*, **86**, 389 (1933).

in the direction of the slower component, which parallels the long direction of the crystal.

As observed perpendicular to the 010 plane, the unit prism makes an angle of about 32° with the base pinacoid. This view displays the maximum birefringence and oblique extinction, the slower component making an angle of about 8° with the *c* crystallographic axis.

End views of the crystals are very rare. This view is diamond-shaped, and shows symmetrical extinction and an acute interference figure. The plane of the optic axes parallels the faster component, which vibrates parallel to the acute diagonal.

Ammonium pentacalcium sulfate is biaxial, positive, with 2V near 90° (86° calculated) with v > r distinct.



Ammonium pentacalcium sulfate monohydrate, $(NH_4)_2SO_4 \cdot 5CaSO_4 \cdot H_2O$.

Potassium pentacalcium sulfate monohydrate, $K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$.

Fig. 1.—Comparison of ammonium pentacalcium sulfate and potassium pentacalcium sulfate (46 ×).

$Y = b$, $Z(B_{x_a}) \wedge c = 8°$. The optic plane is 010. Elongation, positive. Refractive indices: $\alpha = 1.567$ (± 0.003), $\beta = 1.580$ (± 0.003), $\gamma = 1.595$ (± 0.003).

The colorless crystals of the anhydrous salt ammonium dicalcium sulfate, $(NH_4)_2SO_4 \cdot 2CaSO_4$, are isometric, pyritohedral, with an index of refraction of 1.532. (Fig. 2.)

The double salt ammonium calcium sulfate monohydrate, $(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O$ (ammonium syngenite), occurs as colorless, lath-shaped monoclinic crystals that correspond in habit to those of the potassium calcium sulfate monohydrate, syngenite. (Fig. 3.)

As observed perpendicular to 100 the crystal displays a simple rectangular face, which is long and narrow. This view shows low birefringence, parallel extinction and a nearly symmetrical acute interference figure. The plane of the optic axes lies in the direction of the slower component, which parallels the long direction of the crystal. Y is parallel to the axis *b*. As observed normal to 010, the crystals are exceedingly narrow. This view shows the maximum birefringence and oblique extinction, the slower component making an angle of about 3° with the *c* axis.

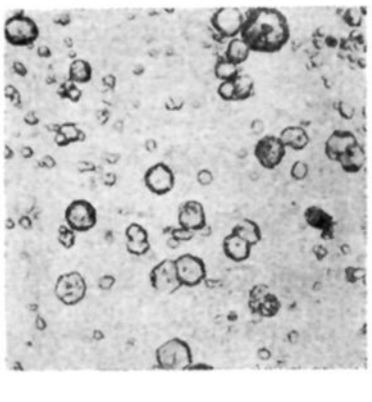
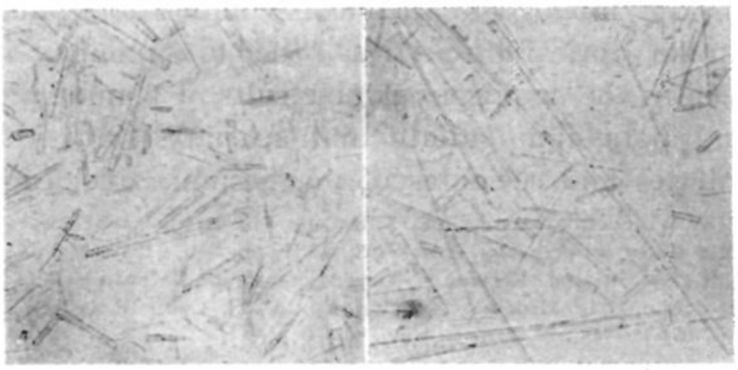


Fig. 2.—Ammonium dicalcium sulfate, $(NH_4)_2SO_4 \cdot 2CaSO_4$ (16 ×).

The material is biaxial, negative, with 2V about 50° and dispersion v > r distinct. $Y = b$, $Z(B_{x_a}) \wedge c = 3°$. The optic plane is 010. The sign of elongation positive. Refractive indices $\alpha = 1.521$ (± 0.003), $\beta = 1.529$ (± 0.003), $\gamma = 1.531$ (± 0.003).

Merz, Hardesty and Hendricks[5] report the crystals to be optically negative with indices of refraction n_D: $\alpha = 1.522$, $\beta = 1.527$, $\gamma = 1.529$.

The Hydration of Ammonium Calcium Sulfate.—A survey of the literature discloses a divergence of opinion as to the degree of hydration of ammonium "syngenite" (ammonium calcium sulfate). Bell and Taber[4] assigned two molecules of water of hydration to the salt, and subsequently were supported by the work of Merz, Hardesty and Hendricks.[5] D'Ans and Schreiner[1] found but one molecule of water of hydration, their work being substantiated recently by the careful investigation of Hill and Yanick.[6]



Ammonium calcium sulfate monohydrate, $(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O$.

