Cohesion

All of the substituent fluorine atoms in the polytetrafluoroethylene chain have strong, identical electrostatic fields which are mutually repellent. Because of this effect, interchain bonding forces (except for van der Waals forces) are absent in the polymer, and the molecular cohesion is very low. As a result the polymer is easily fractured above the transition point at 327°. The polymer is mechanically anisotropic; applied stresses are localized along certain lines within the mass and fracture of the mass occurs along these lines as the stress is increased. These fracture lines can be observed by heating a block of polymer to about 350°, subjecting it to compression in a chamber having an orifice, then cooling and sectioning. Once the polymer mass is fractured, the high viscosity and absence of interchain bonding preclude its fusing together except very slowly and under considerable direct pressure.

Insolubility

Polytetrafluoroethylene resembles polyethylene in being insoluble in organic solvents at room temperature, but it has not been found to exhibit the increased solubility at elevated temperatures that is shown by polyethylene around 70°.[18] The separation of polymer chains from each other when a non-polar, crystalline polymer is dissolved must involve the same relative motion of the chains as that occurring in the viscous flow of the molten polymer, hence the surmounting of the same energy barrier in both situations. While this factor should not affect the equilibrium solubility of the polymer, it would make the rate of solution of polytetrafluoroethylene in any solvent extremely low. However, it is probable that polytetrafluoroethylene is not just slowly soluble, but is quite insoluble, because of the very low order of associative forces between a fluorocarbon and other organic molecules.

Acknowledgment.—We wish to acknowledge the assistance of Mr. H. S. Young in the high pressure work on the polymerization of tetrafluoroethylene, of Miss Janice Sutter for X-ray diffraction data, and of Dr. J. R. Downing for the infrared spectrum of polytetrafluoroethylene.

Summary

An improved method for the polymerization of tetrafluoroethylene is described.

The properties of polytetrafluoroethylene include abnormally high melt viscosity, insolubility in all organic solvents, extreme chemical inertness, and very low dielectric loss factor.

Evidence that the polymer is a linear, highly crystalline fluorocarbon, and an explanation of its properties in terms of such a structure, are presented.

WILMINGTON, DELAWARE RECEIVED APRIL 5, 1946

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[18] Ref. 11, p. 98.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reaction between Ferric Oxide and Barium Carbonate in the Solid Phase. Identification of Phases by X-Ray Diffraction[1]

BY MICHAEL ERCHAK, JR.,[2] I. FANKUCHEN AND ROLAND WARD

An investigation of the kinetics of the reaction between barium carbonate and ferric oxide in presence of oxygen was made by Struthers and Ward.[3] By chemical analysis, they inferred that one of the products was probably $BaFeO_3$. Rosenstein[4] further investigated this system and established, by X-ray analysis, the presence of barium oxide in many of the products and the existence of a compound which seemed to have a perowskite-like structure. The latter was taken as further evidence for the compound $BaFeO_3$. In these preparations, however, the valence number of iron rarely exceeded 3.3 and never reached 4. A more thorough investigation of this system seemed to be called for especially with regard to the determination of the solid phases produced in the reaction at various temperatures with a wide range of mixtures. Chemical analysis has decided limitations for this purpose. X-Ray analysis, on the other hand, permits not only of the recognition of phases and their intersolubilities but also an approximate determination of the relative extent to which the phases are formed. Structural changes in a phase may also be observed. H. Forestier[5] found that a compound corresponding to $BaOFe_2O_3$ crystallized in a hexagonal close-packed lattice. Hilpert[6] also found evidence of formation of crystalline products. Hüttig[7] prepared many ferrites of the alkaline earth metals. Calcium ferrite was identified as having a spinel structure. Adelsköld[8] found evi-

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[1] Abstracted from a thesis submitted by Michael Erchak, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn, 1945.

[2] Present address: Central Research Lab., Allied Chem. and Dye Corp., Morristown, N. J.

[3] R. Ward and J. D. Struthers, THIS JOURNAL, **59**, 1849 (1937).

[4] R. D. Rosenstein, Thesis for Bachelor of Science degree at Polytechnic Institute of Brooklyn, 1943.

[5] H. Forestier, *Compt. rend.*, **192**, 842 (1937).

[6] S. Hilpert and A. Wille, *Z. physik. Chem.*, **18 B**, 291 (1932).

[7] G. F. Hüttig, *et al.*, *Z. Elektrochem.*, **40**, 306 (1934); THIS JOURNAL, **57**, 2470 (1935).

[8] V. Adelsköld, *Arkiv. Kemi Mineral. Geol.*, **12A**, No. 29 (1938).

dence that the compound ($BaO \cdot 6Fe_2O_3$) has a structure similar to that of magneto-plumbite ($PbO \cdot 6Fe_2O_3$) the structure of which he established.

This paper presents the results of a systematic study of the barium carbonate–ferric oxide system. Changes occurring in the mixtures after heating at definite temperatures were followed by Debye–Scherrer diffraction patterns. Phase boundaries were located approximately by the "Disappearing Phase" method frequently used in the investigation of alloys.[9]

The catalytic activity of all the preparations was also studied and good correlation was found with the properties revealed by the X-ray investigation. A paper on this phase of the work follows.

Experimental

I. Preparation of Mixtures.—C. P. barium carbonate and ferric oxide, dried forty-eight hours at 400°, were intimately mixed and about 2 g. of the mixture was placed in a tube furnace maintained at constant temperature. The carbon dioxide liberated in the ensuing reaction was swept, by a steady stream of dry oxygen, into absorption tubes filled with ascarite. These were weighed at definite intervals of time in order to follow the course of reaction. The mixtures were periodically removed from the furnace, cooled in a desiccator, reground and placed again in the furnace until the liberation of carbon dioxide had ceased. This was invariably accomplished within forty-eight hours.

The appearance of the products differed considerably and some of them were found to be ferromagnetic. It was necessary to prepare over one hundred samples in order to describe adequately the whole system. A two number system is used to identify samples, thus 20-600 designates a mixture containing 20 weight per cent. barium carbonate and 80% ferric oxide which was heated at 600° as described above.

II. X-Ray Analysis.—Debye–Scherrer diagrams were taken using filtered Kα radiation from an iron target tube and 5-cm. radius cylindrical camera.

