where t_1 is the drop time. If it is supposed that diffusion of B may be considered negligible if the second term of the right side of equation (6) is less than 5% of the first, equation (9) will hold for $k_b >$ about 100 sec.$^{-1}$ for normal t_1 values. Though $E_{1/2}$ is a function of k_b, the shape of the wave remains unaltered, as seen from equation (8). The expressions obtained by Smith and Vavřín have a similar form, though they do not contain k_b and t_1. Since E_0 is not known for the reactions studied and k_b cannot be varied in a controlled manner, there are as yet no data available to test equation (9). However, it is planned to investigate the dependence of $E_{1/2}$ on t_1, which has not yet been studied for this type of reaction.

It should be pointed out that the analogy between this and the kinetic case is not complete, because there the surface concentration of reactant remains constant, whereas here it may diminish under the influence of a high reaction rate. It is possible that under such circumstances, the restriction on diffusion is somewhat relaxed. In a study of the second-order kinetic case,[17] in which the surface concentration of reactant is variable, it was found that equations of type (6) held quite well over a wide range of reaction–diffusion ratios.

The $E_{1/2}$ of Catalytic Waves.—It is interesting to compare this relationship of $E_{1/2}$ and k_b with that obtaining in the ordinary catalytic wave. It is found by the argument given below that in the latter case $E_{1/2}$ and k_b are independent.

The equations for the rising part of the curve are

$$\partial C_A/\partial t = D_A(\partial^2 C_A/\partial x^2) + k_b C_B$$
$$\partial C_B/\partial t = D_B(\partial^2 C_B/\partial x^2) - k_b C_B$$

with the boundary conditions $C_A = a$ and $C_B = 0$ for $t = 0$; and for $x = 0$, $\partial C_A/\partial x = -(D_B/D_A)\cdot\partial C_B/\partial x$ and $C_A/C_B = [nF/RT] \exp (E_0 - E)$. If D_A and D_B are assumed equal, application of the Laplace transformation in the usual manner yields the result

$$(\partial C_A/\partial x)_{x=0} = (1 + q)^{-1}[a\sqrt{k_b/D}(e^{-k_b t}/\sqrt{\pi k_b t} + \operatorname{erf} \sqrt{k_b t})]$$

where $q = [nF/RT] \exp (E_0 - E)$. The term inside the square brackets is the expression for $(\partial C_A/\partial x)_{x=0}$ under limiting current conditions. It follows that $E_{1/2} = E_0$ and that the current dependence on E is exactly what it would be if the limiting current were a normal diffusion current.

CAMBRIDGE, MASS.

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(17) To be published in THIS JOURNAL.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Solubility Product of Ferrous Hydroxide and the Ionization of the Aquo-Ferrous Ion

BY D. L. LEUSSING AND I. M. KOLTHOFF

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The solubility products $S_{1\text{Fe(OH)}_2} = a_{\text{FeOH}^+} \times a_{\text{OH}^-}$ and $S_{2\text{Fe(OH)}_2} = a_{\text{Fe}^{++}} \times a^2_{\text{OH}^-}$ have been determined in air-free suspensions of ferrous hydroxide at 25°. Average values of S_1 of 4×10^{-10} and of S_2 of $8 \pm 3 \times 10^{-16}$ were found. The ferrous ion forms an unstable complex with ammonia. The ionization constant of the aquo-ferrous ion $a_{\text{FeOH}^+}a_{\text{H}^+}/a_{\text{Fe}^{++}}$ was calculated to be equal to 5×10^{-9}. A brief discussion is given of the relation between our results and those in the literature.

In an investigation of the complexes formed between ferrous iron and thioglycolate it was necessary to know the value of the solubility product of ferrous hydroxide. Many and varying values of the solubility product have been reported in the literature. A summary of these values is given in Table I.

All these values have been calculated on the basis of the dissociation of an aqueous solution of ferrous hydroxide into ferrous and hydroxyl ions.

