tures up to 100° failed to give any new materials, the unchanged reactants always being recoverable.

Reaction of Fluorine Fluorosulfonate with Iodine.—Fluorine fluorosulfonate was admitted to a bulb containing iodine at room temperature. Reaction occurred immediately with the evolution of heat and the production of a black liquid. Further addition of the hypofluorite caused the liquid to become green, then yellow and finally very light yellow, almost colorless. The volatile material was removed by distillation and was found to contain fluorine fluorosulfonate and peroxydisulfuryl difluoride which were identified by molecular weight determinations after separation by distillation at Dry Ice temperature.

The non-volatile liquid residue amounted to 2.4392 g. from 0.8157 g. of iodine, which was 99.36% of the calculated 2.4548 g. of product for the composition $IF_3(SO_3F)_2$. This composition was established by analysis after long digestion with aqueous base. Aliquots for sulfur and fluorine were reduced with hydrazine to destroy the iodate prior to precipitation of barium sulfate; aliquots for iodine were reduced with sodium bisulfite prior to the Volhard determination. Calcd. for $IF_3(SO_3F)_2$: I, 33.2; S, 16.8. Found: I, 33.4, 33.2; S, 16.3, 16.2. From these data it is clear that the preparation reaction must have followed the equation

$$I_2 + 6SO_3F_2 \longrightarrow 2IF_3(SO_3F)_2 + S_2O_6F_2$$

Properties of Iodine Trifluoride Bisfluorosulfonate.—The pentavalent nature of the iodine in $IF_3(SO_3F_2)$ was established by hydrolysis of the compound. Reaction with water was violent and rapid producing iodate but only traces of iodine. Iodometric titration showed 5.88 and 5.90 oxidizing equivalents per mole. Titration of the hydrolysis solution after 3 days' digestion showed 10.51 and 10.48 (theory = 10.0) equivalents of acid per mole of original compound. These slightly high values are the result, at least in part, of action of the hot base on glass during the long digestion and the absorption of carbon dioxide. Hydrolysis evidently proceeds according to the equation

$$IF_3(SO_3F)_2 + 3H_2O \longrightarrow HIO_3 + 3HF + 2HSO_3F$$

with subsequent further hydrolysis of the HSO_3F.

The density of the $IF_3(SO_3F)_2$ was determined in a graduated straight tube 3 mm. in diameter which had been calibrated with water and mercury. At 25°, $IF_3(SO_3F)_2$ has a density of 2.63 g./ml. The nuclear magnetic resonance spectrum of $IF_3(SO_3F)_2$ showed two fluorine peaks with a separation of 31.8 p.p.m. The peak caused by SO_3F groups was quite sharp; that due to the other three fluorine atoms came at a higher field strength and was very broad. This clearly established the existence of two different environments for the fluorine atoms in the molecule. Areas under the curves, however, differed from the expected ratio of 3:2, approaching 4.5:2. The cause of this discrepancy was not apparent but in view of the synthetic and analytical data, it was considered not to constitute proof of a ratio truly different from 3:2. The simple nature of the n.m.r. spectrum indicated the sample to be a single substance rather than a mixture.

Attempts to crystallize the compound yielded only a glass; the freezing point is therefore unknown.

The measurement of the temperature dependence of vapor pressure was attempted but slow decomposition, becoming appreciable at 35 cm. and 123°, made accurate measurements impossible. Extrapolation from the data obtained, however, indicated a boiling point in the vicinity of 150°.

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Reactions of Solid Alkaline Earth Oxides. II.[1] CaO and MgO

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The reactions of salts of oxy-acids with CaO and MgO are re-examined. The supposed phenomenological similarity of the CaO reactions with those of BaO and SrO is not borne out by the data. The thesis that the "reactivity" is a function only of the oxide and the associated "reaction temperature" concept are shown to be invalid.

The reactions of BaO, SrO, CaO and MgO with salts of oxy-acids have been the subject of extensive investigation and speculation in the past, the results of which are recorded in most modern references on solid state chemistry.[2-5] The unusual rate behavior reported for these reactions is the subject of this series of communications.

According to Hedvall and co-workers,[2,6] the alkaline earth oxides begin to react rapidly with salts of oxy-acids at a temperature characteristic of the oxide only (see, for example, Table II, ref. 5). Furthermore, it was postulated that in each case the reaction occurs in the solid state.[2,7,8]

It was shown[1] previously that for BaO and SrO, the reaction phenomenon observed by Hedvall is due to the appearance of a liquid phase. At the so-called "reaction temperature," a barium (or strontium) hydroxide-containing eutectic melts and the reaction proceeds *via* this liquid phase. In these terms, the sudden "triggering-off" of the reaction at a temperature independent of the salt component and the substantial completion of reaction in a matter of seconds is readily understood.

