3. A thermometric method for the determination of the V. C. has been devised and the apparatus and calculations are described.

4. Measurements of the V. C. of three solutes, urea, acetanilide and ammonium nitrate made in various solvents and mixtures by the thermometric method, indicate that the important factor in altering the V. C. of a given solute in such solvents and mixtures is the viscosity of the solution. The relation between the viscosity of the solution, η, and the velocity constant, K, is given by the expression: $K = \text{Const.}/\eta^{0.59}$.

5. The results of these experiments have been discussed in relation to some of the present theories of crystallization.

6. The temperature coefficient of the V. C. of acetanilide in two solvents was found to be due only to the decrease in viscosity of the solution at the higher temperature.

7. Measurements of the V. C. of lactose from water indicate that the process is retarded by the slow formation of the hydrate in solution by the reaction: lactose anhydride + $H_2O \rightleftharpoons$ lactose hydrate. Ammonia in very dilute solution greatly increases the V. C.

8. Some determinations of the rate of solution have been made and a formula has been suggested and tested for the rate of solution of small crystals in a medium whose volume is so great that its concentration is not appreciably altered during the process.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEVADA]

CRITICAL STUDIES ON THE FUSION OF RARE-METAL ORES
I. THE PYROSULFATE FUSION OF TITANIUM ORES[1]

BY GEORGE W. SEARS AND LAURENCE QUILL

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Although fusion methods have long been in use for the decomposition of ores, apparently no very careful study of the reactions taking place or of the conditions affecting these reactions has been made. When the analyst is forced to use fusion for the decomposition of his sample, he receives little help from the literature as to the method of procedure, the proportion of flux necessary, the time of fusion or the temperature most desirable. Furthermore, he is not always sure of obtaining a complete decomposition in one fusion but often finds a second and sometimes a third fusion necessary. Because of this lack of definiteness in the treatment of ores and a desire to clarify if possible the reactions concerned, a series of investigations is being carried on in this Laboratory in a critical study

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of the decomposition by fusion of certain rare-metal ores. In order to obtain the relative value of the acid radical, the sodium salts were selected as the flux for both acid and alkali fusions, since they are more available and with the exception of the pyrosulfate are more generally used.

The present investigation has to do particularly with the conditions affecting the decomposition of titanium ores by fusion with sodium pyrosulfate.[2] Under present conditions considerable difficulty and uncertainty are experienced in the decomposition of these ores.

While fusion with alkali pyrosulfate seems to be more generally applicable a number of other methods are described, among which are fusion with a mixture of the pyrosulfate and alkali fluoride,[3] with alkali,[4] with alkali peroxide[5] and with alkali carbonate.[6]

Of those methods using pyrosulfate, Washington,[7] in his determination of iron and titanium, recommends the use of fifteen to thirty parts of the flux to one of ore. The melt is treated with 10 cc. of sulfuric acid and 150 cc. of water. The solution is filtered, the silica driven off and any residue fused a second time with the pyrosulfate. Browning[8] states that the mineral is fused with six parts of bisulfate and the cooled mass extracted with water. Ullman and Boyer[9] calcine limestone containing titanium below the point of vitrification, mix it with pyrosulfate and fuse the mixture for an hour with a slow evolution of sulfur trioxide. No mention is made of the proportion of pyrosulfate used. Winch and Chand-Ratreya[10] use ten parts of bisulfate. Pampfil[11] heats a mixture of ferric and titanic oxides with fifteen parts of bisulfate, at first gently and then intensely, until it becomes a dark red. Marden[12] uses from ten to twelve parts of bisulfate in his treatment of ore and slag but mentions the possibility of three fusions before securing complete decomposition. He recommends fusion at a dull red heat for one hour. Faber[13] goes a little more deeply into the reactions concerned and shows that a basic sulfate ($TiOSO_4$) is formed in addition to the normal sulfate. He states that two to three hours are necessary to dissolve the melt in sulfuric acid (d., 1.10–1.12) and thirty-six hours in water. It is evident, therefore, that little attention has been given to the effect of time, temperature or the ratio of flux to ore on the decomposition of titanium ores by means of the pyrosulfate fusion.