TABLE I

DATA ON THE SOLUBILITY OF FERROUS HYDROXIDE REPORTED IN THE LITERATURE

A. Solubility of ferrous hydroxide in water

Solubility (*M*)	Reference	
6.7×10^{-5}	Whitman, *et al.*	1
1.35	Lamb	2
7.5	Bineau	3
0.73	Murata	4

B. Solubility product of ferrous hydroxide in water

$S\text{Fe(OH)}_2 =$ $[\text{Fe}^{++}][\text{OH}^-]^2$	Method	Reference	
3.2×10^{-14}	Solubility	Whitman, *et al.*	1
9.9×10^{-15}	Conductivity	Lamb	2
8.7×10^{-14}	Solubility	Krassa	5
2.9×10^{-15}	Conductivity	Murata	4
1.56×10^{-15}	Solubility	Murata	4
2.13×10^{-15}	Colorimetric *p*H	Murata	4
4.5×10^{-21}	Potentiometric	Britton	6
4.8×10^{-16}	titration	Elder	7
3.9×10^{-15}	*p*H	Shipley & McHaffie	8
7×10^{-13}	Polarographic	Shrager	9
1.7×10^{-15}	E.m.f.	Randall	10
2.4×10^{-14}	Potentiometric titration	Arden	11

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(1) W. G. Whitman, R. P. Russell and G. H. P. Davis, THIS JOURNAL, **47**, 70 (1925).

(2) A. B. Lamb, *ibid.*, **32**, 1214 (1910).

(3) M. A. Bineau, *Compt. rend.*, **41**, 509 (1879).

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(6) H. T. S. Britton, *J. Chem. Soc.*, **127**, 2110 (1925).

(7) S. W. Elder, *Trans. Am. Electrochem. Soc.*, **57**, 383 (1930).

(8) J. W. Shipley and I. R. McHaffie, *Can. Chem. Met.*, **8**, 5, 121 (1924).

(9) B. Shrager, *Collection Czechoslov. Chem. Communs.*, **1**, 275 (1929).

(10) M. Randall and M. Frandsen, THIS JOURNAL, **54**, 40 (1932).

(11) T V. Arden, *J. Chem. Soc.*, 882 (1950).

Lindstrand[12] reports the existence in solution of the species, $FeOH^+$. The *p*H of solutions of known concentration of ferrous perchlorate in water was determined and from this Lindstrand calculated a value of the "hydrolysis" constant, K_h, to be 1.20×10^{-6} at 20° for the equilibrium $Fe^{++} + H_2O \rightleftarrows FeOH^+ + H^+$.

This value indicates that in all of the experiments referred to in Table I, a considerable portion of the iron is present as the monohydroxy ferrous ion.

Schikoor[13] states the possibility of ferrous hydroxide being oxidized by water. Evans and Wanklyn[14] report that there is no evidence of hydrogen evolution from suspensions of ferrous hydroxide either with ferrous sulfate or alkali in excess. If platinum chloride or colloidal platinum, nickel, etc., are present before the addition of the alkali hydrogen evolution was observed at room temperatures.

In the present paper we report the results of a careful study of the solubility and solubility product of ferrous hydroxide in various media and of the ionization constant of the aquo-ferrous ion. We find this ion to be a much weaker acid than indicated by Lindstrand.

Experimental

In the preparation of suspensions of ferrous hydroxide air-free ferrous chloride solutions were added to air-free sodium hydroxide solutions. Pure, freshly prepared ferrous hydroxide is white but even traces of oxygen turn it green. The experimental technique used in the present work enabled ferrous hydroxide to be prepared white and to be maintained reasonably so for periods of several weeks while being rotated at 25° in contact with its mother liquor.

Narrow mouth screw-cap bottles of about 200-ml. capacity were used. A self-sealing Buna N gasket was placed in the metal screw-cap. Small holes had previously been punched through the metal cap so access to the interior of the bottle through the gasket could be had by hypodermic needles of about 20 gage. In this way reagents could be added to the bottles by means of syringes and the solutions in the bottles could even be bubbled out with nitrogen by means of a 6-inch needle which reached to the bottom of the bottle and through which nitrogen could be passed. A smaller needle was, of course, inserted into the air space in the top of the bottle to allow for the escape of the gas during this process. Solutions also could be transferred quite satisfactorily under air-free conditions from one bottle to another with a syringe. The nitrogen used was Linde 99.99% pure.

