where T_r is the reduced temperature, T/T_c. By combining this equation with the equation for the sum of the densities

$$\rho_L + \rho_V = \alpha + \beta t + \gamma t^2$$

the densities can be calculated from room temperature to within about 5° of the critical point. The values of the constants k, m, n, α, β, and γ evaluated for each of the compounds from the experimental data are given in Table II. Included in this table are the average deviations of the observed from the calculated values for both the vapor pressure and density. The agreement between the observed and calculated values is within the experimental error in the data.

A comparison of the vapor pressure and density data calculated for *n*-hexane and 2,3-dimethylbutane with data reported by Young[1] is shown in Table III.

Summary

1. The critical constants of all of the isomeric hexanes and the standard boiling points of all except 2,2-dimethylbutane were carefully determined. Values of the liquid density at 20° were obtained by interpolation of the density–temperature curves.

2. The vapor pressures and saturated liquid and vapor densities of the isomeric hexanes were determined from near their atmospheric boiling points to their critical points. The data have been represented by empirical equations: (a) the vapor pressure data by equations of the type $\log P = A + (B/T)$ with the aid of deviation curves; (b) the density data by means of the equation of Fales and Shapiro, $\log \log \rho_L/\rho_V = \log k + m \log (1 - T_r^2) - n \log T_r$ together with the equation for the sum of the liquid and vapor densities, $\rho_L + \rho_V = \alpha + \beta t + \gamma t^2$. Values of the constants in the equations are given for each hydrocarbon.

RECEIVED[11] NOVEMBER 5, 1942

---

[11] This manuscript was originally received on November 5, 1942, and after examination by the Editorial Board was accepted for publication in the Journal. It was, however, referred to the National Defense Research Committee, and at their request was withheld from publication, in a confidential file, until clearance was granted on January 10, 1946.

[CONTRIBUTION FROM THE WESTERN REGIONAL RESEARCH LABORATORY[1]]

The Composition, Optical and Crystallographic Properties of Two Calcium Oxalate–Chloride Double Salts

BY FRANCIS T. JONES AND LAWRENCE M. WHITE

When microscopical methods[1a] were employed for the identification of minute crystals of calcium oxalate found in asparagus juice and hemlock bark, two crystalline substances were observed whose optical properties indicated that they were probably new compounds. Analysis shows that these compounds are the double salts $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$ and $CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$.

A careful search of the literature failed to reveal any work on the calcium oxalate–chloride double salts later than that of G. Rainey[2] in 1865. He investigated the oxalate–chloride double salts of the alkaline earth elements and, among others, described the compound $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$ that appears to be the same as one of the two reported here in detail. This compound had been prepared earlier by Fritzsche,[3,4] who also described another double salt of the composition $3CaC_2O_4 \cdot CaCl_2 \cdot 8H_2O$. Souchay and Lensen[5] in 1856 reported a double salt having the formula $4CaC_2O_4 \cdot CaCl_2 \cdot 24H_2O$ the existence of which was later doubted by Fritzsche.[4]

Experimental

Microscopical Observations.—When crystals obtained from asparagus juice or hemlock bark were recrystallized on a microscope slide[6] from a drop of 3 N hydrochloric acid, a few relatively large plate-like crystals were obtained in addition to crystals characteristic of calcium oxalate monohydrate. On contact with water these plate-like crystals changed quickly to a fine grained mass. The behavior, shape and optical properties of the plate-like crystals could not be reconciled with any of the hydrates of calcium oxalate reported by Winchell[7] but references[2,3,4,5] found in Beilstein[8] indicated that the plate-like crystals might be a double salt of calcium oxalate–chloride, and analysis proves that they are $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$. Rainey's[2] method (reaction of saturated calcium chloride solution with solid calcium oxalate on a microscope slide) gave identical plate-like crystals after standing several days. During attempts to prepare large quantities of the new compound by recrystallizing calcium oxalate from 6 N hydrochloric acid, crystals of oxalic acid and of tetragonal $CaC_2O_4 \cdot 3H_2O$ were recognized by their optical properties as being mixed with the plate-like crystals of the new compound. A homogeneous preparation of the plate-like crystals was obtained by the method described below. When hot concentrated hydrochloric acid was saturated with calcium oxalate and cooled

---

[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[1a] Chamot and Mason, "Handbook of Chemical Microscopy," John Wiley & Sons, New York, N. Y., 1938.

