

and pentasalt must be below 40° and not far above 31.8° (point O).

With regard to the general problem of separating potassium sulfate from calcium sulfate by solubility differences, the complete diagram gives a somewhat disappointing picture; it indicates

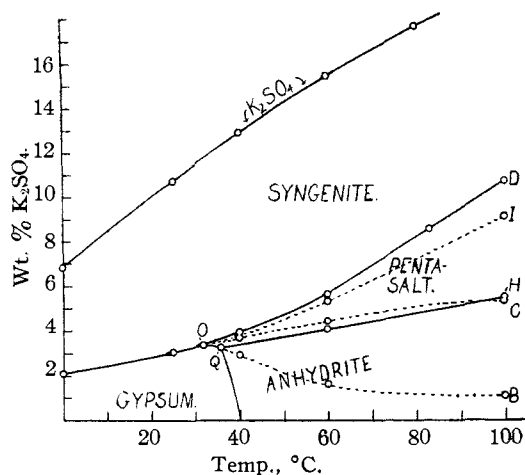


Fig. 4.—Polytherm for CaSO₄-K₂SO₄-H₂O.

that as far as stable equilibria are concerned, the rise of temperature from 25 to 100° improves the possibilities only slightly; at 25° potassium sulfate could be concentrated in solution up to 3.067%, which could be increased at 100° only up to 5.46% (points on line H) without leaving some of the potash in one of the insoluble double salts. However, the very low rate at which an-

hydrite combines to form pentasalt or syngenite makes it seem probable that if any of the complex salts could be so decomposed at higher temperatures as to convert the calcium sulfate into anhydrite, solutions might be concentrated up toward the neighborhood of 10.6% at 100° (point D) or at least to 9.1% (point I).

Summary

1. Complete isotherms for the system CaSO₄-K₂SO₄-H₂O have been studied at 40, 60 and 100°, and the fields for the various equilibria, stable and metastable, between 0 and 100° have been indicated.

2. A preliminary report is made on the determination of the solubility of anhydrite in water; the solubility appears to vary with the mode of preparation of the salt, and the approach to equilibrium is extremely slow.

3. The results in the ternary system indicate that so far as the stable equilibria are concerned the separation of potassium sulfate from calcium sulfate in natural polyhalite, by solubility differences, is not materially favored by increase in temperature, but that a substantial concentration of potassium sulfate may prove possible through the metastable precipitation of anhydrite, in view of the great retardation in the formation of pentasalt and syngenite even at 100°.

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Microdetermination of Fluorine in Organic Substances

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The present method was devised to titrate fluorine in small quantities of gaseous organic fluorides. As it may be applied to the titration of halogens in any substance which can be volatilized or burned, its publication may be justified.

The principle of the method consists in decomposing the organic molecule over silica heated to 900° in a combustion tube. Under these conditions, the decomposition is rapid and complete and the fluorine of the organic molecule is transformed into silicon tetrafluoride. The latter is then collected in water or in a weak alkaline solution where the fluorine ion is then titrated by

means of cerous nitrate. To ensure correct results it is essential to sweep the combustion tube with hydrogen in order to remove adsorbed silicon fluoride and to reduce silicon oxyfluoride.

Procedure.—The gases analyzed were organic substances containing both fluorine and chlorine. As the method used to titrate fluorine permits a simultaneous measurement of the chlorine, and as the chlorine and fluorine are present in the organic molecule in a known ratio, it is convenient to check the accuracy of the fluorine titration by the titration of chlorine. (The Volhard method is a very sensitive and well-known procedure.) The following paragraphs describe the analysis

of CF_2Cl_2 , mixtures of CF_2Cl_2 and CCl_3F , and mixtures of $\text{C}_2\text{H}_2\text{F}_3\text{Cl}$ and $\text{C}_2\text{F}_3\text{Cl}_3$.

A mercury gas buret is used to measure the sample, and to force it through the heated silica into the absorption device. The same buret is subsequently used to deliver the nitrogen and the hydrogen used to sweep the combustion tube. The silica used for the decomposition is contained in a small quartz tube heated to 900° by means of an electric furnace. This silica tube is connected to the gas buret on one side, and to a slightly modified Péligré tube on the other side. A more detailed description of the equipment follows.¹

Detail of Equipment

(1) **Electric Furnace.**—The core is a silica tube 17.5 cm. long, 15.5 mm. internal diameter and 22 mm. external diameter. A nichrome wire No. 30, 7.2 m. long is wound over 15 cm. of its length and protected with a coat of aluminum cement. An insulating packing of mixed magnesium oxide and asbestos, 6 cm. thick is wrapped around, and the whole furnace is encased in an aluminum sheet, with transite ends bearing the binding posts. A small rheostat, made of the same wire, permits adjustment of the temperature. The voltage used is 220 volts.

