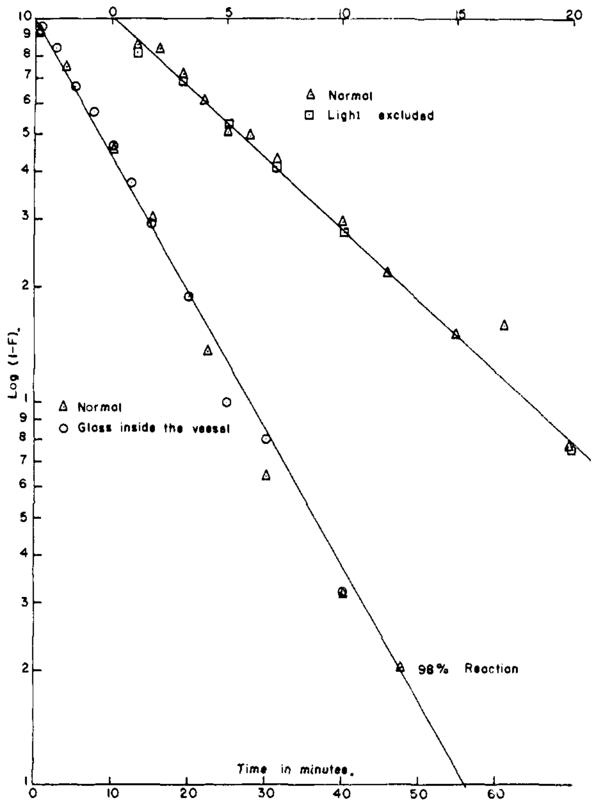

Fig. 1.—Logarithms of the fractions unexchanged *versus* time in minutes.

values for pure water, measured by Rona.[3] It is seen that the great increase in rate at the high alcohol concentrations, found previously,[1] can be correlated with the decrease in the activation energy. The shape of the curve activation energy *versus* alcohol concentration is rather similar to that found for the conductivity of UO_2Cl_2 in the water-alcohol system.[4] Figure 1 shows that under the conditions used in this investigation there are no detectable wall or light effects, so that the orders close to zero, found previously,[1] must be interpreted otherwise.

A comparison of the activation entropies for this reaction under different conditions seems impossible due to the fact that the over-all orders in water and in the various mixtures (30, 60, 90, 100% ethanol) are, respectively, 0.0, 0.3, 0.98, 1.93, 1.44.[1,3] A change in the concentration units would alter not only the absolute values of ΔS^* but also their comparative magnitude.

TABLE II

ACTIVATION ENERGY OF THE REACTION U(IV) → U(VI) AS A FUNCTION OF THE ALCOHOL CONCENTRATION

Alcohol concn., vol. %	*A*	*B*	ΔE, kcal.
0	...	..	33.4[a]
30	16.21	6032	27.6
60	15.32	5741	26.3
90	12.07	5047	23.1
98	6.41	3141	14.4

[a] From Rona, see ref. 3.

This reaction is not a simple one and hydrolysis equilibria probably are involved, as it seems proven by the influence of the hydrogen ion concentration. The measured activation energy itself is therefore not a simple quantity but could involve the energetic parameters related to the hydrolysis processes. However, the magnitude of the change is so great that it strongly suggests that non-electrostatic and specific phenomena prevail in determining the change in rate due to the change in the solvent composition. The electrostatic part of the activation energy is in fact usually of the order of 5–6 kcal.[5] The study of this reaction in other solvent systems could be therefore of a certain interest.

The authors wish to thank the Atomic Energy Commission for the financial support of this investigation.

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(4) N. Goldenberg and E. S. Amis, Presented before the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(5) E. S. Amis, "Kinetics of Chemical Change in Solution," the Macmillan Co., New York, N. Y., 1949, p. 106.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE GENERAL ENGINEERING LABORATORY, GENERAL ELECTRIC COMPANY]

Reactions of Solid Alkaline Earth Oxides. I. BaO and SrO[1]

BY HANS J. BORCHARDT AND BARBARA A. THOMPSON

RECEIVED MARCH 13, 1959

The "solid state" reactions whereby BaO and SrO react with salts of oxyacids to yield the reciprocal pairs are re-examined. The generally held view that the reactions proceed by solid state diffusion processes is shown to be incorrect. The reactions only occur in the manner described by Hedvall[2] when impurities originating from the atmosphere (H_2O, CO_2) are present. The rate behavior can be understood readily in terms of the formation of a liquid phase.

