

structure of the organic radical have a greater effect on the thermochemical properties of these solutions than the location of the amino group. Over most of the concentration range studied the ΦL_2 values for glycine solutions³ are negative. The addition of a methyl group in α -alanine and an ethyl group in α -amino-*n*-butyric acid are accompanied by large increments in ΦL_2 values. Only one case of radical isomerism is available for examination; the two methyl groups in α -amino-*i*-butyric acid seem to have a greater influence on the property measured than the normal radical. In the alanines and the four amino butyric acids, the location of the amino group seems to be the factor of least importance. The magnitude of the

ΦL_2 values for *dl*-valine solutions⁵ is in general agreement with these considerations.

Summary

The heats of dilution of aqueous solutions of α -amino-*i*-butyric, α -amino-*n*-butyric, β -amino-*n*-butyric, and γ -aminobutyric acids at 25° have been measured from 0.8 to 0.001 *m*. Linear equations for ΦL_2 as a function of *m* have been derived for each of the four acids. The slopes of these curves are as follows: α -*i* = 165; α -*n* = 128; β -*n* = 115; γ = 131. Relative partial molal heat contents of the solutes and the solvent have been evaluated.

PITTSBURGH, PA.

RECEIVED MARCH 7, 1946

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

Preparation and X-Ray Diffraction Studies of a New Cobalt Carbide¹

BY L. J. E. HOFER² AND W. C. PEEBLES³

At atmospheric pressure and 226–230° carbon monoxide and finely divided cobalt will react to form a product whose composition (9.3% carbon) corresponds to the formula Co_2C .⁴ The reaction is slow under the above conditions, requiring some five hundred hours to come to completion. The product reacts readily and completely with hydrogen at 240–250° to form cobalt metal and methane. When the temperature of carburization is higher than 230°, the rate of reaction is greater; furthermore, the amount of carbon deposited is not limited to 9.3% but increases without apparent restriction as long as the metal is exposed to carbon monoxide. The product so formed does not react completely with hydrogen at 240–250° to form methane and cobalt; instead a residuum of carbon remains, which reacts with hydrogen only at temperatures above 350°, and complete reaction of the carbon is not achieved even at 620°. The amount of carbon in the product which reacts readily with hydrogen at 240–250° or lower may equal but never exceeds the amount which corresponds to the formula Co_2C . Carbon may thus be deposited upon or in cobalt metal in two forms, which are quite sharply differentiated by the temperature ranges at which they react with hydrogen. No sample carburized above 315° contained appreciable amounts of carbon capable of hydrogenation at or below 250°. Bahr and Jessen called the easily hydrogenated carbon (capable of hydrogenation below 250°) "carbide carbon"; the residuum they called "free carbon." Bahr and Jessen infer that carbon combined with cobalt to

form a homogeneous phase is more highly reactive than free carbon. However, this homogeneous phase may be either a terminal solid solution of carbon in α -cobalt (hexagonal close-packed) or a carbide of a distinct crystal structure. Meyer⁵ made an X-ray diffraction study of cobalt carburized at various temperatures with illuminating gas. He concluded that the easily hydrogenated carbon produced by carburization in the 225–300°, range was held in solid solution in the interstices of the lattice of α -cobalt. However, he did find a distinct crystalline carbide isomorphous with cementite, Fe_3C , in samples carburized between 450–600°. The present paper will demonstrate that the easily hydrogenated carbon is combined with cobalt to form a distinct new crystalline species.

Experimental

Materials.—The carbon monoxide gas was prepared by the action of concentrated sulfuric acid on A. C. S. specification formic acid, density 1.2, at 120–150°. The gas was passed over solid sodium hydroxide pellets and stored in a gas-holder over water. It was then passed over calcium chloride, copper at red heat, soda lime, calcium chloride, and magnesium perchlorate.

Electrolytic hydrogen from tanks was further purified by passing over palladized asbestos at 300° and then successively over soda lime, calcium chloride, and magnesium perchlorate.

Nitrogen from tanks (99.7% pure), was passed over copper at red heat, soda lime, calcium chloride and magnesium perchlorate.

The cobalt oxide was prepared by precipitation. A 0.1 *M* solution of cobalt nitrate, A. C. S. specification, was heated to 85°. Ammonium hydroxide, 24% solution, was then added with stirring until further addition caused no more precipitation. The rose-colored precipitate was washed by decantation with a very dilute ammonium hydroxide solution (0.028%) until a sample of the precipitate dissolved in hydrochloric acid gave a negative nitrate test. The X-ray diffraction pattern of this pre-

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Physical Chemist, Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

(3) Assistant Physicist, Bureau of Mines, Central Experiment Station, Pittsburgh, Pa.