The samples were prepared for X-ray investigation by coating a 1-cm. Pyrex glass rod about 0.3 mm. in diameter with a uniform layer of the mixture. The exposures were two hours at 12 ma. and 30 Kv.

The intensity of the important reflections was measured by a North American Philips Co. X-ray spectrometer (using nickel-filtered copper radiation) which gives the relative intensities of the diffracted beams directly by means of a Geiger counter. A typical spectrum is shown in Fig. 1. Specimens in this instance were prepared by mixing a little of the sample in melted vaseline and spreading it on a glass slide over an area of about 1 × 3 cm. and just thick enough to be opaque. The prepared slides were then clamped in place on the spectrometer and number counts recorded.

Interplanar distances were determined in the usual manner from Debye–Scherrer diagrams. These were, however, calculated in terms of d^*, where $d^* = 2 \sin \theta$, which is equivalent to $d^* = \lambda/d$. Since a large number of films were involved, it was found convenient to make a paper scale so that the d^* values could be read off directly by simply placing the scale on the film. Where higher precision was desired, the patterns were measured with a steel ruler.

III. Measurement and Interpretation of Diffraction Patterns.—Relative intensities of all the reflections on each film were first estimated visually and were represented by numbers between zero and ten. After noting the intensities on any one film, it was further necessary to adjust these values relative to intensities obtained from other films. This was facilitated by arranging the patterns as shown in Plate 1. Relative intensities of similar lines were then readjusted by tracing each reflection from film to film. This was done for all mixtures having the same original composition. A similar comparison was made of the patterns obtained from all mixtures heated at the same temperature. By such a procedure relative intensities of all the lines may be estimated within about 20%.

A cursory examination of the films and the corresponding intensity data revealed that ferric oxide and barium carbonate lines begin to decrease in intensity at rather low temperatures with simultaneous or subsequent appearance of new lines. Closer inspection showed that some of the new reflections fitted those of barium oxide while others were due to unknown compounds. To interpret the complex diffraction patterns from mixtures containing so many phases, it was found advantageous to eliminate all known lines and arrange the intensity data in two ways. First, the intensity of the lines was listed with respect to the temperature. This was done for the products of each mixture. Secondly, the intensity of the lines was listed with respect to the composition of the mixtures. This was done for each temperature. A careful study of the data arranged in this way made it possible to select families of lines which showed the same trend and therefore could be attributed to one compound.

Four distinct phases identified in this manner besides ferric oxide and barium carbonate are barium oxide and compounds designated as D, E and F. A reasonably intense line which could be

TABLE I

Compound	$d^* = 2 \sin \theta$
Fe_2O_3	0.78
$BaCO_3$	.75
BaO	.62
D	.57
E	.70
F	.68

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[9] A. J. Bradley and A. Taylor, *Proc. Roy. Soc.* (London), **A159**, II, 56 (1937).

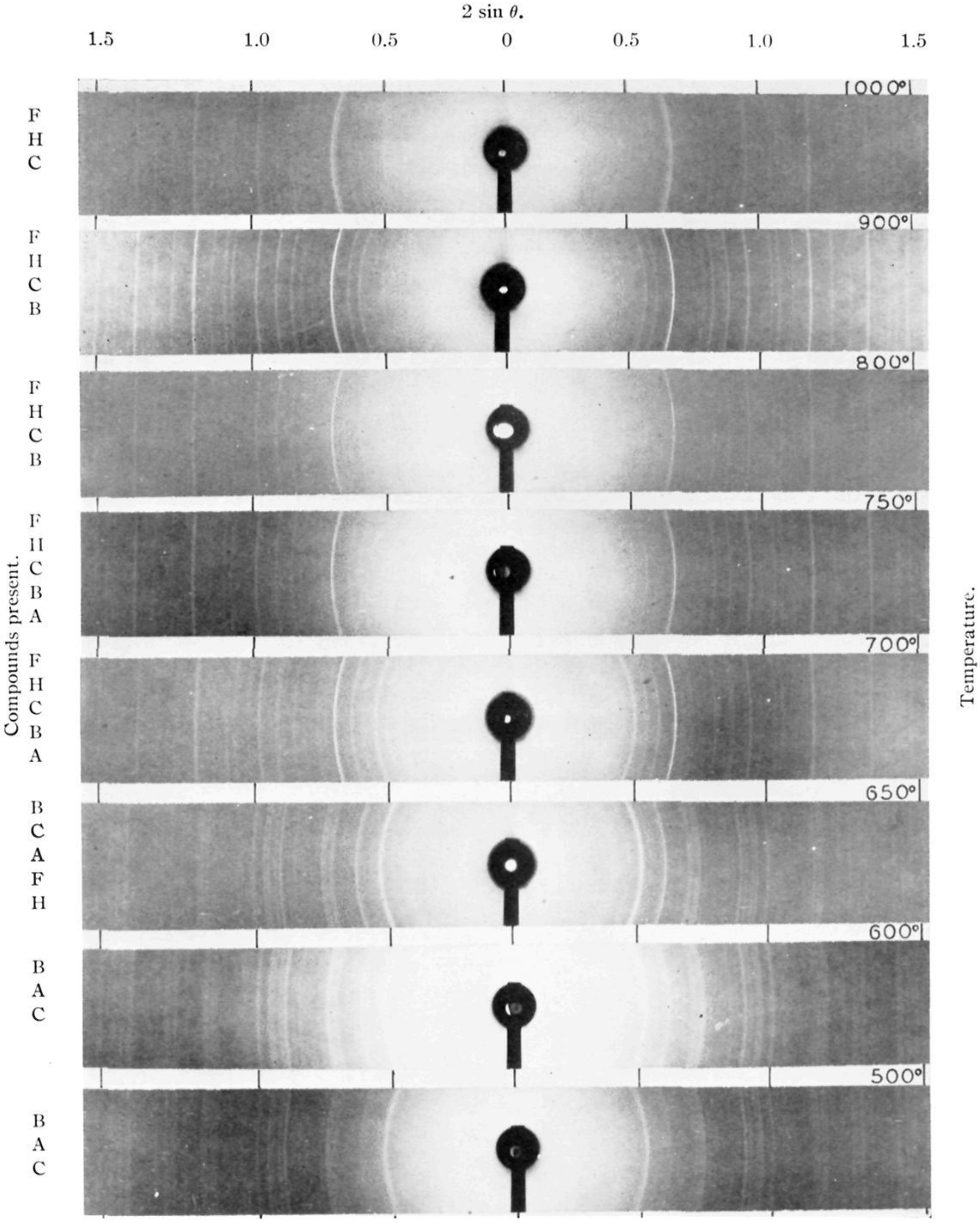

Plate I.—X-Ray diffraction patterns of products obtained at various temperatures from barium carbonate–ferric oxide mixtures containing 70% ferric oxide: A, ferric oxide; B, barium carbonate; C, barium oxide; D, $BaO\cdot 2Fe_2O_3$; E, $BaO\cdot 6Fe_2O_3$; F, $Ba_8Fe_8O_{21}$; H, extra lines in pattern of F.