The sodium hydroxide solutions (0.01–0.05 *N*) were freshly prepared for each set of experiments from saturated sodium hydroxide stock solutions kept in wax-lined bottles. These solutions were standardized against standard acid.

Ferrous chloride stock solutions free from ferric iron were freshly prepared in sealed bottles. A known volume of standard 1.0 *N* hydrochloric acid was placed in the bottle and bubbled out with nitrogen for a few minutes. A quantity of iron powder (Baker C.P.) in slight excess of the amount required to react completely with the hydrochloric acid was then added and the bottle quickly capped with a metal cap and self-sealing gasket. Nitrogen was passed over the surface of the solution through needles inserted in the gasket. The hydrogen evolved provided for adequate deaeration of the solution. After about one-half hour when the vigorous hydrogen evolution quieted down the needles were removed and the bottle placed on a shaker. In 24 hours about 99% of the hydrochloric acid was consumed and in 48 hours the reaction could be considered to have gone to completion, at least within the experimental error of the iron determination. In some of the experiments described below the reaction had not gone to completion. The concentration of free hydrochloric acid in these solutions was obtained when necessary by analyzing for both total iron and chloride, the hydrochloric acid being obtained by difference.

Aliquots of the ferrous chloride stock solution were removed from the sealed bottle by means of a syringe inserted through the gasket. The hydrogen pressure built up inside the bottle allowed the easy removal of samples without introducing air into the bottle.

For the preparation of the suspension of ferrous hydroxide, 100 ml. of 0.01–0.05 *N* sodium hydroxide was pipetted into bottles and the bottles sealed as described above. The solutions within the bottles were then deaerated by vigorously bubbling nitrogen through them for one-half hour. The needles were then withdrawn and an excess of the ferrous chloride solution was injected into the bottles by means of a syringe.

The bottles containing the precipitates were then rotated in a water-bath at 25 ± 1°. It was observed that at least 48 hours was required for the *p*H of the solution to decrease to a constant value. This constant value was maintained up to two weeks after which time no tests were made. Most of the solutions were rotated for 72 hours or longer.

After a sufficient period of time of rotation the suspensions in the bottles were sampled by means of a syringe and the *p*H of the solutions was determined in a nitrogen atmosphere. The Beckman model G *p*H meter was used with a glass electrode. The instrument was standardized with Eimer and Amend buffer of *p*H 7.00.

The bottles were then centrifuged and a sample of the supernatant liquid removed and analyzed for iron by titration with standard ceric sulfate.

Results

Composition of Precipitate.—In order to determine whether the precipitate consists of a basic salt or ferrous hydroxide suspensions of the precipitate were prepared as described above and the supernatant liquids were analyzed for chloride after 72 hours. The 0.5 *M* ferrous chloride stock solution was analyzed to be 1.005 *M* in chloride and was injected into the sodium hydroxide solution using calibrated syringes. The iron content was only approximately 0.5 *M* as the stock solution contained about 0.01 *M* of unreacted hydrochloric acid. This free acid does not interfere in the present experiment. From 10 sets of experiments at varying concentrations and under various conditions, described in detail in the doctor's thesis of the junior author, it was found that all of the chloride was in solution and none in the precipitate. The precipitate thus consists of $Fe(OH)_2$ or some hydrate.

The solubility of undissociated ferrous hydroxide and ferrite was found to be less than 10^{-6} *M* in 0.1 *N* NaOH. No color was observed with *o*-phenanthroline when the *p*H was adjusted to 4.5 with concentrated acetic acid. Thus, these species need not be considered in the present experiments.

Evidence for the Existence of $FeOH^+$ in Solution.—One hundred ml. of sodium hydroxide solution was pipetted into a bottle and made air-free. Excess ferrous chloride solution was then injected into the bottle using a calibrated syringe and the bottle rotated on the water-bath at 25° for 140 hours.

The *p*H and iron and chloride concentrations were determined as described above. The results are given in columns 1–6 of Table II.

Calculations.—The initial volume of ferrous chloride added to the solution was calculated from

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(12) F. Lindstrand, *Svensk. Kem. Tids.*, **56**, 282 (1944).

(13) G. Schikoor, *Z. Elektrochem.*, **35**, 65 (1929).