The study of the reactions of solid alkaline earth oxides represents one of the more prominent chapters of classical solid state chemistry. The work originated with Hedvall and Heuberger[2] in 1922 and was followed by a decade of intense investigation which involved the laboratories of Tammann, Jander and other European scientists. Details on the results of these studies can be found in most modern references[3–6] on solid state chemistry. Hed-

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(1) Presented in part at the 135th National Meeting of the American Chemical Society, Boston, Massachusetts, April, 1959.

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

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

vall[3] presents a particularly thorough treatment.

A singularly unusual finding of Hedvall and Heuberger[2] was that the alkaline earth oxides begin to react rapidly with a large number of other solids at a temperature characteristic of the oxide. This is illustrated in Table I where the "reaction temperatures" of BaO and SrO with various carbonates and sulfates are listed. It is seen that a "characteristic reaction temperature" of approximately 350° may be associated with BaO; 450° with SrO.

TABLE I

REACTION TEMPERATURES OF EXCHANGE REACTIONS BETWEEN ALKALINE EARTH OXIDES AND SALTS OF OXYGEN-CONTAINING ACIDS[6]

Salt component	Reaction temp. with BaO, °C.	Reaction products	Reaction temp. with SrO, °C.	Reaction products
Carbonates				
$SrCO_3$	395	$BaCO_3 + SrO$		
$CaCO_3$	345	$BaCO_3 + CaO$	465	$SrCO_3 + CaO$
$MgCO_3$	345	$BaCO_3 + MgO$	455	$SrCO_3 + MgO$
Sulfates				
$SrSO_4$	370	$BaSO_4 + SrO$		
$CaSO_4$	370	$BaSO_4 + CaO$	450	$SrSO_4 + CaO$
$MgSO_4$	370	$BaSO_4 + MgO$	440	$SrSO_4 + MgO$
$ZnSO_4$	340	$BaSO_4 + ZnO$	425	$SrSO_4 + ZnO$
$CuSO_4$	345	$BaSO_4 + CuO$	420	$SrSO_4 + CuO$

Various explanations for this phenomenon have been offered. Fischbeck[7] suggested that the "reaction temperatures" are analogous to "self-ignition temperatures," namely, that at a particular temperature the rate of heat evolution due to reaction exceeds the rate of heat dissipation which leads to a catastrophic temperature rise and very rapid reaction at a fairly well-defined initial temperature. Hedvall[3] rejected this postulate since ignition temperatures should be dependent on such quantities as heat capacity, rate of temperature rise, etc., and the "reaction temperatures" are independent of these variables.

Balarew[8] pointed out that BaO and SrO react readily with atmospheric moisture and CO_2 and that Hedvall probably was not working with the pure oxides. He suggested that the "reaction temperatures" correspond to the melting points of alkaline earth hydroxide–carbonate eutectics and that the reaction proceeds *via* the liquid phase, *i.e.*, the reactants dissolve in the melt and the products precipitate out. This postulate was vigorously rejected both by Hedvall[9] and Tammann[10] for various indirect reasons.

Hedvall[3] postulated that the reactions proceed by solid state diffusion processes and that the "reaction temperature" corresponds to the knee in the exponential rate constant temperature curve. This was expanded upon by Jagitsch[11] who rationalized the lack of dependence of the "reaction temperatures" on the reactant salt by assuming that solid state diffusion of some species from the alkaline earth oxide is rate limiting. Further credence was lent to this postulate by the finding that at the "reaction temperature," each of the alkaline earth oxides has the same electrical conductivity ($\sim 10^{-9}$ ohm^{-1} cm.$^{-1}$). In addition, the ratio of "reaction temperature" to melting point (in degrees Kelvin) was found to be virtually the same constant for each oxide, namely, 0.28.

Since the work of Jagitsch[11] in 1942, no detailed study of these reactions has been made and the unusual rate behavior still remains as a somewhat obscure subject, although recent references[3–6] seem to favor the solid state diffusion mechanism. As part of an effort to re-assess our present state of knowledge of the reactivity of solids, it was considered appropriate that this subject be reexamined.

Measurements first were performed to reproduce the phenomenon reported by Hedvall. The latter made use of heating curves (thermal analysis) to detect the occurrence of a reaction. In the present work, differential thermal analysis is utilized for this purpose. The DTA curves, shown in Fig. 1, were obtained under the conditions described below.