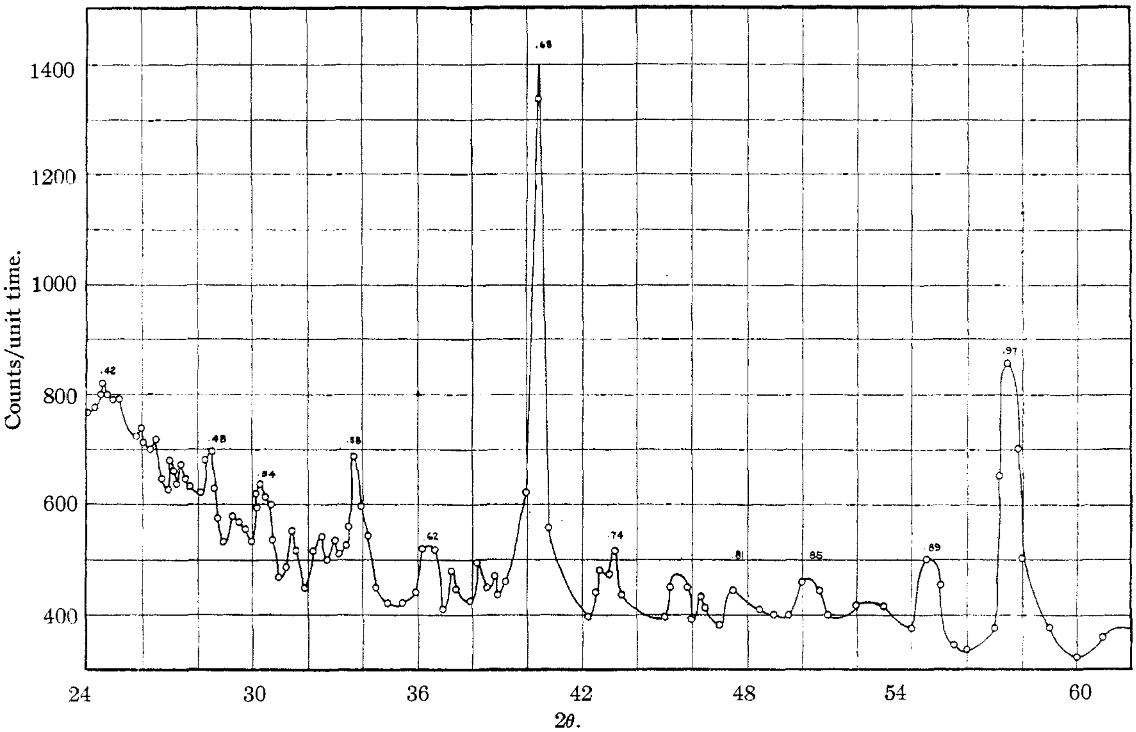

Fig. 1.—Partial diffraction pattern of the product at 800° from $BaCO_3 + Fe_2O_3$. The numbers at the peaks are d^* values.

attributed unequivocally to each of the phases was selected. Overlapping lines were avoided so that it was not always possible to choose the strongest reflection. The d^* values of the selected lines are shown in Table I.

The intensities of the reflections at these d^* positions were then determined for all the products using the X-ray spectrometer, where the accuracy was about 1% for any one observation and about 5% for different runs. The general method used in recording the intensities of these lines is illustrated in Fig. 2 where the Geiger count of the barium carbonate line ($d^* = 0.75$) is compared for products obtained at different temperatures.

A more careful study of the spacing of the lines in the back-reflection patterns revealed no appreciable shifts in the reflections, and it was therefore not necessary to consider intersolubility limits. The range of temperatures and mixture composition within which each compound is formed was estimated by plotting the intensity of the selected line of each family against the com-

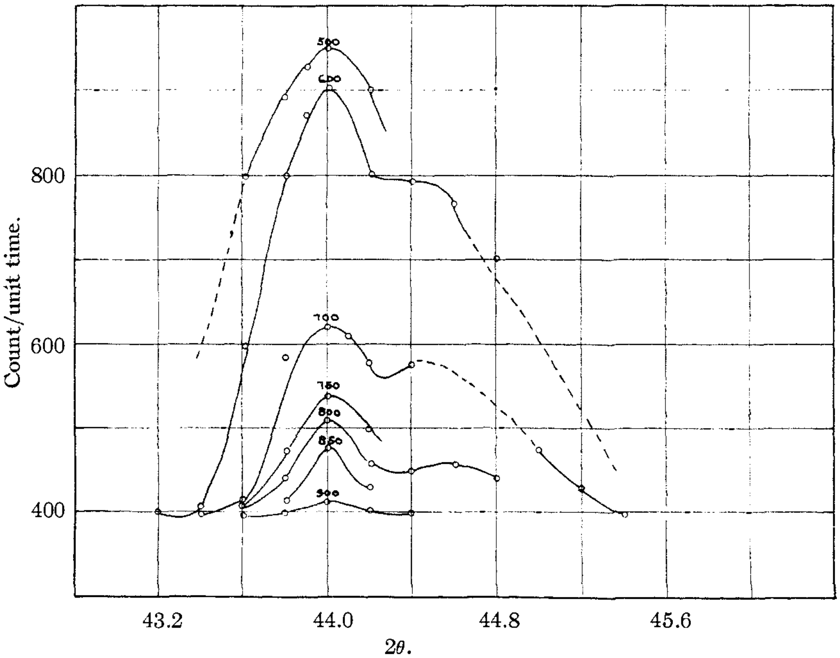

Fig. 2.—Intensity of barium carbonate line ($d^* = 0.75$) in mixtures containing 55% barium carbonate and 45% ferric oxide heated at temperatures ranging from 500 to 900°.