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[2] Since the potassium salt is usually employed and in some ways is considered more desirable for general analytical purposes, a few decompositions were carried out with potassium pyrosulfate for comparison.

[3] Ball and Smith, THIS JOURNAL, **36**, 1838 (1914). Baskerville, *J. Soc. Chem. Ind.*, **19**, 419 (1900).

[4] Knecht, *Z. angew. Chem.*, **26**, 734 (1913).

[5] Walton, THIS JOURNAL, **29**, 481 (1907). Neumann and Murphy, *Z. angew. Chem.*, **26**, 613 (1913).

[6] Newton, *Am. J. Sci.*, **25**, 343 (1908). Barnebey and Isham, THIS JOURNAL, **32**, 957 (1910).

[7] Washington, "Chemical Analysis of Rocks," John Wiley and Sons, Inc., first ed., **1904**, p. 107. The directions are somewhat less definite in the third edition, p. 159 (1919).

[8] Browning, "Introduction to the Rarer Elements," third ed., p. 102.

[9] Ullman and Boyer, *Chem. Eng.*, **10**, 163 (1910).

[10] Winch and Chand-Ratreya, *Chem. News*, **124**, 231 (1922).

[11] Pampfil, *Mon. Sci.*, **24**, 643 (1911); *C. A.*, **5**, 1720 (1911).

[12] Marden, Bur. Mines, *Bull.*, **212**, 284 (1923).

[13] Faber, *Chem.-Ztg.*, **31**, 263 (1907); *C. A.*, **1**, 1528 (1907).

Experimental Part

While the greater part of the work done in connection with this paper has to do with rutile, some investigation was made of titanite, columbite and tantalite. All fusions were made in platinum with sodium pyrosulfate on ore ground to about 150 mesh. The rutile used was a high grade commercial product containing small amounts of iron and silica. The sodium pyrosulfate used was prepared by fusing the C. P. crystallized sodium bisulfate of commerce.

In a number of the earlier experiments the temperature was raised as rapidly as possible and the progress of decomposition followed by noting the fine particles of ore floating on top of the mass. Although the proportion of flux in these first experiments was varied and gradually increased to eleven times that of the ore, complete decomposition could not be obtained, but in several cases after prolonged heating the proportion of ore seemed to increase and spread out over the surface as a gray, metallic-looking film. The substitution of a Meker burner to increase the temperature resulted only in the formation of the gray film in a shorter time.

Two possible explanations for the appearance of the gray film presented themselves, namely, lack of sufficient flux for holding the titanium sulfate in solution, and the decomposition of the titanium sulfate by the high temperature. In order to eliminate as far as possible the effect of temperature and decompose as little flux as possible, a series of fusions was made in which the temperature was kept just high enough to keep the mass liquid. The ratio of flux to ore was varied somewhat but not increased beyond that of the previous experiments. In all cases, however, the gray film appeared before all the dark particles of ore were decomposed. It seemed evident, therefore, that a ratio greater than eleven parts of sodium pyrosulfate to one of ore would be necessary to effect a complete decomposition.

During the course of the fusions so far discussed a rather distinct change of color was apparent when the dirty green mass began to change to a clear red. While the time of heating before this color appeared varied from ten minutes to half an hour, the time from this change until the appearance of the gray film was fairly constant for a given ratio of flux to ore. In Table I are listed a number of experiments in which the time of heating after this color change is recorded. In all these experiments the cooled melt was treated with 100 cc. of water and the mixture allowed to stand usually overnight, although disintegration was complete in about three hours. The solution was then filtered and the residue washed free from titanium (absence of color with hydrogen peroxide) with hot 6 *N* hydrochloric acid[14]

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[14] Hot 6 *N* hydrochloric acid was found to be most satisfactory for washing the residue undissolved by cold water. Both sulfuric and nitric acids of various concentrations were tried.

ignited, fused again with pyrosulfate and tested for titanium with hydrogen peroxide. In all cases in which the gray film appeared during fusion a positive test for titanium was obtained in the residue. While no attempt was made to determine the exact nature of this, it was probably the basic sulfate ($TiOSO_4$) mentioned by Faber[13] although it may have contained a smaller concentration of sulfate, since he states that this basic sulfate is soluble in an excess of sulfuric acid.