(14) U. R. Evans and I. N. Wanklyn, *Nature*, **162**, 27 (1948).

Table II

Solubility Product $a_{FeOH^+} \times a_{OH^-}$ at 25°

Vol. $FeCl_2$ added by syringe, ml.[a]	$FeCl_2$ soln. added, ml.[b]	Cl^- concn. in supernatant liq. (M)	Fe concn. in supernatant liq. (M)	Initial concn. NaOH (M)[c]	pH at equil.	Concn. $FeOH^+$ $M \times 10^3$	γ[d]	$S_{1Fe(OH)_2} \times 10^{10}$
24.5	23.4	0.1903	0.0765	0.0495	7.37	2.5	0.75	4.4
9.5	9.46	.0871	.02155	.0495	7.57	1.4	.80	4.1
22.5	22.3	.183	.0895	.00987	7.05	3.7	.75	3.1

[a] 0.496 M in $FeCl_2$, 0.013 M in HCl. [b] Calculated from final chloride concentration. [c] 100 ml. of NaOH originally used. [d] γ is the activity coefficient of a univalent ion.

Table III

Solubility Product $a_{Fe^{++}} \times a^2_{OH^-}$

Initial concn. NaOH, (M)	0.5 M $FeCl_2$, ml.	pH at equil.	Total Fe in soln. (M)	a_{FeOH^+}, $M \times 10^3$[b]	γ_1[c]	γ_2[c]	$S_{Fe(OH)}$ $a_{Fe^{++}} \times a^2_{OH^-} \times 10^{16}$
0.0241	5	7.63	0.0095	0.9	0.79	0.45	6.8
.0241	5	7.60	.0109	1.0	.79	.46	7.1
.0241	5	7.60	.0116	1.0	.80	.47	7.8
.0495	10	7.57	.0215	1.1	.80	.47	13
.01	3	7.55	.0091	1.1	.87	.60	6.1
.01	4	7.52	.0113	1.2	.87	.60	6.5
.01	4	7.46	.0112	1.4	.87	.60	4.8
.0514	10	7.46	.0234	1.4	.80	.47	8.6[a]
.01	5	7.45	.0183	1.4	.84	.55	7.3
.01	10	7.42	.0377	1.5	.85	.57	14
.0514	15	7.42	.0373	1.5	.78	.44	11
.01	6	7.40	.0203	1.6	.84	.56	6.6
.01	7.5	7.37	.0256	1.7	.82	.51	6.6
.01	6	7.35	.0205	1.8	.84	.56	5.2[a]
.0495	25	7.33	.0765	1.9	.75	.40	14
.0514	18	7.26	.0541	2.2	.76	.41	6.9
.0099	8.3	7.23	.0338	2.3	.81	.48	4.3
.0514	25	7.15	.0827	2.8	(.75)	(.40)	6.3
.0099	22.5	7.05	.0895	3.6	(.75)	(.40)	4.3
						Average	8 ± 3

[a] Cooled at 5° for 120 hours then brought back to 25° for 120 hours. [b] The activity of $FeOH^+$ was obtained from the relationship $a_{FeOH^+} \times a_{OH^-} = 4 \times 10^{-10}$. [c] γ_1 is activity coefficient of univalent, γ_2 that of divalent ion.

the chloride concentration of the final solution in order to circumvent the errors inherent in measuring a known volume with a syringe. Let $[Fe]_t$ represent the total concentration of iron found in the supernatant liquid at equilibrium and $[Fe]_i$ and $[OH]_i$ represent the initial concentrations of iron, and hydroxide, the latter being corrected for the free hydrochloric acid in the ferrous stock solution. Then

$$[Fe]_t = [FeOH^+] + [Fe^{++}]$$
$$[Fe]_i - [Fe]_t = [Fe(OH)_2]_s$$
$$[OH]_i = 2[Fe(OH)_2]_s + [FeOH^+]$$

Solving for $[FeOH^+]$

$$[FeOH^+] = [OH]_i - 2([Fe]_i - [Fe]_t)$$

$[Fe(OH)_2]_s$ is expressed as the concentration of iron that has been removed from solution as solid $Fe(OH)_2$.