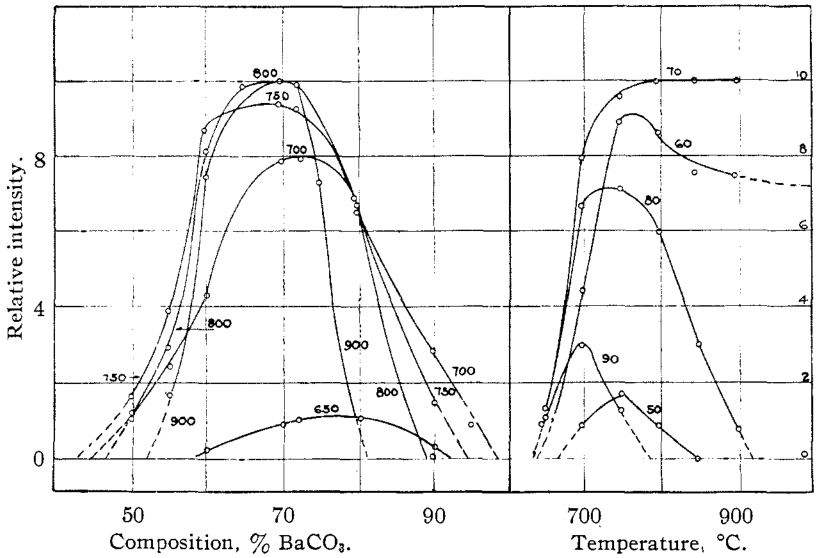

Fig. 3.—Variation in intensity of $Ba_8Fe_8O_{21}$ line $d^* = 0.68$ with composition of mixture and temperature of preparation.

position of the original mixture and extrapolating to zero intensity. This is illustrated by Fig. 3 where the variation of the intensity of the line, $d^* = 0.68$, is shown. This is taken as representing the variation in concentration of Compound F. The curves on the left show the change in relative intensity with composition of original mixture while those on the right illustrate the change with temperature of preparation.

Results

I. Conditions for Formation of Compounds

In order to study the change in concentration of each phase as a function of original mixture composition and temperature of preparation, it was found convenient to use contour diagrams. The ordinates represent temperature of preparation and the abscissa the composition of the original mixture. Points of equal concentration are located from the intensity-temperature and intensity-composition graphs (such as Fig. 3), and a smooth line drawn through them. The method is illustrated in Fig. 6 where the set of curves at the right is derived from those in Fig. 3. Inspection of such diagrams reveals at a glance not only the limit of formation of this component but its approximate relative concentration throughout the area of formation.

The contour diagrams (Figs. 4, 5 and 6) show the regions of existence of the main compounds formed in the reaction. These are barium oxide, $BaO \cdot 6Fe_2O_3$ (E), $BaO \cdot 2Fe_2O_3$ (D), and the compound whose idealized formula is $BaFeO_3$ (F).

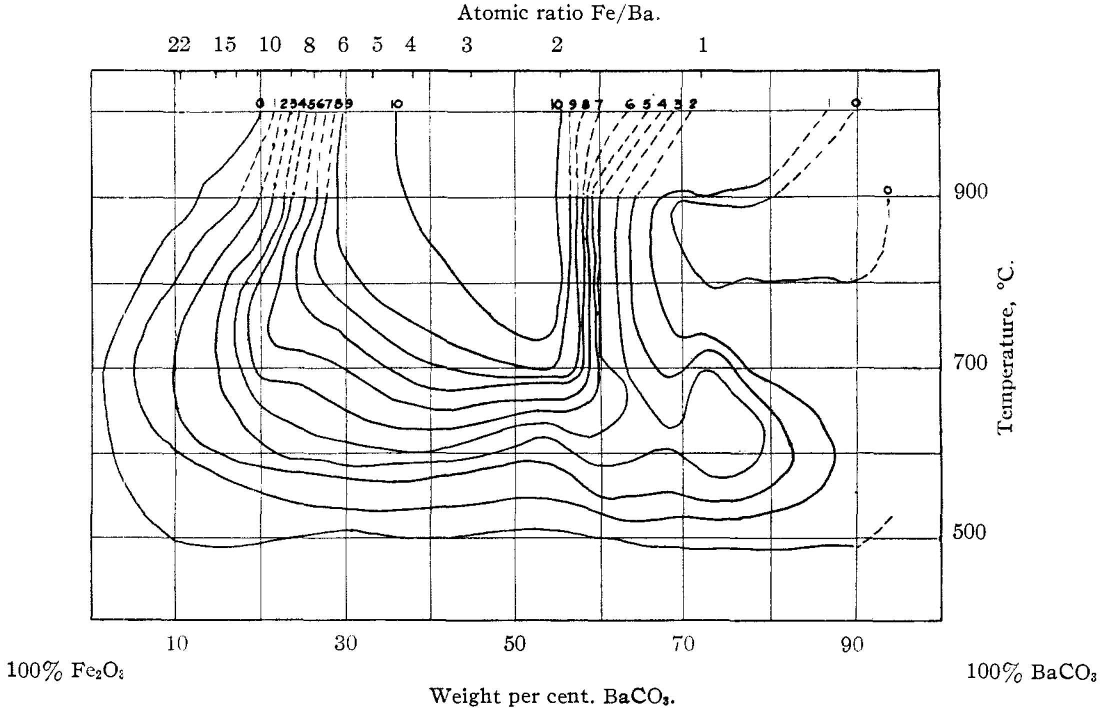

Fig. 4.—Variation in concentration of barium oxide with composition of mixture and temperature of preparation.

