

density data in dilute potassium ferrocyanide solutions.

For a 1-4 electrolyte, the limiting law of the theory for the diffusion coefficient is

$$D = D_0 - s(D)\sqrt{c} \quad (5)$$

where

$$D_0 = 11.1705 \times 10^{10} T \left(\frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right) \quad (6)$$

and

$$s(D) = \frac{29.679 \times 10^{-3}}{D^{3/2} T^{1/2}} \left(\frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right) + \frac{2.9117 \times 10^{-8}}{\eta_0 D^{1/2} T^{1/2}} \left(\frac{4\lambda_1^0 - \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \right)^2 \quad (7)$$

For potassium ferrocyanide at 25°, these equations yield

$$D \times 10^6 = 1.4731 - 10.925\sqrt{c} \quad (8)$$

The values of the diffusion coefficient computed by equations (1) to (3) and given in the third column of Table I agree surprisingly well with the observed results. In Fig. 1, the diffusion coefficient is plotted against the molar concentration. The upper curve represents the values obtained from the complete theory. The middle graph is ob-

tained when the mobility term, $(3\pi/c)$, is constant and equal to its value when c equals zero. The difference between the upper and middle curves represent the contribution of electrophoresis. The lowest curve represents the limiting law.

It would be presumptuous to take too seriously the agreement between theory and experiment for an electrolyte as complicated as potassium ferrocyanide since the calculated values are derived by a theory which assumes complete dissociation. Such a calculation involves only the mean mobilities of the ions, K^+ and $Fe(CN)_6^{4-}$. A completely detailed computation would require a knowledge of the degrees of dissociation and mobilities of other ions such as $KFe(CN)_6^{3-}$, $K_2Fe(CN)_6^{2-}$ etc. which are probably present and this information is not available. A second difficulty resides in the long extrapolation required to evaluate the thermodynamic term due to lack of information regarding the activity coefficient of potassium ferrocyanide in dilute solution. However, it may be stated that there is evidence that the experimental observations approach the expected theoretical values as the concentration approaches zero.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Barium Cobalt Oxide of the Perovskite Type^{1,2}

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The system barium-cobalt-oxygen was studied over the temperature range 500 to 1300°. Three distinct new phases were found by means of X-ray and chemical analysis. The formulas assigned to these phases are $BaCoO_{2.72}$, $BaCoO_{2.31}$ and $BaCoO_{2.23}$. The latter has the perovskite structure.

The reaction of cobalt oxides with barium peroxide was studied by Hedvall and von Zweiberg⁵ by means of heating curves from which they concluded that a reaction occurred and suggested that a cobaltite was formed. The composition of the product was not determined. Some previous investigations⁶⁻⁹ in this Laboratory established that ternary compounds in this system were formed in which the average valence of the cobalt in the reaction products was greater than 3. X-Ray analysis showed that more than one new phase was formed. The expected perovskite type structure was not obtained in these investigations although this is readily obtained when lanthanum is substituted for barium.¹⁰ The results reported here offer

an explanation of the barium-cobalt-oxygen system within a limited composition range.

Experimental

The materials used were Baker analyzed C.P. chemicals. Intimate mixtures of barium nitrate and cobaltous nitrate were heated in platinum boats in an atmosphere of oxygen at constant temperatures over a temperature range of 500 to 1300°. The products were examined with X-rays and the average valence of the cobalt was estimated by determining the amount of chlorine liberated on dissolving a sample in dilute hydrochloric acid.

It was found that mixtures, in which the barium to cobalt atomic ratios were greater than one, gave products the diffraction pattern of which contained the lines of barium oxide. The barium oxide could be extracted with water leaving a residue in which $Ba/Co = 1$. When the barium to cobalt atomic ratio in the starting mixture was less than one, the product gave the lines of Co_3O_4 in the diffraction pattern. With equimolar mixtures the diffraction patterns of the products obtained by prolonged heating above 650° corresponded to new phases. Attempts to prepare a cobalt compound analogous to $BaO \cdot 6Fe_2O_3$ ¹¹ were not successful.