(2) **Combustion Tube.**—It is a 30-cm. silica tube packed with crushed silica (broken dishes), graded to 20–40 mesh, and held in place with glass wool. Moist strips of cloth dipping into beakers containing water are used to keep the ends cool.

(3) **Absorption Tube.**—It is a 12-mm. diameter U-tube constricted several times to make nine successive bulbs, with an horizontal branch closely connected to the combustion tube by a small piece of rubber hose. It contains 10 cc. of 0.1 sodium hydroxide solution and 1 cc. of superoxol.

(4) **The Gas Buret.**—It is equipped with a three-way stopcock, to permit the drawing in of the sample as well as its expulsion into the combustion tube. Mercury is used in the leveling bulb.

Experimental Procedure.—Take about 10 cc. of sample in the buret, measuring it accurately; increase the volume of gas to 100 cc. by admitting 90 cc. of air or oxygen. Force the gaseous mixture slowly through the combustion tube. Admit another 100 cc. of air or oxygen in the buret, then force it through the furnace. Sweep with 100 cc. of nitrogen, 200 cc. of hydrogen and finally 100 cc. of nitrogen. When this is done, the fluorine has been carried into the absorption tube as silicon tetrafluoride, and the chlorine as such. In the absorption tube, silicon tetrafluoride is hydrolyzed, while chlorine is reduced to hydrogen chloride.

The content of the absorption tube is now ready for analysis of the fluoride and chloride ions. The chlorine is titrated by the Volhard method. The titration of the fluorine is done by the cerous nitrate method of Batchelder² slightly modified; it was found that the addition of brom cresol green to the methyl red indicator enhanced the sensitivity of the end-point.

(1) Liquid samples (weighed in fragile ampoules) are placed in an "evaporator" inserted between the furnace and the buret. The "evaporator" is progressively heated, and air from the buret carries the vapors into the combustion tube.

(2) Batchelder and Meloche, *THIS JOURNAL*, **53**, 2131 (1931).

Wash the contents of the absorption tube with 150 cc. of distilled water into a 250-cc. beaker, add a bumping stone and 1 cc. of superoxol. Boil to remove the excess of hydrogen peroxide thus reducing sodium hypochlorite to sodium chloride. Filter to remove silica, cool and dilute to 250 cc. Take a 25-cc. aliquot, add 2 drops of phenol red indicator as described by Clark. Neutralize with *N* nitric acid, finishing with 0.02 *N* nitric acid. After each addition of acid, the solution is heated to expel carbon dioxide, until the yellow color of the indicator becomes permanent. This neutralization must be done very carefully. Reduce the total volume by evaporation to not over 5 cc.; add 2 drops of methyl red indicator and 10 drops of brom cresol green indicator. A green color develops. Titrate at 80° with a solution of 7.6206 g. of cerium nitrate hexahydrate in two liters (1 cc. of solution is equivalent to 5 mg. of fluorine). Shake constantly. It is best to light the sample from the back (artificial light through frosted glass), to use a microburet, and to approach the end-point rapidly as the color is changing from green to purplish-red. The end-point is taken when the maximum strength of purplish-red is attained.

Verification.—The purity of the cerous nitrate was checked by igniting to cerous oxide; sodium fluoride, used as standard was converted to sodium sulfate; the cerous nitrate solution was standardized through sodium fluoride.

In order to gage the effect of sodium chloride and sodium nitrate on the results, the fluorine titration was carried out in the presence of such an amount of these salts as would be present in a complete analysis of organic fluorides. Table I shows that the results remain correct.

TABLE I

NaNO_3 added, mg.	0	0	85	85	0	0
NaCl added, mg.	0	0	0	0	58.5	58.5
F added, mg.	9.80	9.80	9.80	9.80	9.80	9.80
F found, mg.	9.77	9.70	9.67	9.70	9.77	9.75

To test the sensitivity of the titration, under conditions similar to those encountered in practice, decreasing amounts of sodium fluoride were added to a 50-cc. solution of *N*/50 sodium hydroxide solution, then neutralization and titration were performed as outlined. Table II summarizes the results.

TABLE II

F added, mg.	9.80	9.80	7.84	7.84	5.88	5.88
F found, mg.	9.75	9.60	7.78	7.75	5.80	5.85
F added, mg.	3.92	3.92	1.96	0.98	0.98	
F found, mg.	3.90	3.90	2.00	1.00	1.00	

Complete Analysis.—The chemical compound CCl_2F_2 was then analyzed as described; its melting curve indicated that the sample used was pure. Since CCl_2F_2 is not a perfect gas, it is impossible to compute its fluorine and chlorine content by weight, from the analysis of a known volume. However, the theoretical weight ratio of these two elements in CCl_2F_2 is known to be $35.46/19.00 \pm 1.866$, and this ratio is determinable by the present procedure. On the basis of 10-cc. samples of gas at 0° and 760 mm. pressure, the following results were obtained.