An R. L. Stone Company DTA apparatus was utilized, the measurements being made in air with a rate of temperature rise of 15°/min. The preparation and/or source of these materials were: BaO, decomposition of Baker reagent grade BaO_2 at 900° *in vacuo;* SrO, decomposition of Baker reagent grade $SrCO_3$ at 950°; $CaCO_3$, Fisher reagent grade; $CuSO_4$, decomposition of Baker reagent grade $CuSO_4 \cdot 5H_2O$ at 270° *in vacuo*. 50–50 mole % mixtures of the reactants were used, the total sample weight being approximately 0.8 g.

The DTA pattern of $BaO + CaCO_3$ is shown in Fig. 1. The sharp exotherm which appears at 375° can be associated with the reaction $BaO + CaCO_3 \rightarrow CaO + BaCO_3$ for these various: (1) the $CaCO_3$ decomposition endotherm which generally appears in the neighborhood of 800° is absent; (2) the peak at 810° is reversible (appears on cooling and reheating) and corresponds to the $\beta \rightarrow \alpha$-$BaCO_3$ transition which occurs at 810°; (3) X-ray analysis of the material after heating shows the presence of CaO and $BaCO_3$, while BaO and $CaCO_3$ are absent. Note that the time interval between the observed initiation and termination of the 375° peak is one minute. Thus, the reaction which does not occur at a detectable rate below 375° goes essentially to completion in no more than one minute (probably much less) when this temperature is attained. With the exception of the differences in "reaction temperature" (345°—Hedvall, 375°—this work) and the extra endotherm at approximately 500°, the phenomenon observed is as described by Hedvall.

Note, also, the value of ΔT. A temperature rise of 12° occurs before the peak goes off scale. The measurable temperature rise is probably two or three times this value and the actual local ΔT's much greater than this. The magnitude of this temperature rise as well as the fact that it is established in the order of a few seconds is indicative of a very

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(4) K. Hauffe, "Reaktionen in und an Festen Stoffen," Springer Verlag, Berlin, 1955.

(5) W. E. Garner, "Chemistry of the Solid State," Butterworths, London, 1955.

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

(7) K. Fischbeck, *Z. anorg. Chem.*, **165**, 53 (1927).

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

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

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

(11) R. Jagitsch, *K. Vet. Akad. (Stockholm) Ark. Kemi, Mineral. Geol.*, **15A**, No. 71 (1942).

abrupt change in reaction rate. It is difficult, at the very least, to reconcile this observation with a normal exponential increase in reaction rate as Hedvall proposed.

Substantially the same observations are made with BaO + $CuSO_4$, SrO + $CaCO_3$ and SrO + $CuSO_4$, the respective DTA patterns being shown in Fig. 1.

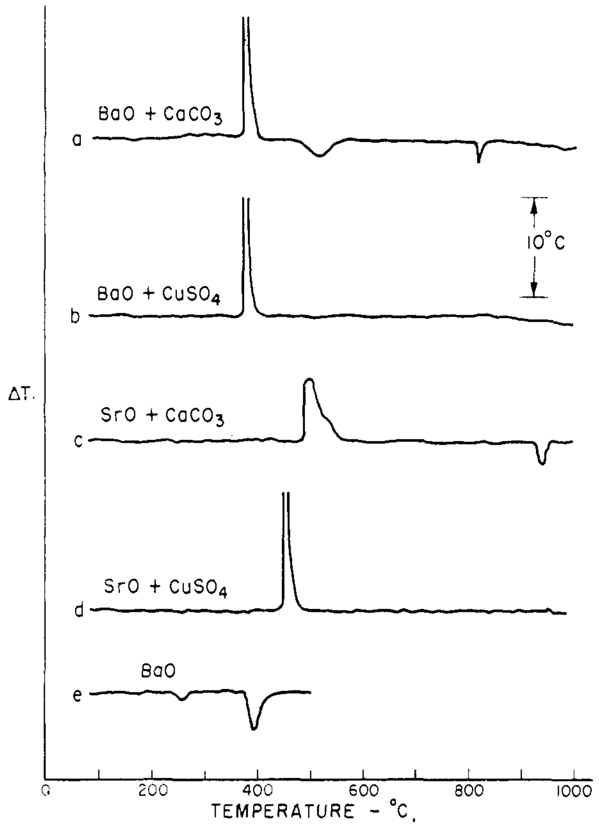

Fig. 1.—DTA patterns of materials as indicated. The sharp exotherm in each case is due to reaction to form the reciprocal pair. The endotherm at approximately 500° in curve a probably is due to decomposition of $Ca(OH)_2$, which forms at 375° as a result of the presence of $Ba(OH)_2$ contaminants in BaO. The endotherm at 810° of curve a is due to a phase transition in $BaCO_3$. The endotherm in curve c at 930° corresponds to a phase transition in $SrCO_3$. The endotherm in the BaO pattern at 375° probably is due to fusion of a $Ba(OH)_2$–$BaCO_3$ eutectic, present in BaO as a contaminant.