The product obtained by heating the equimolar mixture of barium nitrate and cobaltous nitrate at 650°, an opaque material with a metallic luster, gave an average oxidation number for cobalt of 3.44. The spacings from the diffraction pattern correspond to a cubic structure with a primitive cell $a = 4.82 \text{ \AA}$. and are listed in Table I. The measured density of the product was 3.72 g./cc. which is about 5.4% higher than the calculated density based on the formula $BaCoO_{2.72}$. Virtually no change occurred upon

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(3) National Bureau of Standards, Washington, D. C.

(4) University of Connecticut, Storrs, Connecticut.

(5) J. A. Hedvall and N. von Zweiberg, *Z. anorg. Chem.*, **106**, 119 (1919).

(6) N. G. Wittenbrock, M.S. Thesis, 1940.

(7) F. C. Brenner, M.S. Thesis, 1942.

(8) R. C. Ryder, B.S. Thesis, 1943.

(9) S. W. Strauss, B.S. Thesis, 1944.

(10) F. Askham, I. Fankuchen and R. Ward, *THIS JOURNAL*, **72**, 8799 (1950).

(11) M. Erchak, Jr., I. Fankuchen and R. Ward, *ibid.*, **68**, 2085 (1946).

heating this product in oxygen at 700° but, when the temperature was raised to 760°, the appearance of a new phase was observed.

Two additional weak lines were obtained in the diffraction pattern corresponding to $d = 3.336$ and $d = 2.838$ lying between the strongest lines ($d = 3.399$ and $d = 2.786$) of the low-temperature phase. The product at 820° gave a diffraction pattern in which these four lines were of about equal intensity but that obtained at 900° appeared to consist entirely of the second phase. The pattern contained none of the lines of barium oxide or cobalt oxides. The average oxidation number of the cobalt was 2.62. The pattern for this second phase (see Table I) does not correspond to a cubic lattice. Because of the proximity of its strong lines with those of the low temperature phase, it appears likely, however, that the phases are structurally similar. The formula assigned to the phase which is stable at 900° is $\text{BaCoO}_{2.31}$.

In the temperature range from 1000 to 1300° a third phase appeared. Prolonged heating (1300°) gave a uniform product in which the oxidation number of the cobalt was found to be 2.46. The diffraction pattern corresponded to a cubic structure ($a = 4.072$ Å.) of the perovskite type (see Table I). The formula assigned to this phase is $\text{BaCoO}_{2.23}$. The density was found to be 5.62 which is about 0.88% lower than the calculated density.

By heating $\text{BaCoO}_{2.72}$ *in vacuo* at 700° for several hours a mixture of this phase and $\text{BaCoO}_{2.31}$ is obtained while at 820° *in vacuo* a mixture of $\text{BaCoO}_{2.31}$ and $\text{BaCoO}_{2.23}$ is obtained.

Discussion

There are two implications in these results to which some attention should be given. The first is that no evidence was found for the presence of a typical non-stoichiometric phase. No observable

TABLE I

X-RAY DIFFRACTION PATTERNS FOR COMPOUNDS IN THE BARIUM-COBALT-OXYGEN SYSTEM
The relative intensities of the more pronounced reflections are indicated in parenthesis

$\text{BaCoO}_{2.72}$, d ($a = 4.82$ Å.)	$\text{BaCoO}_{2.31}$, d ...	$\text{BaCoO}_{2.23}$, d ($a = 4.072$ Å.)
8.42	3.336 (1)	4.073 (3)
3.72	2.838 (1)	3.151
3.399 (1)	2.453	2.883 (1)
2.786 (1)	2.252 (3)	2.440
2.597	2.159 (1)	2.347 (3)
2.421	2.047 (3)	2.174
2.396	1.995	2.125
2.159 (1)	1.962	2.034 (2)
2.017	1.882	1.822 (3)
1.962	1.763 (3)	1.658 (2)
1.808	1.72 (2)	1.631
1.705 (2)	1.658 (5)	1.501
1.611	1.639 (5)	1.438 (3)
1.514	1.613	1.357
1.451	1.537	1.287 (3)
1.398	1.494	1.226
1.342	1.463	1.178
1.291	1.433 (2)	1.133
1.205	1.419 (2)	1.089 (3)
1.168	1.395	
1.140	1.363	
1.103	1.349	
1.08	1.322 (4)	
1.055	1.307 (4)	
1.026	1.281 (5)	
	1.200 (5)	
	1.187 (5)	
	1.168 (4)	
	1.097 (5)	
	1.074 (5)	

change in the interplanar spacings occurred in any of the phases. The gradual lowering of the oxidation state of cobalt with rising temperature is to be explained by the coexistence of varying proportions of two distinct phases each of quite definite composition. The formulas of these phases are assigned on the assumption based on evidence from diffraction patterns that the phases analyzed were reasonably pure. It can only be asserted that in the low temperature phase $\text{BaCoO}_{2.72}$ represents the minimum value for oxygen content and in the high temperature phase $\text{BaCoO}_{2.23}$ represents a maximum value for oxygen content since both of these might have been contaminated by small amounts of the intermediate phase.