[2] Rainey, *Proc. Roy. Soc.* (London), **14**, 144 (1865).

[3] Fritzsche, *Pogg. Ann. d. Physik u. Chemie*, **28**, 121 (1833).

[4] Fritzsche, *Jahresbericht uber de Fortschritte der Chemie*, **372** (1864).

[5] Souchay and Lensen, *Ann.*, **100**, 317 (1856).

[6] Chamot and Mason, ref. 1a, Vol. II, 1940.

[7] Winchell, "Optical Properties of Organic Compounds," University of Wisconsin Press, Madison, Wis., 1943.

[8] "Beilstein Handbuch," 4th ed., Vol. II, Julius Springer, Berlin, 1920, p. 515.

slowly, there separated monoclinic, prismatic crystals, whose optical properties were unlike those of any other oxalate reported in the literature. Sometimes the plate-like crystals of the heptahydrate developed at first but redissolved and transformed to the prismatic type after standing overnight. This transformation was observed in a preparation on a microscope slide. The prismatic crystals react slowly with water becoming covered with a granular crust after an hour or two. A pure preparation of the prismatic crystals was made and analyzed as reported below, proving that the new compound is $CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$.

Preparation and Composition of the Double Salts.—The calcium oxalate–chloride heptahydrate was prepared by heating 1 part calcium oxalate monohydrate with 15 parts by weight of 8.6 *N* hydrochloric acid in a glass-stoppered flask until the solid phase completely disappeared. On cooling to room temperature the heptahydrate crystallized in well-defined plates.

The calcium oxalate–chloride dihydrate was prepared by digesting at 100° 1 part calcium oxalate monohydrate with 12 parts by weight of concentrated hydrochloric acid in a securely stoppered flask to prevent loss of hydrochloric acid. The prismatic crystals of the dihydrate began to separate before the calcium oxalate was completely dissolved and crystallization continued on cooling to room temperature. Each of the double salts was separated from its mother liquor by centrifugal filtration on a fritted glass plate, washed once with absolute ethanol and centrifuged as before. The crystals were air-dried and stored in glass-stoppered bottles. Microscopic examination showed that the ethanol washing, air-drying and storage had no effect on the crystallographic properties of the salts.

When digested with hot water the double salts gave liquid phases containing only traces of oxalate and residues free from chloride. Analysis showed that these residues were calcium oxalate monohydrate. The liquid phase of each of the digests contained calcium and chloride in the atomic ratio of 1 to 2 and the amount of calcium found in each residue was equal to that found in the corresponding liquid phase. It is therefore apparent that the double salts are equimolar compounds of calcium oxalate and calcium chloride and differ only in their water content.