Table I

Fusion Data

One gram of ore was taken for each fusion

Result: A = gray film on melt; basic sulfate formed. B = clear yellow; decomposition complete.

	A	B	B	A	A	A	A	B	B	A	B	B	B	B	B	A	A	A	A	A	B	A	A
$Na_2S_2O_7$, g.	11	14	14	14	14	14	14	16	16	16	16	16	16	18	18	18	23	23	23	23	14[a]	18[a]	18[a]
Time, min.	20	20	22	25	30	27	25	21	25	29	27	18	21	18	18	34	11	..	53	53	15	29	32
Excess of $Na_2S_2O_7$, g.	..	..	..	..	3.9	..	..	..	..	..	4.8	7.8	5.8	..	..	..	11.2	5.4	5.9	..	5.8	4.7	..

[a] These experiments differed from the others in that the heating was more rapid and the evolution of sulfur trioxide was more vigorous. They are represented by solid circles in Figs. 1 and 2.

In several of the fusions the time of heating was purposely carried beyond the point of complete decomposition. Some of these fusions were stopped before the appearance of the gray film and some as soon as it was noticed. By plotting the ratio of flux to ore against the time of fusion (shown in Fig. 1) and connecting the points representing the appearance of the gray film, also those representing the shortest time necessary for a complete decomposition, the effect of time and ratio is brought out more clearly. The point of intersection of the two curves represents the minimum ratio of sodium pyrosulfate necessary for a complete decomposition of rutile, and the area between the two curves shows the range over which a complete decomposition may be secured when the temperature is maintained just high enough to keep the mass liquid. At this temperature there is a slow evolution of sulfur trioxide. According to the equation, $TiO_2 + 2Na_2S_2O_7 \longrightarrow Ti(SO_4)_2 + 2Na_2SO_4$, 5.5 g. of sodium pyrosulfate is required for the decomposition of 1 g. of titanium dioxide. The point of intersection of the two curves shows that approximately 12.5 g. is necessary for complete decomposition, an amount more than double that necessary for the reaction. While a portion of this is decomposed into sodium sulfate and sulfur trioxide the remainder, about 3.5 g. as will be shown later, must be required either as solvent for the titanic sulfate or as a means of lowering the temperature of the melt.

In a number of the fusions noted in Table I, a portion of the original of solution of the melt was titrated with standard alkali from which the excess pyrosulfate given in Row three was calculated. By plotting this value against the original ratio and, as before, connecting the points representing those in which the decomposition was just complete as well as those in which the gray film appeared, the amount of unnecessary flux is shown by the distance between the two curves (Fig. 2). By extending the curves to their point of intersection the minimum ratio necessary for complete decomposition is obtained. This agrees well with the ratio-time curve, Fig. 1.

In order to determine the effect of more rapid heating, three experiments represented by solid circles in both Figs. 1 and 2 were carried out in which the temperature was increased more rapidly, as evidenced by a more rapid evolution of sulfur trioxide. As was to be expected, these points fall to the left of the original curve in Fig. 1, showing that complete decomposition as well as formation of the basic sulfate is obtained in a shorter time. The final result, however, is unchanged as is shown by these points in Fig. 2.

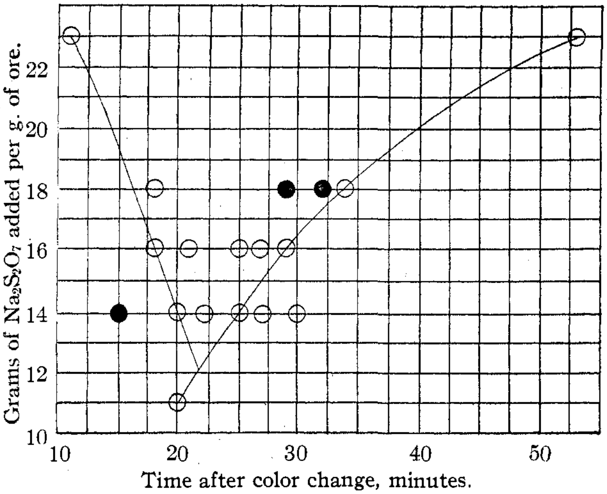

Fig. 1.—The heavy circles represent samples to which CaO was added; the solid circles represent fusions in which the temperature was raised more rapidly, as evidenced by a more vigorous evolution of SO_3.