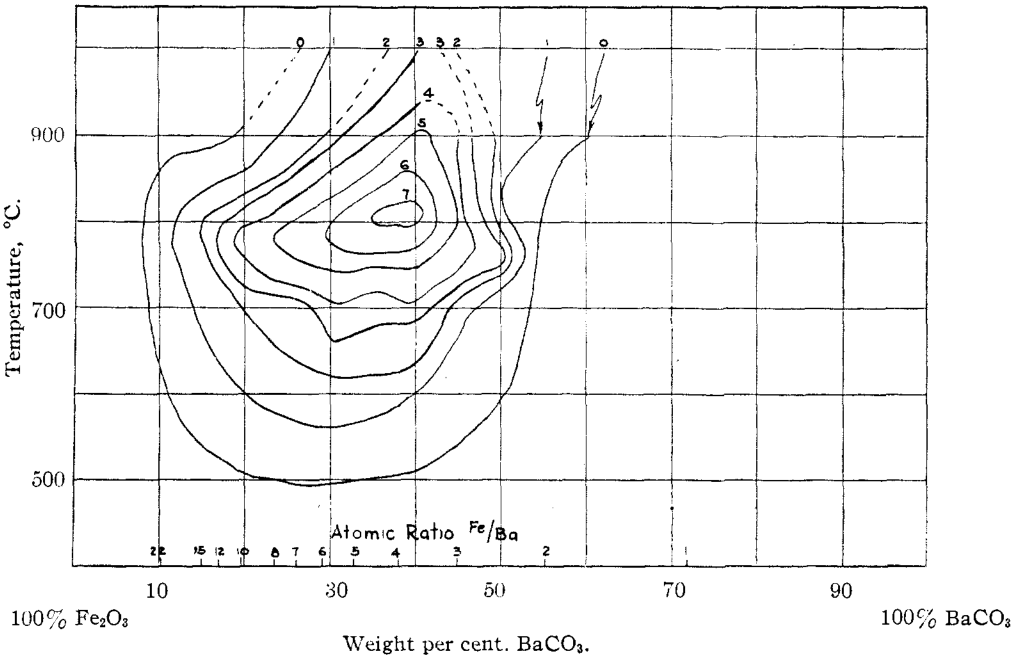

Fig. 5.—Variation in concentration of $BaO \cdot 2Fe_2O_3$ with composition of mixture and temperature of preparation.

Besides these definite phases some evidence was obtained for the existence of another phase formed in the region below 10-750 to 20-750. The characteristic line for this phase is $d^* = 0.48$ but the low intensity of the reflections did not permit of certain identification.

The preparations obtained in the area below 80-750 to 99-750 gave no unknown lines in the diffraction patterns. The stability of the products in moist air and their initial color, however, suggest that some significant changes had occurred. It is interesting to note that products obtained in the region above 80-750 to 99-750 gave very poor diffraction patterns in which two new lines, $d^* = 0.64$, and $d^* = 0.66$, were obtained. It is possible that these might be attributable to barium

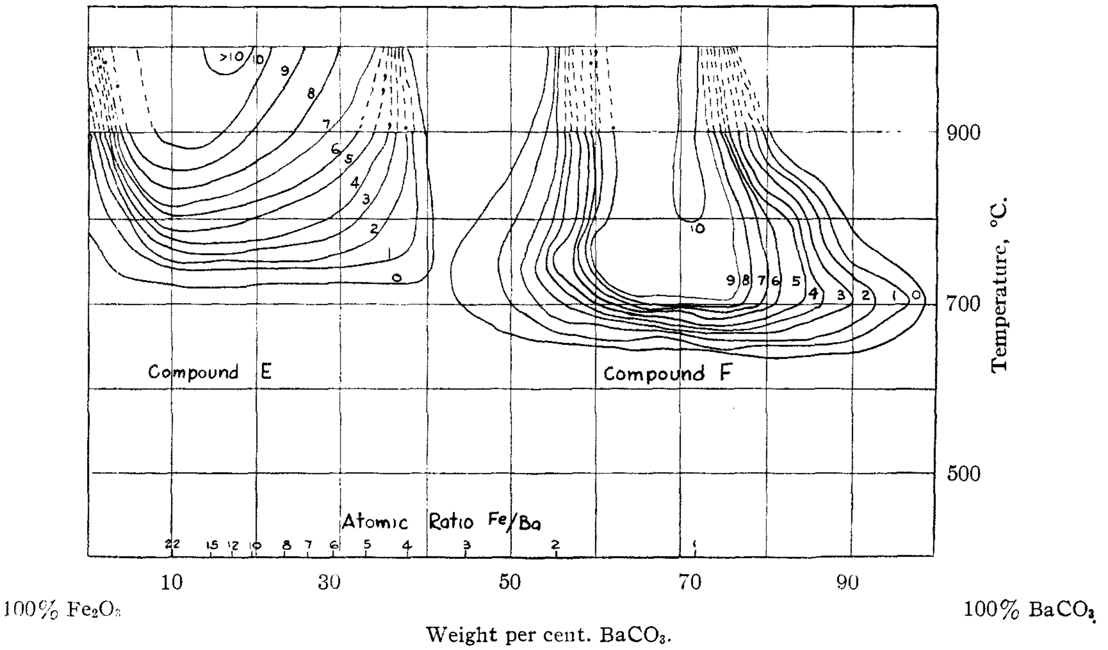

Fig. 6.—Variation in concentration of $BaO \cdot 6Fe_2O_3$ (E) and $Ba_8Fe_8O_{21}$ (F) with composition of mixture and temperature of preparation.