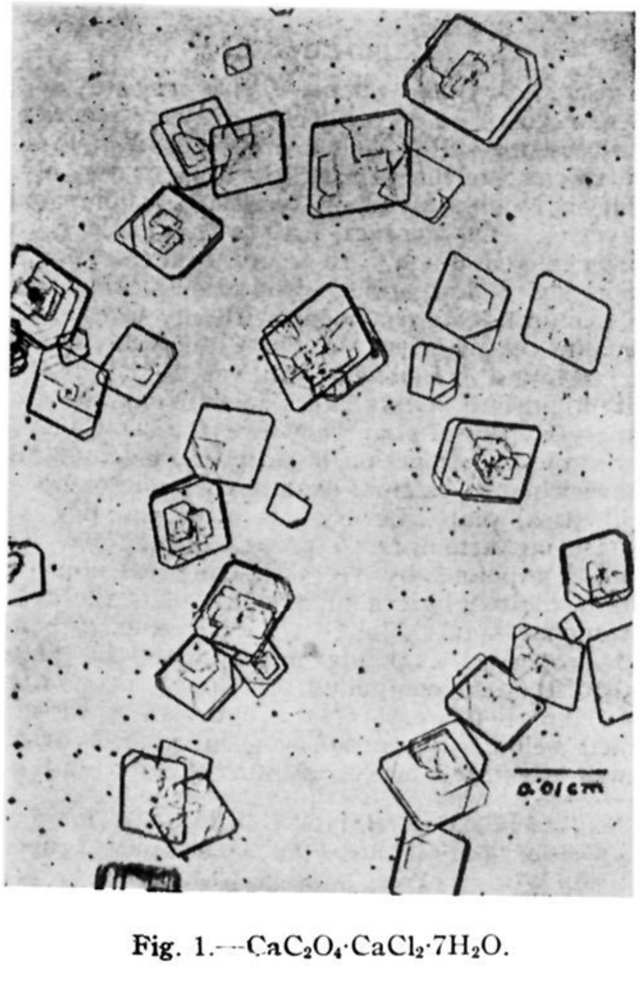

Fig. 1.—$CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$.

The air-dry heptahydrate lost five-sevenths of its water on vacuum drying over Anhydrone at 25°. No further loss occurred on heating in air at 100° but at 205° the remaining water was driven off. Heating at 250° did not cause further change. The air-dry dihydrate did not lose weight on heating up to 205° and its optical properties remained unchanged after being heated at this temperature. It did, however, lose all of its water on being heated at 250°. Table I shows the composition of the double salts. Calcium and oxalate were determined by titration with permanganate according to Scott[9] and chloride was determined gravimetrically as silver chloride in the oxalate-free liquid phase.

TABLE I

COMPOSITION OF CALCIUM OXALATE–CHLORIDE DOUBLE SALTS

	$CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$, %		$CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$, %	
	Found	Calculated	Found	Calculated
Calcium	21.87	21.95	28.92	29.14
Oxalate	23.86	24.10	31.71	31.99
Chloride	19.47	19.42	25.87	25.78
Water	34.50	34.53	13.16	13.09

Optical and Crystallographic Properties.—Refractive indices were determined at about 25° by immersion methods using light from a sodium vapor lamp. The values listed in Table II are regarded as correct to ± 0.001 except the highest value which is ± 0.002. The calculated values of 2 *V* listed in Table II were obtained from the refractive indices by the exact formula given by Larsen and Berman.[10]

TABLE II

OPTICAL PROPERTIES OF CALCIUM OXALATE–CHLORIDE DOUBLE SALTS

	$CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$	$CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$
α	1.500 ± 0.001	1.571 ± 0.001
β	1.545 ± 0.001	1.648 ± 0.001
γ	1.568 ± 0.001	1.718 ± 0.002
n_1 common view	....	1.698 ± 0.001
n_2 common view	....	1.596 ± 0.001
Crystal system	Monoclinic	Monoclinic
Axial angle, calcd.[10]	$2V = 71°$	$2V = 87°$
Axial angle, observed	$2V = 71°$[a]	$2V = 85°$[b]
Dispersion	$(r < v)$ weak	$(r < v)$ weak
Optical character	(−)	(−)

[a] By conoscopic observation. [b] Estimated from curvature of isogyre.

The colorless, monoclinic thin plates of the compound $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$ are illustrated in Fig. 1. Figure 2 shows the principal view and optic orientation. Twinning is common; it is not noticeable in ordinary light but is conspicuous when the crystals are examined between crossed nicols. Birefringence is moderate for the common view. Ordinarily one layer of the twin overlies the other in bands, although adjacent segments which do not overlap may also be seen. Twinned crystals do not extinguish sharply in any position if the portions of the twin overlie each other. The acute angle between the planes of vibration of the slow rays in adjacent portions of the twin is about 21°. Crystals which are not twinned show sharp

---

[9] N. H. Furman, Ed., "Scott's Standard Methods of Chemical Analysis," 5th ed., Vol. I, p. 212 and Vol. II, p. 2253, D. Van Nostrand Co., New York, N. Y., 1939.