The solubility product, $S_{1Fe(OH)_2} = a_{FeOH^+} \times a_{OH^-}$ was then calculated using also the pH and assuming an average activity coefficient of univalent ions as given by Kielland.[15] The values found are in the last column of Table II, the average value being 4×10^{-10} at 25°.

Solubility Product, $S_{2Fe(OH)_2}$, for the Equilibrium $Fe(OH)_2(s) \rightleftarrows Fe^{++} + 2OH^-$.—The concentration of free ferrous ion $[Fe^{++}]$ in a solution containing excess ferrous chloride in equilibrium with ferrous hydroxide can be calculated given the total iron concentration, pH and $S_{1Fe(OH)_2}$ equal to 4×10^{-10}. The activity product, $S_{2Fe(OH)_2}$, is then obtained using average values of the activity coefficients.[15] Results obtained are given in Table III. The average of the value of $S_{2Fe(OH)_2}$ is $8 \pm 3 \times 10^{-16}$.

It was found that within the experimental error the chloride ion concentration (at least to 0.2 M) has no effect on $S_{2Fe(OH)_2}$, therefore the concentration of such ions as $FeCl^+$ is negligible.

Effect of Oxidation upon the Solubility Product of Ferrous Hydroxide.—As solid ferrous hydroxide becomes oxidized it undergoes color changes from white to green and then to a deep purple. Feitknecht and Keller[16] studied the effect of oxidation by means of X-rays. They report that in up to 10% oxidation no change in crystal lattice of ferrous hydroxide occurs. With further oxidation lines of α-FeOOH appear in the X-ray pattern.

This behavior is also reflected in the change of the solubility product with oxidation. A sample which had inadvertently become oxidized and was green yielded a value of the solubility product $S_{2Fe(OH)_2}$ of 3.8×10^{-16} while a very dark green sample yielded a value of the solubility product of 3.2×10^{-16}. It is thus seen that oxidation tends to decrease the value of the solubility product but not as much as reported by Arden.[11]

Discussion

The values of $S_{1Fe(OH)_2}$ and $S_{2Fe(OH)_2}$ found in this work yield a value of K_h equal to 5×10^{-9} at 25°. This value differs greatly from that reported by Lindstrand.[12] This discrepancy in the value of K_h is probably accounted for by traces of free acid in the ferrous perchlorate used by Lindstrand.

In a curve presented by Arden[11] for the titration of a solution 0.05 M in $FeSO_4$ and 0.05 M in H_2SO_4 with 0.1 M NaOH the pH at the first end-point lies between 5 and 6. The value of K_h reported by Lindstrand gives a calculated value of pH of about 3.8 at this first end-point while the value of K_h reported in this paper gives a calculated value of about 5.

The value of the solubility of ferrous hydroxide in pure water is calculated to be 1.9×10^{-5} M from the present values of $S_{1Fe(OH)_2}$ and $S_{2Fe(OH)_2}$ neglecting activity coefficients. This is in fair agreement with the value of 6.7×10^{-5} M found by Whitman[1] and 7.5×10^{-5} M found by Bineau.[3]

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(15) J. Kielland, This Journal, **59**, 1675 (1937).

(16) W. Feitknecht and G. Keller, *Z. anorg. Chem.*, **262**, 61 (1950).

In a saturated solution of only ferrous hydroxide it is calculated that [FeOH$^+$] is 1.76×10^{-5} *M* and [Fe^{++}] is 0.18×10^{-5} *M*. The *p*H of this saturated solution is calculated to be 9.32 in good agreement with the value of 9.4 reported by Shipley and McHaffie.[8]

If the iron in such a solution is present mostly as FeOH$^+$ then the solubility of Fe(OH)$_2$ reported by Lamb[2] from conductivity measurements (1.35×10^{-5} *M*) would be approximately half as great as the true value, since Lamb assumed completely dissociation into Fe^{++} and OH$^-$ ions. The results of Lamb, therefore, do not disagree with ours.