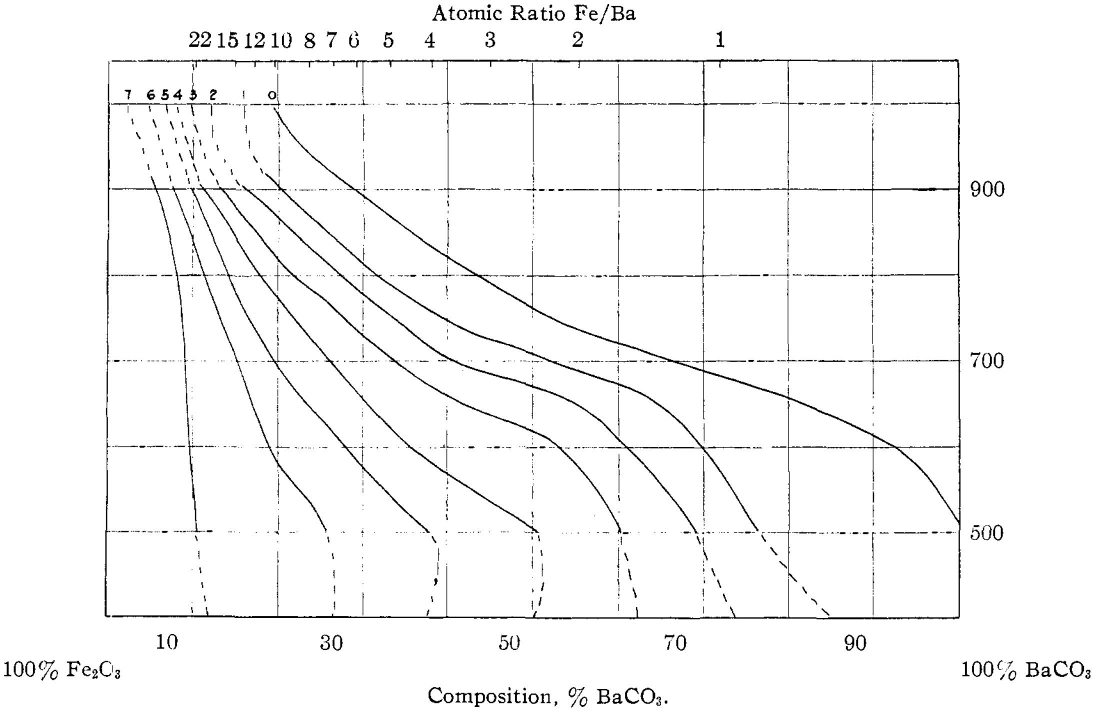

Fig. 7.—Variation in concentration of ferric oxide with mixture composition and heating temperature.

carbonate which undergoes crystallographic modification above 800°.

The following information concerning the formation of the four main products of the reaction can be derived from the contour diagrams.

1. **Barium Oxide.**—The widespread formation of barium oxide at temperatures above 525° is shown in Fig. 4. Maximum concentration is reached above the line 36-900 to 55-750 while little or no barium oxide is found above the line 70-750 to 90-500 or in the area above 0-600 to 20-1000. The rate of change in barium oxide concentration is slow in some directions for example along the line 40-500 to 40-800 and is rapid from 55-800 to 60-800 or from 18-900 to 30-900.

It is of some interest to correlate these facts concerning barium oxide with the conditions of formation of the other compounds.

2. **Compound D: $BaO \cdot 2Fe_2O_3$.**—Superposition of Fig. 4 upon Fig. 5 shows that barium oxide is coexistent with this compound and that, with rising temperature and increasing proportions of the barium carbonate up to 40%, the concentration of each compound increases. This would suggest that the two compounds may be formed simultaneously perhaps by the decomposition of the thermally unstable substance whose detection has been referred to above.

In the region of maximum concentration of barium oxide there is a definite decrease in the formation of D with rising temperature and with increasing proportions of barium carbonate.

The change in concentration of D also seems to be related to that of compounds E and F (compare Fig. 6 with 5). Along the line 12-1000 to 40-800 the concentration of E decreases while that of D increases. Likewise from 60-800 to 40-800, the concentration of F decreases while D increases.

3. **Compound E: $BaO \cdot 6Fe_2O_3$.**—No evidence from X-ray analysis was obtained for the formation of this substance below 750° or in the products from any mixture containing more than 40% of barium carbonate (see Fig. 6). Within the limits of observation, the region of maximum concentration is in the neighborhood of 18-1000. The decrease in concentration of E appears to be rather slow from 15-900 to 30-900 and rapid from 30-900 to 40-900 while the concentration of barium oxide increases rapidly from 15-900 to 30-900 and changes very little thence to 40-900. One would suspect that the formation of barium oxide, in mixtures containing less than 50% barium carbonate, was more closely associated with the formation of D than with that of E.

4. **Compound F: $BaFeO_3$** (idealized formula).—Evidence for the existence of compound F at about 700° in the products from all mixtures containing 50 to 97% barium carbonate is shown in Fig. 6. The range of mixtures giving rise to F narrows considerably with increasing temperature of preparation, however, and its presence was detected only in 55 to 80% mixtures at 900°. The maximum concentration was reached in a narrow region above 70-800 to 72-800. In this region, the barium oxide concentration is at a minimum.

Figures 7 and 8 represent the contour diagrams for ferric oxide and barium carbonate respectively so that Figs. 4 to 8 present all the necessary in-

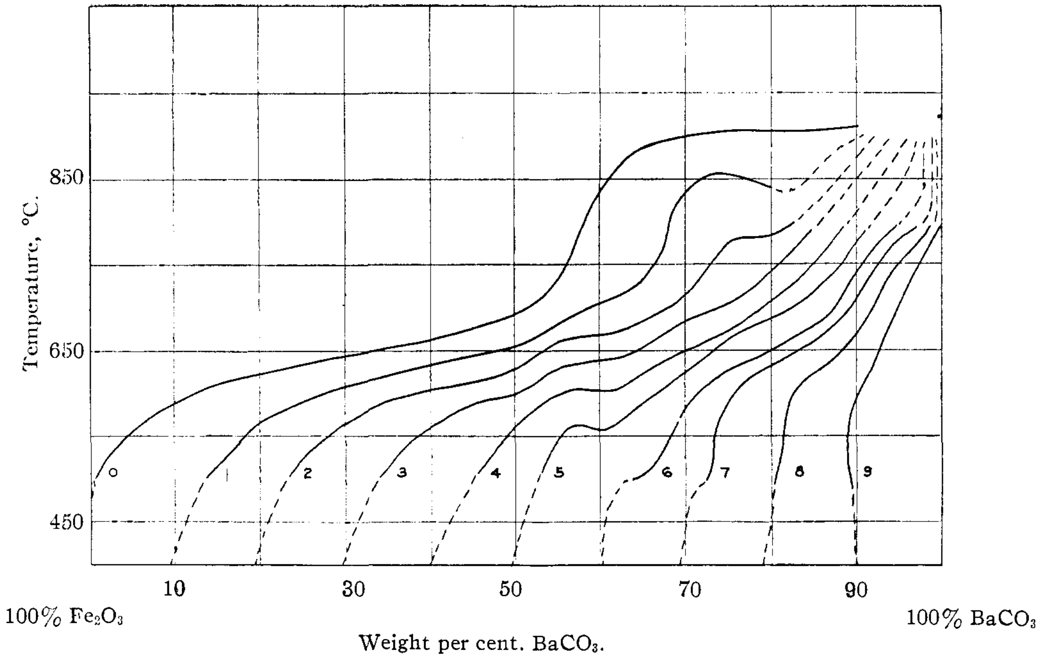

Fig. 8.—Variation in concentration of barium carbonate with mixture composition and heating temperature.

formation concerning the main ingredients of the products. Certain other facts follow from these diagrams.