[10] Larsen and Berman, "The Microscopical Determination of the Non-opaque Minerals," U. S. Geol. Survey Bulletin, 2nd Ed., 1934, p. 848.

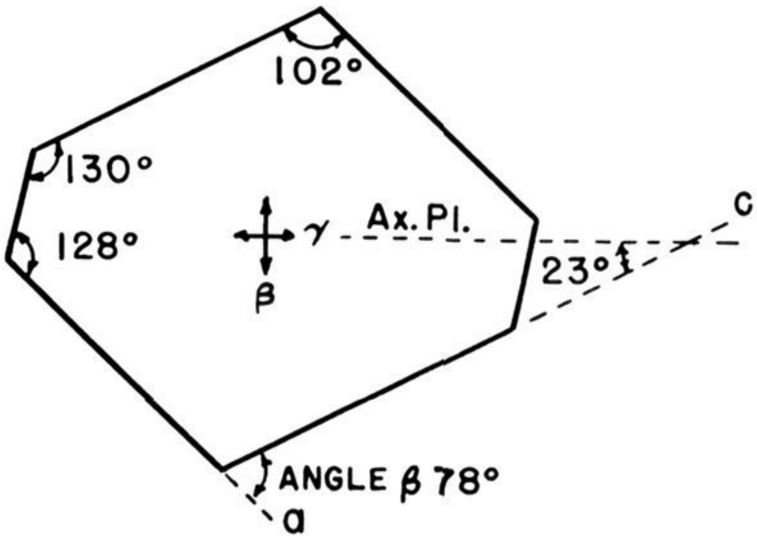

Fig. 2.—$CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$, principal view.

oblique extinction. The extinction angle between the slow ray and the nearest edge is 23°. Edge views give parallel extinction with the vibration direction for the index α normal to the plate. Conoscopic observation using an apertometer-calibrated eyepiece scale, shows a negative acute bisectrix interference figure of 2E ≈ 126° from which 2 *V* is calculated to be approximately 71°. The acute bisectrix is normal to the plate. The optic axial angle for blue light is slightly greater than that for red light. None of these observations conflict with the meager description given by previous workers.

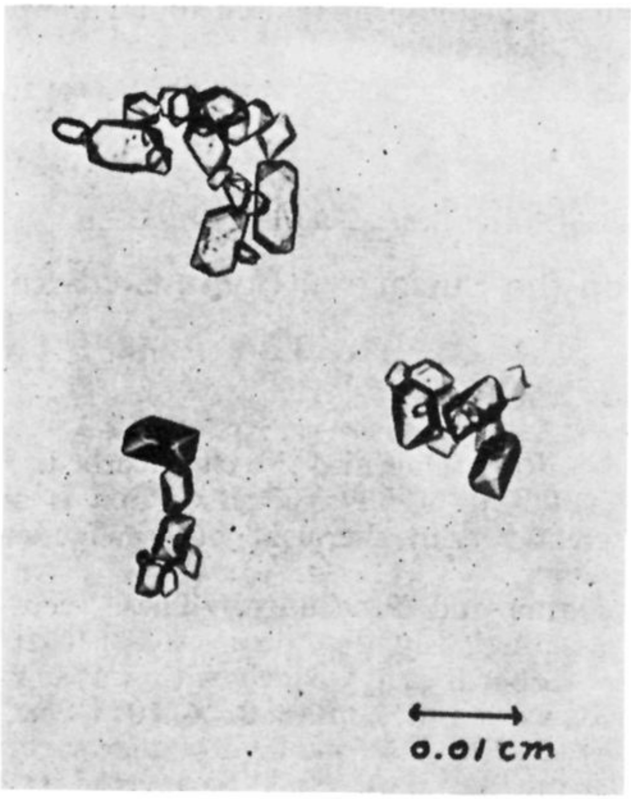

Fig. 3.—$CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$.