The appearance of a liquid phase, however, cannot account for the behavior of CaO and MgO since the hydroxides of Ca and Mg decompose below the "reaction temperature." Indeed, this fact was used by Hedvall and co-workers to counter the criticism of contemporaries[9] who originally proposed that the reactivity of BaO and SrO is due to a hydroxide melt. The argument that Hedvall[2] and Jagitsch[10] present is as cited:

> In the case of CaO, the constancy of the "reaction temperature" cannot be due to the formation of a liquid phase. The reaction phenomenon is substantially the same for CaO as for BaO and SrO and a single explanation is required. Therefore, the behavior of BaO and SrO cannot be explained in terms of the formation of a liquid phase.

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(1) For part I, see H. J. Borchardt and B. A. Thompson, THIS JOURNAL, **81**, 4182 (1959).

(2) J. A. Hedvall, "Einfuhrung in die Festkorperchemie," Fr. Vieweg and Sons, Verlag, Braunschweig, 1952.

(3) K. Hauffe, "Reaktionen in und an Festen Stoffen," Springer Verlag, Berlin.

(4) W. E. Garner, "Chemistry of the Solid State," Butterworth Publishing Co., London, 1955.

(5) G. Cohen, *Chem. Revs.*, **42**, 527 (1948).

(6) J. A. Hedvall and J. Heuberger, *Z. anorg. Chem.*, **122**, 181 (1922); **128**, 1 (1923); **140**, 243 (1924).

(7) J. A. Hedvall, *ibid.*, **162**, 110 (1927).

(8) G. Tammann, *ibid.*, **160**, 101 (1927).

(9) D. Balarew, *ibid.*, **160**, 92 (1927).

(10) R. Jagitsch, *Arkiv Kemi, Mineral. Geol.*, **15A**, 1 (1942).

The reactions of CaO and MgO have been reexamined in order to clarify the seeming contradiction that our previous findings and the above argument present as well as to learn the cause for the anomalous rate behavior reported by Hedvall and co-workers.

The "reaction temperature" reported for CaO is approximately 530°.[2] This number is the average of several observed "reaction temperatures" of calcium oxide with carbonates, sulfates, phosphates and silicates. The specific data for the carbonate and sulfate reactions are[2]: $MgCO_3$, 525°; $MgSO_4$, 540°; $ZnSO_4$, 520°; $CuSO_4$, 515°. For MgO, "reaction temperatures" are not reported by Hedvall since well-defined temperatures could not be measured. This difficulty is attributed to the small heat effect associated with the reactions of MgO. Jagitsch, however, has calculated that the "reaction temperature" of MgO should be approximately 570°.[10]

Recently, a group of Russian investigators have reëxamined some of the reactions of CaO and MgO.[11] One of their techniques consisted of placing pellets of the reactants in close proximity of one another but avoiding direct contact. The fact that the products were observed to form under these conditions at temperatures very close to Hedvall's "reaction temperatures" clearly shows that a gas phase mechanism cannot be ruled out, contrary to the statements of Hedvall[7] and Tammann.[8] However, the claim that the cited experiments prove Hedvall's interpretation to be erroneous is also subject to criticism.[12]

In the present work, the following reactions were studied: $CaO + MgCO_3$, $CaO + CuSO_4$, $CaO + ZnSO_4$, $CaO + MgSO_4$, $MgO + CuSO_4$ and $MgO + ZnSO_4$.

Experimental

Measurements were performed to reproduce Hedvall's observations using differential thermal analysis (d.t.a.), a refinement of the method of the thermal analysis which was used in the original work. The experimental procedures were essentially the same as before.[1] Pertinent data on the material are

Material	Preparation or source	Particle size, μ
CaO	Decompn. of Fisher reagent grade $CaCO_3$ at 800°	8.6
MgO	Matheson reagent grade	0.5
$MgCO_3$	California Magnesite, Wards Natural Science Establishment	7.4
$CuSO_4$	Decompn. of Baker reagent grade $CuSO_4 \cdot 5H_2O$ at 400°	4.5
$ZnSO_4$	Decompn. of Mallinckrodt reagent grade $ZnSO_4 \cdot 7H_2O$ at 450°	11.5
$MgSO_4$	Decompn. of Fisher reagent grade $MgSO_4 \cdot 7H_2O$ at 450°	5.3

The average particle size was measured with a Fisher sub-sieve sizer. The reactants were mixed by grinding them together with a mortar and pestle.