$BaO·6Fe_2O_3$ is obtained free from ferric oxide and barium oxide when prepared from a mixture containing 20% barium carbonate by heating at 1000°. $BaO·2Fe_2O_3$ is best prepared by heating a mixture containing 36% barium carbonate at 800°. It always contains a considerable amount of barium oxide and probably a trace of $BaO·6Fe_2O_3$, but no barium carbonate or ferric oxide.

$BaFeO_3$ is obtained, substantially free from barium oxide, ferric oxide and barium carbonate by heating mixtures containing 72% barium carbonate at 850°.

Mixtures containing equal weights of barium carbonate and ferric oxide when heated at 900° give rise to barium oxide and $BaO·2Fe_2O_3$. None of the other substances are detectable in products prepared in this way.

II. Structure of Compounds Formed

Compound D.—It has been noted that the probable composition of this compound is $BaO·2Fe_2O_3$. The lattice spacings are listed in Table II. Since relatively few lines are obtained and since the majority of these are rather weak, it is not possible to arrive at any definite conclusion regarding the structure.

It should be pointed out that the composition assigned to this compound is advanced only on the evidence that the maximum intensity of its main diffraction line occurs at an atomic ratio Fe/Ba = 4. The evidence would be more convincing were it not that according to X-ray diagrams there is also a high concentration of barium oxide at this point and no evidence of any free ferric oxide. The compound may, therefore, contain more iron than is represented by $BaO·2Fe_2O_3$. No evidence was found for the compound $BaO·Fe_2O_3$.

TABLE II

d, Å.	I	Remarks
4.65	M	Also E (?)
3.80	V.V.W.	
3.41	M	
2.30	V.W.	
2.26	V.V.W.	
2.11	M	Also E
2.02	M	
1.63	St	Also BaO
1.347	W	?

Structure of Compound E.—Adelsköld established the structure of the compound $BaO·6Fe_2O_3$ by comparison with $PbO·6Fe_2O_3$ which he was

TABLE III

$PbO·6Fe_2O_3$		Compound E	
d, Å.	I	d, Å.	I
3.30	w	3.40	v.w.
2.96	m	2.93	m-
2.90	w	2.89	v.w.
2.73	St	2.77	St
2.64	St	2.62	St
2.40	m	2.39	m
2.30	w	2.31	v.w.
2.25	St	2.25	m-
2.14	m	2.11	m-
1.69	w		
1.67	St	1.67	St
1.64	m	1.63	St
1.47	St	1.46	St

able to obtain in large crystals. The X-ray diffraction data for magneto-plumbite ($PbO \cdot 6Fe_2O_3$) and compound E compared in Table III, suggests the identity of Compound E with $BaO \cdot 6Fe_2O_3$ and in a sense corroborate Adelsköld's results.

It has been drawn to our attention[10] that the ferrite $BaO \cdot 2Fe_2O_3$ might conceivably be related to the $BaO \cdot 6Fe_2O_3$, just as the mineral plumboferrite, supposedly $PbO \cdot 2Fe_2O_3$ is related to magneto-plumbite $PbO \cdot 6Fe_2O_3$. There is considerable overlapping of lines of D and E (see Tables II and III) which appears to be a characteristic of the two lead compounds. There is also considerable overlapping of the regions of existence of the two ferrites (see Figs. 5 and 6).

Compound F.—Preliminary examination of the lines attributed to this compound (see Table IV) suggests that it has a cubic structure. All the observed lines can be explained on the assumption of a primitive cell having a = 8.05 Å. From previous chemical analysis and the intensity contours, the atomic ratio of barium and iron is unity. The work of Struthers[3] and of Rosenstein[4] showed that the valence number of the iron is greater than three.

If we assume tetravalent iron, the formula becomes $BaFeO_3$. All of this points to the perowskite structure,[11] which, however, would call for a unit cell of dimension 4.02 Å. All the intense lines of the pattern can be explained by this smaller unit cell and their intensities are in the correct order.[12] But, many weaker lines are present which can only be explained on the basis of the larger unit cell.

A slight, but noticeable, decrease in relative intensity of the lines d(Å.) = 3.35, 2.17, 1.472, 1.338, occurs in the products as the temperature of preparation is raised above 850°. The complete elimination of these lines would indicate a face-centered structure of unit cell dimension a = 8.05 Å. While the change in relative intensity of the lines might be taken as an indication of the presence of two compounds, this explanation does not seem correct since it is unlikely (1) that two compounds would exist together over such a wide temperature range and that (2) all of the lines observed could be explained by one primitive cell. An alternative explanation can be advanced which accounts for all the observed facts.

The large unit cell contains eight perowskite-like units. Each of these units in the ideal situation is a cube with barium ions at each corner, an iron ion at the center and oxygen ions at the face-center position. Barium is therefore in 12-fold coördination with respect to oxide ions. In such an ideal structure, iron must have a valence number of four assuming that that of barium remains two. Since the valence number of iron in this compound seems to be stabilized at about 3.3, we must conclude that some oxide ions are missing from the lattice. The large unit cell in ideal form would correspond to the formula $Ba_8Fe_8O_{24}$ where the valence number of iron is four. Since the valence number is about 3.3 the formula should be nearly $Ba_8Fe_8O_{21}$, which would mean that the large unit cell is lacking three oxide ions.