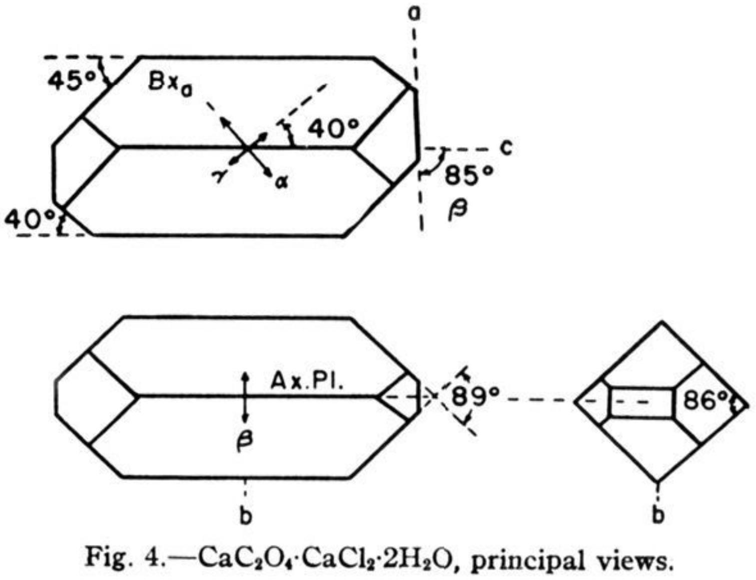

Fig. 4.—$CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$, principal views.

The colorless, prismatic crystals of the new compound, $CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$ are illustrated in Fig. 3. Figure 4 shows the principal views and optic orientation. Figure 5 shows the common view of a crystal lying on a prism face. The face angles and the extinction angle of the slow ray (n_1) relative to the length of the prism are shown. Some crystals in this position can be seen in Fig. 8. No tendency to twin was noticed in this compound. The birefringence is very strong for most views but some edge views parallel to the plane of symmetry show low birefringence. Such views give an optic axis interference figure by conoscopic observation. The optic axial angle is estimated from the slight curvature of the isogyre to be

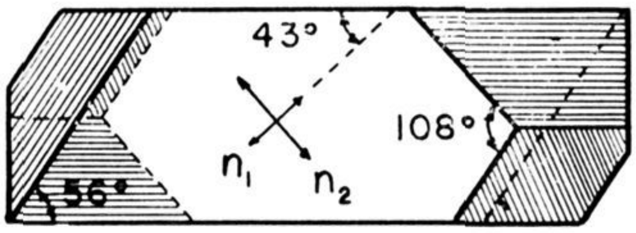

Fig. 5.—$CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$, common view.

TABLE III

X-RAY POWDER DIFFRACTION DATA[a]

Substance	*d*, Å.	Relative intensity[b]
$CaC_2O_4 \cdot H_2O$	5.93	VS
	3.67	S
	2.96	S
	2.50	MW
	2.35	M
	2.26	VW
	2.09	W
	1.96	MW
	1.82	W
	1.74	VW
$CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$	9.87	VS
	6.54	W
	4.46	M
	3.73	M
	3.27	S
	2.79	S
	2.26	M
	2.10	M
$CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$	5.25	M
	3.71	MW
	2.95	VS
	2.63	M
	2.51	M
	2.32	MS
	1.98	M
	1.85	M
	1.75	W
	1.67	VW
	1.59	W

[a] Photographs were taken with MoK_α filtered through a thin zirconium foil. [b] S = strong; M = medium; W = weak; V = very. (Visually estimated.)

about 85°. Dispersion is faint. The optic axial angle for blue light is slightly greater than for red light judging from the optic axis that most nearly coincides with the crystal axis *a*. The other optic axis was not observed.

X-Ray Powder Diffraction.—As an aid to the study of calcium oxalate and its double salts with calcium chloride, the X-ray diffraction lines obtained from powdered samples of calcium oxalate monohydrate and the two double salts described in this paper are listed in Table III.