The perovskite structure is obtained only when the composition becomes $\text{BaCoO}_{2.23}$. This means that the structure lacks about one-fourth of the oxide ions. A somewhat similar phenomenon was found in the case of iron in which the phase having the perovskite structure was given the formula $\text{Ba}_3\text{Fe}_3\text{O}_{21}$.¹¹

The achievement of the perovskite structure in the barium-iron-oxygen and barium-cobalt-oxygen systems appears to require progressively greater departures from the type formula ABX_3 . In the case of the iron compound it was thought that increased oxygen pressure might raise the oxygen content to the stoichiometric value but it is apparent from this investigation that an increase in the oxygen content in the cobalt system causes a change to another structure.

Taking the ionic radii for a coordination number 12 for $\text{Ba}^{+2} = 1.55$ and $\text{La}^{+3} = 1.32$, the tolerance factor (t) in the equation $r_A + r_0 = t \sqrt{2(r_B + r_0)}$ ¹² can be shown to be $t > 1.04$ for BaFeO_3 , $t > 0.98 < 1.05$ for BaCoO_3 , $t = 0.96$ for LaFeO_3 and $t \approx 0.98$ for LaCoO_3 . These were calculated using Pauling's values for ionic radii $\text{Fe}^{+3} = 0.60$, $\text{Fe}^{+2} = 0.75$, $\text{Co}^{+2} = 0.72$,¹³ and assuming that the radius of Co^{+3} is about 0.58. The values of t for BaFeO_3 and BaCoO_3 are appreciably higher than that for BaTiO_3 which is 1.00 using Pauling's value for the radius of Ti^{+4} . Apparently the ionic radii of Fe^{+4} and Co^{+3} are too small relative to the radius of Ba^{+2} to permit a simple perovskite structure. It should also be noted that the radius ratios of Fe^{+4} and Co^{+3} to the oxide ion are close to the lower limit for a coordination number of 6. The compromise apparently reached in the compounds $\text{BaFeO}_{2.63}$ and $\text{BaCoO}_{2.23}$ is to increase the size of the iron and cobalt ions by reduction of the valence, to lower the coordination number of these ions by removal of some oxide ions but to preserve the general features of the cubic perovskite structure. In the case of LaCoO_3 , the distortion of the structure to a rhombohedral modification of the perovskite structure¹⁰ may be due to the small size of the trivalent cobalt ion.

This explanation of these defect structure compounds based on the packing of ions is obviously

(12) For a discussion of the application of this equation see A. F. Wells, "Structural Inorganic Chemistry," second ed., Oxford Univ. Press, 1950, p. 375.

(13) Linus Pauling, "The Nature of the Chemical Bond," second ed., Cornell Univ. Press, Ithaca, N. Y., 1945, p. 350.

superficial since the metallic appearance of the substances indicates that the bonding is by no means ionic. It may serve, however, as a working hypoth-

esis in the preparation of analogous compounds of the transition metals.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE COLLEGE OF ENGINEERING OF THE OHIO STATE UNIVERSITY

High-temperature Reactions in the System Titanium Carbide-Boron Carbide¹

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Titanium carbide and boron carbide are shown to react at temperature above 1920° to produce titanium diboride, carbon and a higher boride of titanium of unknown composition.