Results

The DTA patterns for the several reactions are shown in Fig. 1 and are discussed below:

$CaO + MgCO_3$.—The d.t.a. pattern shows the decomposition of $MgCO_3$ in the temperature range 500–700°. That a small quantity of $CaCO_3$ is formed is indicated by the slight endotherm between 800–900° where $CaCO_3$ decomposes. Several attempts to make the reaction proceed as described by Hedvall (such as using freshly formed CaO, a large excess of CaO, etc.) did not alter the situation. The decomposition endotherm of $MgCO_3$ appeared each time. These observations are consistent with those of Webb and Van der Walt.[13] $CaCO_3$ will, of course, be produced in quantity if marked changes in the experimental conditions are made (such as working in a closed system where CO_2 cannot escape). For the present purposes, however, it is sufficient to show that CaO does not react extensively when the same procedures are followed as in the cases of BaO and SrO. It is interesting to note that the $MgCO_3$ decomposition endotherm is observed to initiate at approximately 25° *below* the "reaction temperature" for "solid state" reaction between CaO and $MgCO_3$.

$CaO + CuSO_4$.—The d.t.a. pattern exhibits a double exotherm which begins at approximately 500° and extends almost to 800°. This observation is at least in approximate agreement with the data of Hedvall. Since $CuSO_4$ decomposes in two stages,[14] it is entirely possible that decomposition of $CuSO_4$ is rate limiting and that the reaction proceeds *via* the gaseous phase.

$CaO + MgSO_4$.—For this curve, it is virtually impossible to assign a "reaction temperature" of any sort. That the reaction under present conditions occurs primarily in the temperature range 800–950° was learned indirectly. The material heated to 800° in the d.t.a. apparatus was subjected to X-ray analysis. It was found that no detectable amount of product had formed. At 1000°, however, only $CaSO_4$ and MgO were present. A weight–temperature trace of $MgSO_4$ shows that decomposition of salt (weight-loss) is readily detectable at 960°. Thus, a gas phase reaction is possible in this case also.

It was pointed out[12] previously that the dissociation pressure of $MgSO_4$ is much too low at 540° (Hedvall's reaction temperature) to allow a gas phase reaction to occur which can be detected by conventional thermal or differential thermal methods. Thus, the reaction that Hedvall observed at this temperature was probably a solid state reaction. However, we have been unable to duplicate this result.

$MgO + CuSO_4$.—The exotherm in this case appears at about 450° and extends to above 600°. Of the reactions studied, this is the least likely to be proceeding by a gas phase mechanism. The initial reaction rate at 490° is approximately 1% conversion per minute.[15] The dissociation pressure of $CuSO_4$ at 490° is only 1.3×10^{-6} atmosphere. Although a gas phase reaction is in principle possible,[12] this case is distinctly in the borderline category. If the reaction $CaO + CuSO_4$ were considered to be proceeding by a vaporiza-

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(11) M. E. Pozin, A. M. Ginstling and V. V. Pechkovsky, *J. Appl. Chem. USSR*, **27**, 273, 376 (1954).

(12) H. J. Borchardt, This Journal, **81**, 1529 (1959).

(13) T. L. Webb and T. Van der Walt, *Nature*, **181**, 411 (1958).

(14) H. J. Borchardt and F. Daniels, *J. Phys. Chem.*, **61**, 917 (1957), Fig. 1.

(15) H. J. Borchardt, *J. Inorg. Nuclear Chem.*, in pres (1959).

tion mechanism with the dissociation of $CuSO_4$ as the rate-limiting step, then the present reaction is not proceeding by this mechanism as evidenced by the marked differences in the d.t.a. patterns.

$CaO + ZnSO_4$.—An exotherm begins at approximately 600°, is interrupted by an endotherm at approximately 745°, then continues to 850°. The pattern can be better understood when compared to that of $ZnSO_4$ alone. It is seen that $ZnSO_4$ alone, after partial decomposition, exhibits the same endotherm. This endotherm has been reported to be a result of a phase transition in $ZnSO_4$.[16] A comparison of the patterns shows that the first evidence of reaction appears at approximately the same temperature as that at which decomposition of $ZnSO_4$ is first detected.