In order to investigate the possible role of atmospheric H_2O and CO_2 in these reactions, DTA and thermogravimetric measurements were performed with BaO and SrO alone.

The DTA measurement was made under the same experimental conditions as above. A weight–temperature curve was obtained on a Chevenard recording thermobalance, the sample being heated in air with temperature rising at 10°/min.

The thermogram of BaO showed a measurable weight gain at temperatures as low as 100°. Weight gain continued at an increasing rate as the temperature was raised and by 375°, the weight increase corresponded approximately to the conversion of 30% of the original BaO to $Ba(OH)_2$.[12] In the case of SrO, the weight increase at 450° (the "reaction temperature" of SrO) corresponded to the conversion of 4% of the original SrO to $Sr(OH_2)$. Although not too much significance can be attached to these values of weight since they are dependent on atmospheric conditions at the time of the measurement, it can be said that an appreciable quantity of H_2O and/or CO_2 has reacted with the oxides by the time the "reaction temperatures" are attained. Thus, even if *initially* pure BaO and SrO are used as reactants, they will become contaminated with hydroxide and possibly carbonate in the course of the measurement and will contain these at the reaction temperature.

The DTA pattern of BaO, shown in Fig. 1, is most illuminating. An endotherm, indicative of fusion, initiates at exactly 375°, the "reaction temperature" for BaO. A similar finding was made with SrO. This observation, as well as the unusual rate behavior which is virtually inexplicable in terms of any reasonable solid state diffusion process, makes the cited postulate of Balarew seem very attractive.

The history of this problem makes it impossible, however, to draw conclusions on the basis of the above data alone. Balarew's thoughts, which were based on similar observations, were rejected. Jagitsch[11] reported that liquid phases did form but maintained that these would only affect the extent of reaction and that the phenomenon was essentially characteristic of the solid. This question can be resolved conclusively if it is demonstrated that the reaction does *not* occur when pure BaO or SrO, free of hydroxides and carbonates, is utilized. An experiment therefore was performed:

> A platinum thimble containing BaO_2[13] was placed in a quartz cell which in turn was attached to a vacuum manifold. Situated immediately above this quartz cell is a side arm which is attached to the vacuum manifold by a standard taper joint. This side arm contained $CaCO_3$ as well as several stainless steel milling balls. The quartz cell was heated slowly to 950° with its contents under vacuum. A pressure rise was noted in the temperature range 550–700°, probably caused by loss of H_2O. A second pressure rise initiated at approximately 750°, due to decomposition of BaO_2 to BaO. After pumping for approximately 1 hr. at 950°, the pressure dropped and, when it was below 1×10^{-5} mm., the cell was cooled to room temperature.
>
> The side arm then was rotated so as to spill its contents into the quartz cell. The quartz cell now was sealed off under vacuum and the reactants mixed by shaking the cell. Whatever lumps were present were broken up by the milling balls. The cell was then laid aside and the identical procedure followed with another sample. In the case of the second sample, however, the cell was *not* sealed off under vacuum but removed so as to expose the sample to the atmosphere. Thereafter, the sample was mixed exactly as in the first case. The cells containing each sample were then inserted into a furnace of 500° (125° above the "reaction temperature") and held there for 20 minutes. Thereafter, the samples were removed from both the open and sealed tubes and subjected to X-ray analysis.

X-Ray analysis of the sample which had been exposed to air showed that the reaction did occur. $CaCO_3$ and BaO were no longer present while Ba-

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(12) Only part of this weight increase can be attributed to H_2O, however, since BaO_2 formation undoubtedly is taking place also.

(13) The platinum thimble is used to prevent reaction between BaO and the quartz vessel. BaO_2 is used as a starting material since the oxide which is formed is readily pulverized. BaO formed from $Ba(NO_3)_2$ or from commercial BaO is badly caked, leading to mixing difficulties in this experiment.

CO_3 and CaO were. However, the sample which was treated *in an identical manner*, except that it was *not* exposed to the atmosphere, showed *no evidence of reaction*. The original BaO and $CaCO_3$ were still present despite that fact that the sample had been heated for 20 minutes at 125° above the "reaction temperature."

This same measurement has been made with BaO + $CuSO_4$, SrO + $CaCO_3$ and SrO + $CuSO_4$ with results the same as described. Specifically, no reaction takes place in any of these other three systems when the reactants are prepared, mixed and heated above the "reaction temperature" *in vacuo*. Under conditions which are otherwise identical, the control which is exposed to the atmosphere does react in each case.