With the development of interest in metal-impregnated refractory carbides as structural materials for jet engines, reactions in the solid state at high temperatures in such systems have assumed ever increasing importance. Whereas various indications that carbon may be removed from the initial carbide body by the impregnating metal phase to form new carbides have been observed, nothing as yet has been published which would indicate that two carbides may react with one another at high temperatures to form a new compound and free carbon. During our investigation of the binary system titanium carbide-boron carbide (TiC-B₄C) we have observed such a phenomenon. We have found that in this system at temperatures of the order of 2000° the reaction represented by the following equation takes place



Preparation of Materials.—Titanium carbide (TiC), 325 mesh, was obtained from Titanium Alloy, Mfg. Division of the National Lead Company. It analyzed Ti, 76.0; C, 20.0; Fe, 1.5; minor impurities 2.5%. Boron carbide (B₄C) #99, 400 grit, was obtained from the Norton Company. It analyzed, B, 78.0; C, 20.0; minor impurities 2.0%.

Five-hundred-gram lots of the crude carbides were wet-milled for 65 hr. in one-quart capacity hardened steel ball mills using steel balls. Methanol was used as the liquid medium. The milled carbides were dried in air and leached with 6 *N* hydrochloric acid. They were then washed with distilled water until free of acid and chloride, washed with methanol, dried in air and granulated through a 200 mesh screen. Particle size distributions in the finished products are given in Table I.

Particle size range, microns	Weight, %	
	TiC	B ₄ C
>20	0.5	3.7
20-10	2.0	2.3
10-5	10.9	26.5
5-1.6	63.2	60.6
<1.6	23.4	6.9

The moisture contents of the processed carbides were TiC, 0.05%, and B₄C, 0.06%. The titanium carbide contained no impurities detectable by X-ray diffraction. The boron carbide contained traces of graphite and FeC solid solution.²

Procedure.—Binary mixtures of the two carbides were prepared at 10% weight intervals. The proper weights of the carbides were wet-mixed for 12 hours in liquid methanol in small bottles packed in ball mills. The separate mixtures were then dried in air and granulated through a 32 mesh

screen. The granulated powders were pressed in a two-punch cylindrical steel die at 850 kg./cm.² The cylindrical specimens thus formed were approximately 1.25 cm. in diameter by approximately 0.75 cm. thick and weighed approximately 2.8 g. These samples were placed in rubber bags, the bags evacuated and the samples repressed hydrostatically at 2400 kg./cm.².

The pressed specimens were placed on thin discs of the same composition, then placed on graphite pedestals after which the assemblies were packed in a graphite crucible. The crucible and contents were placed in a vacuum desiccator which was then evacuated and flushed with argon, the cycle being repeated at least three times. The crucible was then removed and quickly placed in an induction furnace. The firing was carried out in a lamp-grade argon atmosphere using a seven-hour firing schedule. The maximum temperature was attained within six hours at a rate of increase of 350° per hour. All firings were held at the maximum temperature for one hour. Maximum firing temperature ranged from 1920 to 2150°.

To identify the phases present in the first specimens, X-ray diffraction analyses by the powder method were carried out. Molybdenum K_α radiation with a zirconium filter was used at 50 kv. and 20 ma. employing a 114.6 mm. Debye-Scherrer camera. Six hour exposures were used and intensities were estimated visually.

Results and Discussion.—In samples containing less than 60 weight per cent. of TiC, no TiC remained after firing. In samples containing less than 70 weight per cent. of B₄C no lines for that compound could be found for the fired specimen. Except in the case of pure TiC, carbon was found to be present in all fired specimens. The carbon was identified by its X-ray diffraction pattern. The 002 reflection was quite sharp and had an interplanar spacing of 3.36 Å. This seems to indicate that the carbon present was definitely crystalline.

With the exception of the interplanar spacings for TiC, B₄C and C, the interplanar spacings and their estimated intensities for eight fired binary mixtures are tabulated and available on microfilm.³ The majority of these "d" spacings can be grouped into two categories: (a) those whose intensities reach a maximum at about 60 to 70 weight per cent. of TiC, and (b) those whose intensities reach a maximum at about 30 weight per cent. TiC. The first category is designated as "II" in the table and the second as "X." Spacings of the "II" group correspond to titanium diboride, TiB₂. It is believed that the "X" spacings correspond to a boride TiB_x in which, judging from the B/Ti ratio, *x* has a value of the order of 10.

The structure of TiB₂ has been reported as being

(1) This investigation was carried out under USAF Contract No. 33 (038)-16911 between the Air Materiel Command and The Ohio State University Research Foundation.

(2) Konobejewski, *Z. Krist.*, **72**, 386 (1929).

(3) Order Document 3307 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D., C. remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.