$MgO + ZnSO_4$.—The pattern of this mixture does not exhibit a well-defined peak. That reaction occurs is evidenced by the fact that $ZnSO_4$ is no longer present at the higher temperature to undergo the phase transformation at 745°. This is confirmed by X-ray analysis which shows that the final material is $MgSO_4$ and ZnO.

Discussion

Three conclusions may be drawn from the data:

1. The possibility of gas phase step cannot be ruled out for most of the reactions in question. This is in partial agreement with the findings of Pozin, *et al.*[11]

2. The phenomenology of the CaO reactions is distinctly different from that of the BaO and SrO reactions, hence the thesis of Hedvall[2] and Jagitsch,[10] cited above, is ill-founded. The d.t.a. traces of the reactions of BaO and SrO all exhibit a distinct discontinuity (see Fig. 1 and ref. 1). ΔT, which is essentially zero below the "reaction temperature," suddenly rises to a large value at this point, in a time interval of approximately one second. This behavior, indicative of a discontinuity in reaction rate and understandable in terms of the formation of a liquid phase, is not observed with any of the reactions of CaO. The present curves all change slope gradually defying, to some extent, the assignment of a "reaction temperature."

3. The postulate that the "reactivity" of the CaO–salt mixtures is a function only of the oxide and independent of the salt is not borne out by these data. The temperature ranges over which reaction is observed to occur vary widely with the various salts. The least that can be concluded is that the effect Hedvall reported is not readily reproducible; that some condition is required which was not explicitly specified and which was not met in the present work. Although this is possible, it seems highly unlikely. It is more probable that the relatively insensitive thermal analysis measurement gave the illusion of similarities. This illusion disappears when the more sensitive differential thermal method is applied.

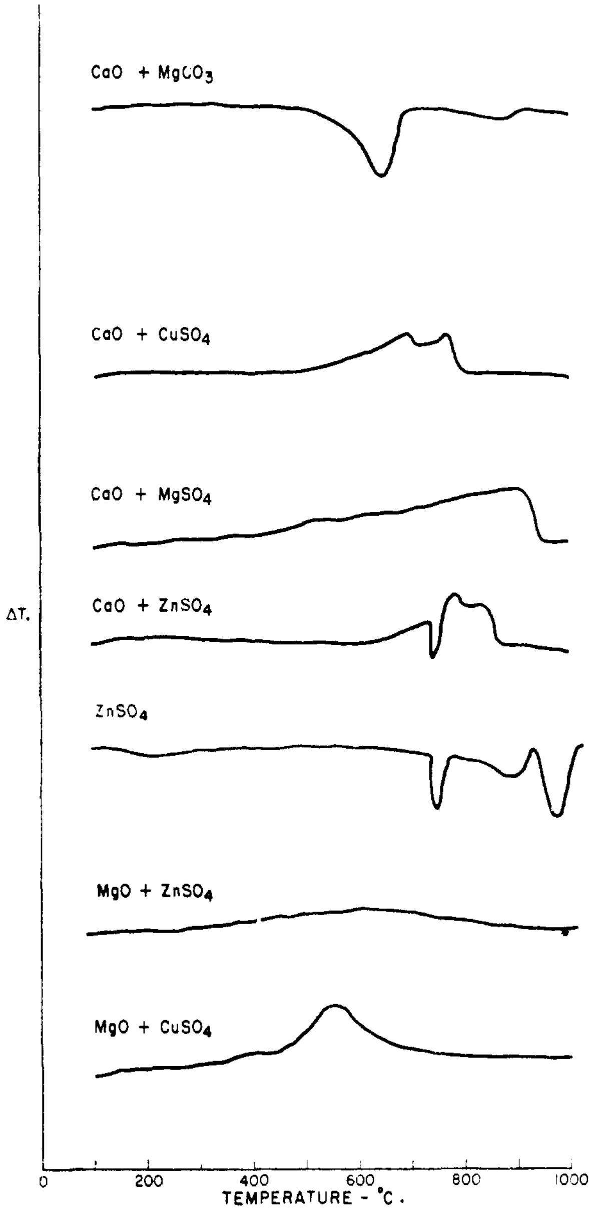

Fig. 1.—D.t.a. patterns of materials indicated.

It is concluded on the basis of this and the previous work[1] that the theory of Hedvall regarding the behavior of alkaline earth oxides with salts of oxy-acids is invalid. The consistencies in the observations with BaO and SrO probably are due to coincidence. With CaO and MgO, there are no anomalous consistencies.

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(16) R. M. Gruver, *J. Am. Ceram. Soc.*, **34**, 353 (1951).