Discussion

The formation of these characteristic crystals by reaction of calcium oxalate with hydrochloric acid can be used to aid in the identification of calcium oxalate in many cases where the unknown does not contain crystals large enough to be identified by optical methods.

No special attempt was made to prepare other double salts of calcium oxalate-chloride, but when conditions of preparation were similar to those described by Souchay and Lensen[5] we did not obtain the compound $4CaC_2O_4 \cdot CaCl_2 \cdot 24H_2O$ that they reported. Consequently it seems possible that their double salt was actually a mixture. In fact they mention the presence of oxalic acid crystals in some of their preparations. Microscopic examination, including a determination of optical properties, would have revealed such a lack of homogeneity in the sample taken for analysis. It is possible that a complete phase study of this system would reveal other double salts.

Acknowledgment.—Acknowledgment is due Merle B. Hartzog for taking the X-ray powder diffraction photographs and for making the measurements given in Table III.

Summary

A microscopical study of the reaction of calcium oxalate with hydrochloric acid has been reported. The composition, optical and crystallographic properties, and X-ray lines of a new double salt, $CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$, and those of the previously reported double salt, $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$, have been determined.

The formation of these crystalline materials can be used as an aid in the microscopical identification of calcium oxalate, and to aid the phase study of this system.

ALBANY, CALIF. RECEIVED MARCH 4, 1946

[CONTRIBUTION FROM RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

The Sorption of Water Vapor at Low Pressure on the Surface of Some Cold-Rolled Steels at 20°

BY MARION H. ARMBRUSTER[1]

Because there are few unexceptionable data relative to the sorption of water vapor on a plane surface, especially of a metal, and because of the possible practical utility of a better knowledge of this matter, several series of careful measurements have been made at 20° at pressures up to 0.15 cm. on some of the identical samples of steel used in earlier measurements of the sorption of other gases.[2] These samples were three cold-rolled surfaces, two of low-carbon steel, the third a stainless alloy containing 18% chromium and 8% nickel, all of which had been carefully preheated to ensure reproducible results comparable with those for the sorption of other gases. At the highest pressures investigated mild steel sorbs what appears to be a complete monolayer physically and a partial layer by chemisorption, the completeness of coverage being estimated by comparison with data for carbon monoxide sorbed reversibly at −183° on the identical sample. On the same basis, the total volume of gas sorbed on the stainless alloy, which is presumably covered by an invisible yet protective oxide film, not reducible by hydrogen at 600°, is three to four times as great as on the mild steel, and of this amount about one-third is chemisorbed. The calculated heat of physical adsorption is about 25% greater than the heat of liquefaction of water vapor.

Apparatus and Procedure.—These were the same as previously described[3] except that the double McLeod gage,[4] which with water vapor could be used only up to 2×10^{-3} cm. was supplemented by a second similar gage such that a higher pressure range could be covered without danger of condensation in the gage during a measurement. This danger was avoided, at the higher pressures, by warming the capillary of the second gage to about 30° during a reading. The correction for this difference in temperature was calculated and checked experimentally by means of hydrogen; it proved to be small. The supplementary gage was calibrated by comparison with the double gage, by use of "spectroscopically

---

(1) Present address, Department of Chemistry, Barnard College, New York, N. Y.

(2) Armbruster and Austin, THIS JOURNAL, **66**, 159 (1944); also unpublished data for stainless alloys.

(3) Armbruster and Austin, *ibid.*, **60**, 467 (1938); **61**, 1117 (1939).

(4) It is of interest to note that in some preliminary measurements condensation of water vapor at 20° in the capillary of this gage was observed at a pressure of about 1.3 cm., whereas 1.7 cm. is the saturation pressure of water at this temperature. Similar condensation at a pressure lower than the saturation pressure of water has been observed by Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927), using the pressure-temperature curve method of determining adsorption; by Frazer, *Phys. Rev.*, (2) **33**, 97 (1929), using the optical method of Drude and Rayleigh modified for greater accuracy; and by Coolidge, THIS JOURNAL, **49**, 708 (1927).