(4) H. A. Bahr and V. Jessen, *Ber.*, **63**, 2226 (1930).

(5) W. Fr. Meyer, *Z. Krist.*, **97**, 145 (1937); *Metallwirtschaft*, **17**, 413 (1938).

TABLE I
 CARBURIZATION AND HYDROGENATION OF COBALT

Identification	Carbiding			Hydrogenation			X-Ray diffraction analysis
	Temp., °C.	Time, hours	Total carbon, per cent.	Temp., °C.	Time, hours	Carbide carbon, per cent.	
Experiment 11							
1 Tube 1, reduced	α -Co
2 Tube 2, partly carburized	218 \pm 2	136.25	2.77	α -Co, Co ₂ C
3 Tube 4, fully carburized	218 \pm 2	1633.58	9.07	Co ₂ C
4 Tube 3, hydrogenated	218 \pm 2	1633.58	9.13	218 \pm 2	149.5	8.50	α -Co
Experiment 17							
5 Tube 3, reduced	α -Co
6 Tube 2, partly carburized	243 \pm 2	93.0	6.29	α -Co, Co ₂ C
7 Tube 4, fully carburized	243 \pm 2	448.5	10.69	Co ₂ C
8 Tube 1, hydrogenated	243 \pm 2	448.5	9.14	243 \pm 2	93.0	5.94	α -Co
Experiment 18							
9 Tube 4, partly carburized	266 \pm 2	20.0	5.33	α -Co
10 Tube 3, partly carburized	266 \pm 2	64.42	16.92	α -Co, Co ₂ C
11 Tube 2, fully carburized	266 \pm 2	341.25	39.27	α -Co, Co ₂ C, C
12 Tube 1, hydrogenated	266 \pm 2	341.25	41.02	266 \pm 2	44.33	7.72	α -Co, C
Experiment 16							
13 Tube 4, reduced	α -Co
14 Tube 2, partly carburized	292 \pm 2	47.12	16.69	α -Co
15 Tube 3, fully carburized	292 \pm 2	112.42	36.51	α -Co, C
16 Tube 1, fully carburized	292 \pm 2	205.42	60.21	α -Co, Co ₃ O ₄ , C
Experiment 19							
17 Tube 4, partly carburized	390 \pm 2	7.75	21.0	α -Co
18 Tube 3, partly carburized	390 \pm 2	12.67	32.64	α -Co, C
19 Tube 2, fully carburized	390 \pm 2	24.33	46.39	α -Co, C
20 Tube 1, hydrogenated	390 \pm 2	24.33	47.27	292 \pm 2	31.42	0.00	α -Co, C

precipitate was identical with that of the pink cobaltous hydroxide described by Weiser and Milligan.⁶ The precipitate was then heated to 150° for twenty-four hours. The resultant product was black and X-ray diffraction analysis showed it to be Co₃O₄ and isomorphous with magnetite. The oxide contained 68.9% cobalt. The determinations of cobalt in all the samples of oxide, cobalt metals, and carburized cobalt described in this paper were made gravimetrically by reduction of the sample with a stream of hydrogen at red heat in a Rose crucible. The product after cooling in hydrogen to room temperature was weighed as cobalt metal.

Apparatus.—The oxide was loaded into Pyrex reaction tubes similar to those used by Bahr and Bahr.⁷ The tubes were connected with ground ball and socket joints to the gas manifold with four outlets on the purification train. Heat was supplied by means of an aluminum block containing four cylindrical holes into which the reaction vessels fitted. The block itself was heated with four strip heaters. The temperature, which was constant to $\pm 2^\circ$ throughout each run, was regulated with a Leeds and Northrup Micromax. The aluminum block was supported by a transite frame in such a manner that all four reaction tubes were horizontal. This arrangement facilitates the removal of the block from the reaction vessels.

Water formation could be followed with absorption tubes containing magnesium perchlorate. The off gas from these tubes passed through flowmeters and into a vent.

Procedure.—Four 4-g. samples of oxide in the reaction tubes were reduced *in situ* by a stream of hydrogen flowing at one liter per hour. This corresponds to a space velocity of over 100 per hour. During the reduction the temperature was gradually raised from room temperature

to 300° and maintained until the reaction vessels had attained constant weight. The reaction vessels could be removed for weighing by removing the block furnace, allowing them to cool, and disconnecting from the gas manifold. All weighings were made with an atmosphere of hydrogen in the tubes to eliminate the buoyancy effect. The time used to bring the samples to temperature averaged about twenty-five hours, and they were maintained at temperature about eighty hours. Experiments 19 and 11 were partial exceptions to the above generalizations. The former was reduced at 400° and maintained at that temperature only forty-four hours, and two hundred and sixteen hours were used to bring the latter up to 300°. During the course of the reaction the samples changed from black to bluish, metallic gray. The residual oxygen after reduction was less than 0.3% as determined from the weight loss during reduction and the cobalt analysis.

