

Subtracting $0.05915 \log m_{\text{IO}_3^-}$ from both sides of (1), we obtain a modified form of a relation employed by Lewis and Randall⁷

$$0.05915 \log (a/m)_{\text{IO}_3^-} = E^\circ - (E + 0.05915 \log m_{\text{IO}_3^-})$$

The $\log a/m$ is equal to zero at infinite dilution and hence $E^\circ = (E + 0.05915 \log m_{\text{IO}_3^-})$. If we plot the quantity in parentheses against the square root of the molality, the intercept on the ordinate at $m = 0$ is equal to E° .

Since extrapolation is precarious in any case, and because of possible errors in determining the potential of the most dilute solution, which was the most difficult to obtain, we have calculated the potential, E_{298}° , by (1), using accepted values⁸ for the activity coefficients of potassium iodate. The values of E° , which should be the same at all concentrations, are given in the last column of Table II. It is evident that the potential of the 0.01 m electrode is too low. Omitting this, we take as the most probable value of the potential of the Ag, AgIO₃, IO₃⁻, ($a = 1$) electrode, $E_{298}^\circ = 0.3569$ volt.

Summary

The electromotive forces of a series of cells of the type: Hg, Hg₂Cl₂, KCl(m), KIO₃, AgIO₃, Ag, have been measured at 25°. By combining these values with the potentials of the corresponding calomel electrodes, the potential of the Ag, AgIO₃, IO⁻ ($a = 1$) electrode is found to be, $E_{298}^\circ = 0.3569$ volt.

(7) Lewis and Randall, "Thermodynamics," 1923, p. 334.

(8) Lewis and Randall, *ibid.*, p. 362.

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The Optical Properties of the Double Salt $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

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During the course of an investigation of the hygroscopicities of mixtures of fertilizer salts not having common ions,¹ one of the solid phases obtained in the systems, $\text{NH}_4^+ \text{Ca}^{++} \text{NO}_3^- \text{SO}_4^{=}$ and $\text{NH}_4^+ \text{Ca}^{++} \text{H}_2\text{PO}_4^- \text{SO}_4^{=}$, was found to be a double salt of calcium and ammonium sulfates. Three double salts, in which the ratios of ammonium sulfate to calcium sulfate are 1:1, 1:2 and 1:5, respectively, have been reported in the literature. The double salt with the ratio 1:2 does not exist below 75°² and, as the vapor pressure measurements were carried out at 30°, it therefore remained to identify the salt as one of the other two compounds. Since the double salt with the ratio, 1:5, cannot exist, in the system $\text{NH}_4^+ \text{Ca}^{++} \text{SO}_4^{=}$, in contact with solid ammonium sulfate,² gypsum was added to a saturated solution of ammonium sulfate which was then evaporated until considerable ammonium sulfate had crystallized and finally allowed to stand for several days. Microscopic examination of the solid phases disclosed both am-

(1) A. R. Merz, W. H. Fry, J. O. Hardesty and J. R. Adams, *Ind. Eng. Chem.*, **25**, 136 (1933).

(2) J. D'Ans and O. Schreiner, *Z. anorg. Chem.*, **62**, 141 (1909).

monium sulfate and the same double salt as was found present during the vapor pressure determinations, thus indicating that the double salt in question had the 1:1 ratio.

D'Ans and Schreiner² state that the double salt of ammonium and calcium sulfate having the 1:1 ratio is an ammonium syngenite, analogous in composition to syngenite, and forms in a saturated ammonium sulfate solution according to the reaction $(\text{NH}_4)_2\text{SO}_4 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} = (\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$. Bell and Taber,³ however, claim that the compound contains two molecules of water of crystallization and should be given the formula $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Since the optical properties

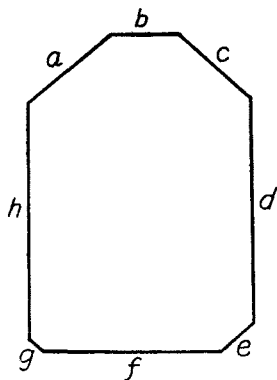


Fig. 1b.



Fig. 1a.

and density of this salt appear not to have been reported, it was considered desirable to determine them, especially as the information thus gained would aid in settling the question as to its composition.

To obtain the double salt as the sole phase in contact with the liquid phase, 251 g. of ammonium sulfate, 36.65 g. of gypsum and 1500 cc. of water were evaporated at 30° over a period of eight days to a volume of 500 cc. to give a point in the field of the 1:1 salt.⁴ Microscopic examination showed the solid phase to consist only of crystals identical with those of the double salt previously obtained. Since washing the salt with water quickly decomposes it, leaving gypsum as a residue, and

washing with alcohol-water and alcohol-ether, as carried out by D'Ans,⁵ has been shown by Bell and Taber to result in decomposition also, the method of residues was used for the chemical determination of the composition. The material used for the optical work was obtained separately by suction filtration and air drying.

Analysis of the mother liquors gave water 63.99%, ammonium sulfate 35.69% and calcium sulfate 0.32%; of the moist crystals, water 32.82%, ammonium sulfate 40.39% and calcium sulfate 26.79%, whence by calculation or graphically, using triangular coordinates, the dry double salt contains 11.47% water of crystallization. This corresponds to the theoretical value, 11.84%.

(3) J. M. Bell and W. C. Taber, *J. Phys. Chem.*, **11**, 492 (1907).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. IV, p. 388.

(5) J. D'ans, *Ber.*, **39**, 3326 (1906).

Optical Properties.—The common crystal habit is that shown in Fig. 1a. A centered acute bisectrix interference figure was obtained from some flat needles of this type. The direction of vibration of the slowest ray, γ , is parallel to the elongation. A very few crystals of the type shown in Fig. 1b were observed in wet samples. The angles ah, cd, and de are equal as measured under the microscope. The crystal section was apparently perpendicular to the optic normal.

The indices of refraction ascertained by the immersion method are N_D : $\alpha = 1.522$; $\beta = 1.527$; $\gamma = 1.529$. The crystals are optically negative.

The density, measured by the centrifugal suspension method, is 2.07. Greater accuracy was impossible owing to the minuteness of the dried crystals.

It is interesting to compare the optical properties of this compound with those of ammonium sulfate and gypsum.⁶

	$(\text{NH}_4)_2\text{SO}_4$ mascagnite	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ gypsum	$(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
α	1.521	1.5195 1.5208	1.522
β	1.523	1.5216 1.5230	1.527
γ	1.533	1.5283 1.5305	1.529
d_{20}	1.7681 ⁷	2.32 ⁸	2.07
Crystal system.....	Orthorhombic	Monoclinic	Orthorhombic?
Mol. vol.....	74.74 cc.	74.2 cc.	147 cc.
Mol. refractivity (calcd. by Lorenz-Lorentz formula)....	22.89	22.67 22.85	45.12

The value of the molecular refractivity of $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is, within the limit of error, equal to the sum of the values for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$. This is likewise true for the molecular volumes. These facts further confirm the composition of the hydrated double salt as being $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

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(6) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1930, Vol. VII, pp. 19, 24.

(7) *Ibid.*, 1928, Vol. III, p. 44.

(8) *Ibid.*, 1926, Vol. I, p. 143.