The data in the present work agree fairly well with the results of Whitman[1] (solubility), Lamb,[2] Bineau,[3] Shipley and McHaffie[8] and Randall.[10] The data of Elder[7] may be in error due to possible coprecipitation and slow precipitation near the end-point in the titration of ferrous chloride with sodium hydroxide. The data of Krassa,[5] Britton[6] and Shrager[9] may be considered not to apply to the present case. An examination of the work of Murata[4] indicates that equilibrium had not been attained in his experiments, consequently the solubility reported by him is low. On the other hand the higher value of the solubility product obtained by Arden[11] in his titration may be due to supersaturation. It was observed in the present work that in the precipitation of ferrous hydroxide the *p*H had not decreased to a constant value within 24 hours.

Solubility of Ferrous Hydroxide in Ammonia Solutions.—Weitz and Müller[17] report that insoluble hexammine salts precipitate upon the passage of ammonia into solutions of ferrous salts. However, in the present work it was found that there was little tendency for the formation of these salts in solutions which were up to 1 *M* in ammonia. On the other hand, evidence for the formation of soluble ammino-iron(II) complexes was obtained. In solutions that were 0.1 *M* in ammonium chloride the solubility of ferrous hydroxide increased with the ammonia concentration. The total iron concentration in an ammoniacal solution that was 0.1 *M* in ammonium chloride and at a *p*H of 10.44 was found to be 2×10^{-4} *M* after 4 days of rotating at 25°. The concentration calculated from our values of $S_{1\mathrm{Fe(OH)}_2}$ and $S_{2\mathrm{Fe(OH)}_2}$ is about 2×10^{-6} *M*. If a coördination number of 4 is assumed the "constant" $[\mathrm{Fe}^{++}][\mathrm{NH}_3]^4/[\mathrm{Fe(NH}_3)_4{}^{++}]$ is calculated from the data to be about 2×10^{-4}. This is about the value expected considering the correlation between the second ionization potential and the stability constant as shown by Martell and Calvin.[18]

Acknowledgment.—We wish to thank the U. S. Public Health Service for a grant which enabled the present work to be carried out.

(17) E. Weitz and H. Müller, *Ber.*, **58**, 363 (1925).

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MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF MINERAL INDUSTRIES, THE PENNSYLVANIA STATE COLLEGE]

Fluoride Models for Oxide Systems of Dielectric Interest. The Systems KF–MgF$_2$ and AgF-ZnF$_2$

BY R. C. DEVRIES AND RUSTUM ROY

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Phase equilibrium relations have been determined in the systems KF–MgF$_2$ and AgF–ZnF$_2$. In the former system, two compounds, KF·MgF$_2$ and 2KF·MgF$_2$, have been found, melting congruently at 1070° and incongruently at 846°, respectively. Only one compound AgF·ZnF$_2$ is found in the second system; this melts congruently and shows a complete series of solid solutions with AgF. Other than the fact that both the 1:1 molar ratio compounds do have the perovskite structure, the "model" relations with the system BaO–TiO$_2$—which has four compounds—are very poor. It has also been found that the difficulties in these fluoride systems are commensurable with the difficulties involved in obtaining the high temperatures required for studying their oxide counterparts.

Introduction

The concept of model structures as introduced by Goldschmidt in 1926,[1] provides a method for the study of higher melting compounds by use of their lower melting models. A common example is that of silicates and their fluoride models. Although structurally the models and their more strongly bonded counterparts are often very similar, their phase relations have not always proved to be exactly the same, though some examples of remarkable similarity exist, *e.g.*, Na$_2$BeF$_4$ and Ca$_2$SiO$_4$.[2,3] Therefore the concept as applied to phase relations has come to be recognized as a tool but one to be used with some reservations. In earlier investigations in this Laboratory this has been amply demonstrated.[3-5]

With the interest in titanates and particularly the perovskite type structure in relation to dielectrics, fundamental research in TiO$_2$-containing systems or in systems containing similar structures is of increasing importance. However, a system such as BaO–TiO$_2$ presents certain technical difficulties, particularly the high temperatures involved and the ease of formation of barium platinates, that make feasible the consideration of lower melting fluoride model systems as one method of attacking the problems. Therefore as an indirect method of attack on the system BaO–TiO$_2$, two fluoride model systems, KF–MgF$_2$ and AgF–

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(3) D. M. Roy, Rustum Roy and E. F. Osborn, *J. Am. Ceram. Soc.*, **33**, 85 (1950).

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