It appears, therefore, that the reactions of BaO and SrO as described by Hedvall do not proceed by solid state diffusion processes but occur *via* the liquid phase. Furthermore, the so-called characteristic "reaction temperature" has nothing to do with the oxide itself but is merely the melting point of what is probably a hydroxide containing eutectic as Balarew suggested,[3] the presence of which presents a low energy path along which the reaction proceeds very rapidly. This is illustrated in Fig. 2 where hypothetical rate constant temperature curves are shown for the liquid phase and solid state mechanisms by curves I and II, respectively. Below the melting point of the third component (T_M), the only path available is the solid state path[14] where, even at T_M, the reaction rate is so small that it may be considered to be zero for all practical purposes. On sudden appearance of a liquid phase, the system finds itself well up on the steep portion of curve I where, because of its exothermic nature, the reaction proceeds with a burst of heat, leading to the high ΔT's observed with DTA.

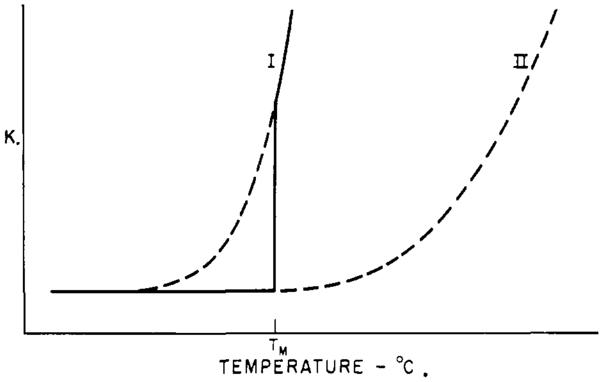

Fig. 2.—Postulated mechanism of the reactions of BaO and SrO. Hypothetical rate constant temperature curves for the liquid phase and solid state mechanisms are shown, respectively, as curves I and II. The reaction path (solid line) follows curve II up to the melting point of the third component at which point the lower energy, liquid phase path becomes available.

(14) We can, of course, only speculate as to the reaction path in the absence of a liquid phase and a better guess, probably, is that the reaction will proceed through the gaseous phase. However, for the purpose of the above, this is of no consequence.

SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Fluoride Complexing of Scandium(III) in Aqueous Solution: Free Energies, Heats and Entropies

BY JOHN W. KURY, ARMINE D. PAUL, LOREN G. HEPLER AND ROBERT E. CONNICK

RECEIVED FEBRUARY 6, 1959

The complexing of Sc(III) in perchlorate solutions at an ionic strength of 0.5 *M* was determined by studying the potential of the ferrous–ferric electrode as a function of the HF, H^+ and Sc(III) concentrations. The data can be interpreted by assuming the presence of the species ScF^{++}, ScF_2^+, ScF_3(aq) and ScF_4^-. Equilibrium constants for the formation of these complexes at 15, 25 and 35° were evaluated and from them the heat and entropy changes of the reactions calculated. The scandium fluoride complexes are more stable than those of other trivalent ions of comparable radius. The extra stability of the complex scandium fluorides arises from an irregularity in the heat term, rather than in the entropy term.

Introduction

This investigation was undertaken because of the work of Dodgen[1] who found the scandium fluoride complexes to be more stable than those of other trivalent ions of similar radius. According to Pauling,[2] In(III) has the same ionic radius (0.81 Å.) as Sc(III). However, the first fluoride complex of Sc(III) is about 280 times more stable than the first fluoride complex of In(III).[3] We wished to determine whether the greater stability of the scandium fluoride complexes arises from the heat term or the entropy term.

The "ferri" method of Brosset and Orring[4] was used. The complexing of Sc(III) was determined indirectly by studying its effect on the ferric fluoride complexing equilibria, as measured potentiometrically through the ferrous–ferric couple.

Experimental

Apparatus.—Descriptions of the cells, electrodes, measuring apparatus and general procedure are given elsewhere.[3,5,6]

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(1) H. W. Dodgen, private communication.

(2) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945.

(3) L. G. Hepler, J. W. Kury and Z. Z. Hugus, *J. Phys. Chem.*, **58**, 26 (1954).

(4) C. Brosset and J. Orring, *Svensk. Kem. Tid*, **55**, 101 (1943).

(5) H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949).

(6) R. E. Connick and M. Tsao, *ibid.*, **76**, 5311 (1954).