TABLE III

Cl found, mg.	32.2	31.5	29.6	31.8	Av. 31.3
F found, mg.	17.3	16.8	15.8	17.0	Av. 16.75
Ratio found	1.86	1.87	1.87	1.87	Av. 1.87
Theoretical ratio	1.866				

A glance at Table III discloses immediately that the analyses were correct, since the ratio of chlorine to fluorine remained constant. The discrepancies in actual weight found are due to the error inherent in the measurement of the volume of the gas sample, and the difficulty of obtaining a sample of such a small size without introducing air. With the device used, the small volume could be read only with a precision of a little less than 1%.

If CCl_2F_2 is assumed to be a perfect gas, it follows that the chlorine content of 10 cc. (standard conditions) should be 31.9 mg., while the fluorine content should be 17.1 mg. Comparing these figures with the experimental values 31.3 mg. and 16.75 mg. (values which are admittedly a trifle low) one finds that the differences are accounted for by the fact that CCl_2F_2 is not a perfect gas, though very close to being perfect.

The method was then applied to the determination of the composition of a small sample of a liquefied gas. This gas was known to be impure CCl_2F_2 , containing CCl_3F as impurity. The limited quantity of material at hand, and the fact that the vapor composition of a mixture is bound to be different from that of the liquid, complicated the sampling problem. Nevertheless, creditable results were obtained, as shown in Table III. The analyses were performed on 10-cc. gas samples.

TABLE IV

Sample	1	2	3	4	5	6	7	8	Av.
Cl, mg.	31.3	35.7	35.3	32.1	32.4	32.2	31.8	32.4	32.9
F, mg.	15.5	17.2	16.9	15.9	15.4	14.8	16.2	15.8	16.0
Ratio	2.02	2.07	2.08	2.02	2.10	2.17	1.97	2.05	2.06

Here, again, advantage could be taken of the fact that in CCl_2F_2 as well as in its impurity, CCl_3F , the ratios Cl/F are constants. Table IV shows that the ratio Cl/F measured is 2.06 ± 0.04 . (The odd results 6 and 7 were readily explained when it was found that an insufficient amount of hydrogen had been used in analysis 6. A somewhat larger amount was used in 7, and the fluorine deficiency was thus promptly recovered.)

Since the theoretical Cl/F is 1.866 in CCl_2F_2 , and 5.598 in CCl_3F , a simple calculation indicates that the experimentally obtained ratio 2.06 corresponds to a mixture of

94.64% CCl_2F_2 and 5.36% CCl_3F . An independent measurement of the sample density indicated 5% of CCl_3F , thus affording a good check.

Analysis of an Unknown Material.—The material was received as a liquid boiling about 8° . Five 10-cc. samples of the gas measured at standard conditions were analyzed with the following results.

TABLE V

Cl, mg.	17.9	17.9	19.1	18.7	20.9
F, mg.	23.6	24.2	23.7	23.2	24.7
Ratio Cl/F	0.76	0.74	0.81	0.81	0.85

The samples were taken while the material was distilling. The results show at once that the sample is a mixture. The fact that the fluorine stays practically constant, while the chlorine content increases progressively (and hence the Cl/F ratio) shows that the number of fluorine atoms is the same in all the constituents of the mixture. On the other hand, the number of atoms of chlorine increases progressively. A simple computation indicates that the mixture contains mainly a compound with 3 atoms of fluorine and 1 atom of chlorine, together with impurities in which 3 atoms of fluorine and more than 1 atom of chlorine are present. A further independent investigation (fractional distillation of one liter of material) shows that only two substances are present, namely, $\text{CF}_3\text{CH}_2\text{Cl}$, which constitutes the bulk of the sample and has a Cl/F ratio 0.60 and $\text{C}_2\text{F}_3\text{Cl}_3$, with a Cl/F ratio of 1.87. From the analysis results it was then computed that the distillation yielded a material with 12.7% impurity in the first stages and with 19.8% of impurity in the last stages. These new compounds are described in a subsequent paper.

Summary

A method is presented for the simultaneous analysis of fluorine and chlorine in minute gas samples. It consists in a decomposition of the gas over heated silica followed by micro-titration of the chlorine and fluorine ions. It is applicable to substances which can be brought to the vapor phase. The accuracy with which the sample can be measured is shown to be the limiting factor in the accuracy of the results.