It will be noted from Curve B, Fig. 2, that an increasing amount of sodium pyrosulfate in the fused mixture is necessary with increasing initial ratio. Since the higher ratios required a much longer time of heating before the appearance of the gray film, a proportionally greater amount of flux would be decomposed, and hence a greater amount of sodium sulfate would be present in the melt. This might act either to reduce the solubility of titanium sulfate in the flux or to produce a higher temperature. Since melting-point curves could not be found that would throw any light on the possible effect on temperature, it was decided to attack the problem from another angle.

So far, all experiments had been carried out with rutile. If the decomposition of the ore is dependent only on the proportion of flux, it should be possible to decompose other ores of titanium by application of the rules found to hold with the rutile. Accordingly, a number of samples of titanite ($CaTiSiO_5$) were fused with the pyrosulfate, in ratios ranging from 14 to 18, and for times that would fall between those indicated in the two curves in Fig. 1. While none of these resulted in complete decomposition of the ore they showed that a much higher temperature was necessary to keep the mass liquid and indicated that the formation of the basic sulfate was caused not so much by the lack of flux as by the high temperature. In view of this, a series of fusions was made in which various proportions of lime were added to rutile in an attempt to find the effect of the calcium as well as to determine the temperature at which the normal titanium sulfate begins to decompose. The results of these experiments are listed in Table II and shown as heavy circles in Fig. 2. The time of heating ranged from 20 to 25 minutes after the color changed. The temperature

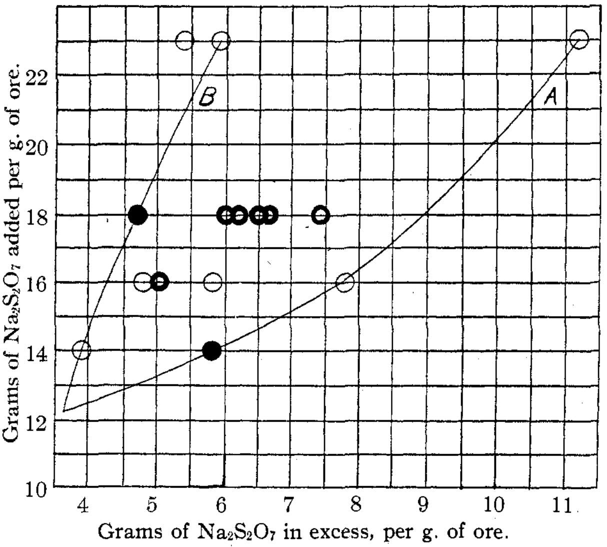

Fig. 2.—The heavy circles represent samples to which CaO was added; the solid circles represent fusions in which the temperature was raised more rapidly, as evidenced by a more vigorous evolution of SO_3.

was measured with a platinum-nichrome thermocouple protected with Pyrex glass tubing and calibrated against the melting points of tin, zinc, antimony, and sodium chloride.

TABLE II

FUSION DATA

One gram of ore was taken for each fusion

Wt. of CaO G.	Wt. of $Na_2S_2O_7$ G.	Temp. °C.	Composition of the melt—2.99 g. of $Ti(SO_4)_2$			Result
			$Na_2S_2O_7$ G.	Na_2SO_4 G.	$CaSO_4$ G.	
None	14	700	...	...	..	Basic sulfate formed
None	16	680	5.8	6.5	None	Decomposition complete
0.05	18	695	6.2	7.2	0.12	Basic sulfate formed
.10	18	710	7.4	6.5	.24	Basic sulfate formed
.10	18	725	6.5	7.2	.24	Basic sulfate formed
.15	18	760	6.0	7.7	.24	Basic sulfate formed
None	23	700	...	...	...	Basic sulfate formed
.05	16	...	5.0	7.1	.12	Basic sulfate formed
.15	18	...	6.6	7.3	.36	Basic sulfate formed

The result of these experiments shows that titanium sulfate even in the presence of an excess of solvent is unstable at the higher temperatures. Some work which was being done with tantalite and columbite involving this principle indicated that this is not peculiar to titanium but is perhaps a general characteristic of the less basic of the rarer metals.