Potassium calcium sulfate monohydrate, $K_2SO_4 \cdot CaSO_4 \cdot H_2O$.

Fig. 3.—Comparison of ammonium calcium sulfate and potassium calcium sulfate (46 ×).

There is close similarity in optical properties of the analogous double salts in the systems $(NH_4)_2SO_4$–$CaSO_4$–H_2O and K_2SO_4–$CaSO_4$–H_2O. Table I shows the close correspondence in the optical character of the two pentacalcium salts and the

TABLE I

OPTICAL PROPERTIES OF ANALOGOUS SALTS IN THE SYSTEMS K_2SO_4–$CaSO_4$–H_2O AND $(NH_4)_2SO_4$–$CaSO_4$–H_2O

Salt	Indices	Optical orientation	Optical angle and sign	Crystal system
K_2SO_4[8]	$\alpha = 1.4935$(D)	X $= b$	67° (+)	Orthorhombic
	$\beta = 1.4927$(D)	Y $= a$ opt. pl. (100)		
	$\lambda = 1.4973$(D)	Z $= c$		
NH_4SO_4[8]	$\alpha = 1.521$	X $= c$	52° (+)	Orthorhombic
	$\beta = 1.523$	Y $= b$ opt. pl. (010)		
	$\lambda = 1.533$	Z $= a$		
$K_2SO_4 \cdot CaSO_4 \cdot H_2O$[a,7,9]	$\alpha = 1.501-1.500$	$X \wedge c$ 87–88°	27–28° (−)	Monoclinic laths
	$\beta = 1.517$	$Y \wedge c$ 2–3° ⊥ (010)		
	$\lambda = 1.518-1.519$	Z $= b$		
$(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O$	$\alpha = 1.521$	$X \wedge c$ 87°	Abt. 50° (−)	Monoclinic laths
	$\beta = 1.529$	Y $= b$ (010)		
	$\lambda = 1.531$	$Z \wedge c$ 3°		
$K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$[7]	$\alpha = 1.550$	$X \wedge c$ 79°	±85° (+)	Monoclinic prisms
	$\beta = 1.565$	Y $= b$ (010)		
	$\lambda = 1.583$	$Z \wedge c$ 11°		
$(NH_4)_2SO_4 \cdot 5CaSO_4 \cdot H_2O$	$\alpha = 1.567$	$X \wedge c$ 82°	±86° (+)	Monoclinic prisms
	$\beta = 1.580$	Y $= b$ (010)		
	$\lambda = 1.595$	$Z \wedge c$ 8°		
$(NH_4)_2SO_4 \cdot 2CaSO_4$ $K_2SO_4 \cdot 2CaSO_4$[b]	$n = 1.532$			Isometric pyritohedrons

[a] Independent examination of $K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$ at this station substantiates the data given by Krüll and Vetter.

[b] This compound apparently has never been formed from aqueous solutions.

agreement in chemical composition. To syngenite, the potassium calcium sulfate, has been assigned the formula $K_2SO_4 \cdot CaSO_4 \cdot H_2O$, the presence of a single molecule of water of hydration having been established by many independent investigators. Since $(NH_4)_2SO_4$ and K_2SO_4 are isomorphous substances, forming isomorphous mixtures in all proportions, it would be expected that they should react in a like manner with calcium sulfate to form "syngenites" having analogous chemical compositions and similar optical properties. Such a similarity is seen in the analogous double salts of ammonium and potassium sulfate and selenates with the sulfates and selenates of magnesium, zinc, cadmium, iron (ferrous), copper and nickel;[10] in the ammonium and potassium acid arsenates and phosphates; in the alums and in numerous other cases.

The analogous chemical compositions and similarity of optical properties of that class of double salts to which ammonium calcium sulfate (ammonium syngenite) and potassium calcium sulfate (syngenite) belong, and the similarity of the syngenites in respect to their long, lathlike monoclinic structure, biaxial negative character, low birefringence and correspondingly small extinction angle would suggest that they possess analogous chemical compositions and, therefore, are hydrated to the same extent.

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(8) Winchell, "Microscopic Characters of Artificial Minerals." John Wiley & Sons, Inc., New York, 1931, pp. 216, 217.

(9) Larson and Berman, "The Microscopic Determination of the Nonopaque Minerals," Second Ed., U. S. Geol. Survey Bull., 848, 154 (1934).

(10) Tutton, from the data tabulated in Winchell, "The Microscopic Characters of Artificial Minerals." John Wiley & Sons, New York, 1931, pp. 240–256.