TABLE IV

UNIT CELL DIMENSION OF $Ba_8Fe_8O_{21}$

		a = 4.02 Å. $h^2 + k^2 + 1^2$		a = 8.05 Å. $h^2 + k^2 + 1^2$	
d, Å.	I	Calcd.	Obs.	Calcd.	Obs.
4.65	0.001			3	3.00
4.02	0.001	1	1.01	4	3.98
3.35	1			6	6.01
2.83	10	2	2.02	8	8.08
2.42	0.1			11	11.06
2.31	0.4	3	3.04	12	12.07
2.17	0.5			14	13.76
2.01	5	4	4.04	16	15.87
1.84	1			19	19.10
1.79	1	5	5.02	20	20.22
1.71	0.1			22	22.17
1.65	6	6	5.96	24	24.23
1.54	0.5			27	27.32
1.472	0.01			30	29.90
1.427	6	8	8.03	32	31.87
1.356	0.01			35	35.25
1.338	0.1	9	9.11	36	36.19
1.311	0.3			38	37.70
1.268	3	10	10.14	40	40.29
1.208	1	11	11.17	44	44.40
1.185	0.8			46	46.15
1.155	0.3	12	12.21	48	48.58
1.123	0.01				
1.071	10				
1.045					

Moreover, since the diffraction pattern shows the presence of an ordered structure, it is probable that the vacant spaces in the lattice are distributed in an orderly fashion. It is very likely that these holes will take positions in each large cell in such a manner as to be as far apart as possible. In any event the removal of the oxide ions would cause a redistribution of the bond energies in the cell with consequent shifts in the positions of the other atoms. The direction and magnitude of these shifts could not be determined from the data at hand. Such defect structures are not uncommon. Pyrrhotite is a mineral having the approximate composition FeS but it always contains sulfur in considerable excess. It is now known that the lattice is deficient in iron. Many other examples, such as silver iodide, γ alumina,[13] can also be given.

The anomalous behavior of the intensity of certain lines in the patterns of the products prepared at the higher temperature can be explained by considering the effect of heat on this structure.

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(10) Private communication from Dr. Cutler D. West, Polaroid Corporation, Cambridge, Mass.

(11) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., Inc., 1931.

(12) Ludo K. Frevel, *Ind. Eng. Chem., Anal. Ed.*, **16**, 209 (1944); **14**, 687 (1942).

(13) R. C. Evans, "An Introduction to Crystal Chemistry," Cambridge, 1939.

Application of thermal energy may induce further redistribution of the "holes" in such a manner that at high temperatures the lattice becomes pseudo face-centered. It is also possible that at the higher temperatures a further loss of oxygen occurs, giving rise to a minor modification in the ionic arrangement but leaving the main features of the structures intact.

Summary

Over one hundred preparations were made by heating mixtures of barium carbonate and ferric oxide whose composition ranged from ten to ninety-nine per cent. barium carbonate. The temperate range was from 500 to 1000°. The composition of the products was determined by means of X-ray analysis.

1. Evidence is found for the formation of a compound having a perowskite-like structure from all mixtures containing fifty to ninety-five per cent. barium carbonate. The composition of this compound is probably represented by $Ba_8Fe_8O_{21}$, the lattice being deficient in oxygen. A unit cell (a = 8.05 Å) containing eight perowskite units best explains the diffraction pattern of this substance.

2. Barium oxide is formed from mixtures with a wide range of composition and is produced in maximum concentrations above 800° for compositions between forty and fifty per cent. barium carbonate.

3. $BaO{\cdot}2Fe_2O_3$ is formed above 550° from mixtures containing between ten and fifty per cent. barium carbonate. Maximum formation occurs at forty per cent. barium carbonate and 800°. The interplanar spacings and intensities of the reflections are recorded for the first time.

4. $BaO{\cdot}6Fe_2O_3$ is formed above 750° from all mixtures having barium carbonate content between five and forty per cent. The diffraction pattern was checked with literature values for a compound prepared at 1100°.

5. X-Ray evidence indicates that an unstable or poorly crystallized phase is present in mixtures containing ten to twenty per cent. barium carbonate which have been heated at temperatures below 750°.

6. Contour diagrams have been shown to be useful in correlating data involving changes of concentration of compounds with composition of mixture and temperature of preparation.

BROOKLYN, N. Y. RECEIVED MARCH 18, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Catalytic Properties of the Products of the Solid Phase Reaction between Barium Carbonate and Ferric Oxide[1]

BY MICHAEL ERCHAK, JR., AND ROLAND WARD

Substances which have been prepared by the interaction of solids in absence of a flux are usually in a very finely divided state provided the temperature of preparation is well below the melting points of any of the reactants or products or their mixtures. Such materials are in very suitable physical condition to act as catalysts and this property has been the subject of many investigations. Hüttig[2] and his students have published many papers on so called "active oxides," which are prepared by solid phase reaction. The results of investigations of this kind on zinc and cadmium ferrites have been taken to indicate that products obtained under conditions in which there is incipient formation of compounds have superior catalytic activity. It was further observed that the more extensive the formation of cadmium ferrite the poorer was the catalytic activity.

An investigation of the products of interaction of barium carbonate and ferric oxide has been reported.[3] This paper describes an investigation in which some correlation is sought between the catalytic activities of these products and their composition as revealed by X-ray analysis.

Experimental

The procedure followed was similar to that of Lamb, Bray and Frazer[4] in which the catalysis of the oxidation of carbon monoxide by oxygen was used as a criterion of relative catalytic activity. One gram of the catalyst was placed in an 8-mm. Pyrex tube and was held in contact with a thermometer bulb by means of glass wool plugs. The tube was placed in a furnace in such a way that the gas which passed over the catalyst was pre-heated. The furnace was adjusted to 325° and dry oxygen was first passed through the catalyst bed to cause activation. A dry mixture of carbon monoxide with excess oxygen (free from carbon dioxide and hydrogen) was then passed over the catalyst at a constant rate. The carbon dioxide formed in the catalyst chamber was absorbed in ascarite and weighed. The remaining carbon monoxide was oxidized by passing the residual gas mixture through a tube filled with Hopcalite maintained at 150°, absorbed in ascarite and weighed. The percentage conversion of carbon monoxide to carbon dioxide by the catalyst could thus be determined.

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(1) Abstracted from a thesis submitted by Michael Erchak, Jr., in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate School of the Polytechnic Institute of Brooklyn, 1945.

(2) G. F. Hüttig, J. Funke and H. Kittel, *Z. Elektrochem.*, **40**, 306 (1936); G. F. Hüttig, *et al.*, *Acta Physicochim.*, **2**, 129 (1935).

(3) M. J. Erchak, I. Fankuchen and R. Ward, THIS JOURNAL, **68**, 2085 (1946).

(4) A. B. Lamb, W. C. Bray and J. C. W. Frazer, *J. Ind. Eng. Chem.*, **12**, 217 (1920).