The decomposition temperature of titanium sulfate is shown to be approximately 700°. In order to secure a satisfactory fusion of titanium ores with sodium pyrosulfate, therefore, sufficient of the low-melting pyrosulfate must be present in the melt to keep the temperature below that point. A comparison of the composition of the melts with their temperatures as shown in Table II indicates that the effect of the sodium pyrosulfate on the temperature is about 2.5 times that of sodium sulfate and 0.09 that of calcium sulfate, the pyrosulfate tending to lower the temperature while the other two raise it. From this it is evident that a much higher proportion of sodium pyrosulfate would be necessary for the decomposition of titanite than would be effective for rutile. Assuming that $CaTiSiO_5$ represents the approximate composition of titanite and calculating on the basis of the above figures, it was estimated that from 30 to 33 parts of the pyrosulfate should be sufficient for complete decomposition of the ore and for holding the temperature below the decomposition point of titanium sulfate. Accordingly, a sample of titanite was mixed with 32 parts of sodium pyrosulfate and the fusion carried out as before. Twenty-two minutes after the color changed, the temperature registered 695°. At this point the flame was removed; the cooled melt, treated in the usual manner, showed complete decomposition. A second sample was fused with 37 parts of the pyrosulfate until the temperature registered 700°, when the flame was removed. On removing the cooled melt from the crucible (this is easily done by gently tapping the crucible) dark specks were noticed along one edge of the bottom of the melt. Closer examination showed them only in the surface next to the crucible, the interior and other side of the melt being entirely free from them. On breaking the melt, dissolving the part containing the dark particles separately from the rest and testing the residue, insoluble titanium was found in the portion containing these particles but not in the other portion. Apparently the basic sulfate was just beginning to form in the hotter portion of the crucible when the flame was removed. There can be little doubt, therefore, that titanic sulfate formed by fusion of titanium material with sodium pyrosulfate is decomposed into an insoluble form if the temperature reaches 700° or higher.

In view of the fact that the potassium salt is usually employed for pyrosulfate fusions, a number of experiments were carried out using 11, 12, 13 and 14 parts of potassium pyrosulfate. Complete decomposition was obtained only in those cases in which 14 parts of the flux were used. This is a somewhat higher ratio than was found for the sodium salt. It would seem, therefore, that the smaller tendency of the potassium pyrosulfate to volatilize is more than offset by the higher-melting potassium sulfate formed. Both the reaction and the disintegration of the cooled melt were markedly slower than when the sodium salt was used.

It is very probable, therefore, that the unsatisfactory conditions which have been connected with the decomposition of titanium material by means of alkali pyrosulfate fusion have been caused by this tendency of the normal titanium sulfate to decompose into an insoluble basic sulfate when the temperature happened to rise too high.

Summary and Conclusion

A critical study of the fusion of titanium ores with sodium pyrosulfate has been made, which has led to the following conclusions.

1. At least 12.5 parts of sodium pyrosulfate to one of ore must be used to secure complete decomposition of the ore and solubility of the titanium content. A higher ratio is more desirable and necessary for ores containing appreciable proportions of other elements having high-melting sulfates.
2. Sodium pyrosulfate is somewhat more efficient than potassium pyrosulfate both in the amount required and in the time consumed.
3. The normal titanium sulfate formed by the fusion is decomposed if the temperature is allowed to reach 700° or higher. Sufficient flux must therefore be used to insure a lower fusion temperature than 700°.
4. The decomposition of the normal sulfate is not characteristic of titanium alone but is probably common to all the less basic metals of Division A in Groups 4 to 7 of the Mendeléeff table.

RENO, NEVADA