Carburization was carried out with a stream of carbon monoxide flowing at a rate of about one liter per hour or a space velocity of 100 per hour. Heating and cooling was always carried out in an atmosphere of nitrogen to avoid carbonyl formation. Likewise, all weighings were made with the tubes filled with nitrogen in order to avoid buoyancy errors. Each carburizing period was timed from the flushing out of the nitrogen from the reaction vessel with carbon monoxide (after they had been brought to temperature) to the reverse process at the end of the carburizing period.

In order to determine the amount of easily hydrogenated carbon (carbide carbon) the carburized samples were treated with hydrogen at the same temperature as the carburization temperature in all cases where the carburization temperature was below 300°. In Experiment 19 hydrogenation was carried out at 292 \pm 2°. In Experiment 11 the temperature of hydrogenation was raised to 290° for 42 hours after 107.5 hours at 216°. A minimum flow rate of one liter of hydrogen per hour was used.

(6) H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **36**, 722 (1932).

(7) H. A. Bahr and Th. Bahr, *Ber.*, **61**, 2177 (1928).

All of the data are tabulated in Table I and represented graphically in Figs. 1, 2, 3, 4 and 5. The percentage of carbon as used here is defined by the equation

$$\text{Per cent. carbon} = \frac{\text{weight carbon} \times 100}{\text{weight carbon} + \text{weight cobalt}}$$

Similarly, the percentage of carbidic carbon is represented by the equation

$$\text{Per cent. carbidic carbon} = \frac{\text{weight loss on hydrogenation} \times 100}{\text{weight loss on hydrogenation} + \text{weight cobalt}}$$

The magnesium perchlorate tubes failed to gain in weight during the hydrogenation of the carburized samples. This may be taken as proof that the weight losses are due to conversion of carbon to methane and not to reduction of oxygen (as oxide) to water.

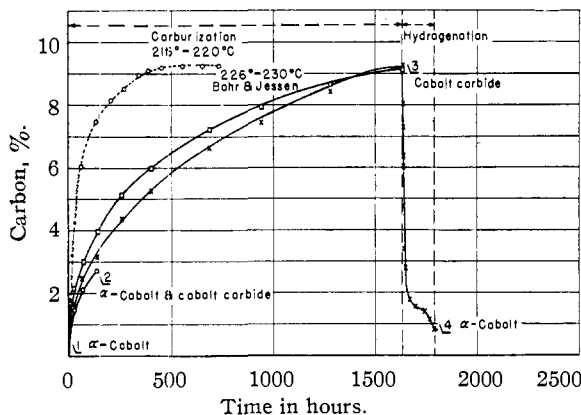


Fig. 1.—Experiment 11.

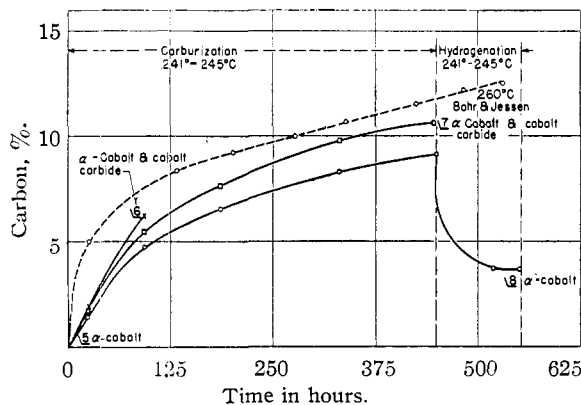


Fig. 2.—Experiment 17.

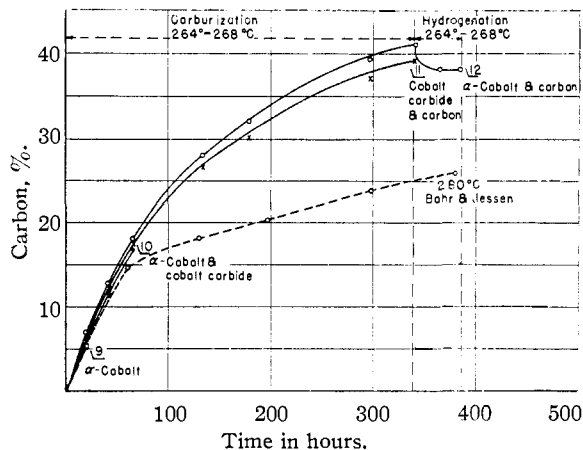


Fig. 3.—Experiment 18.

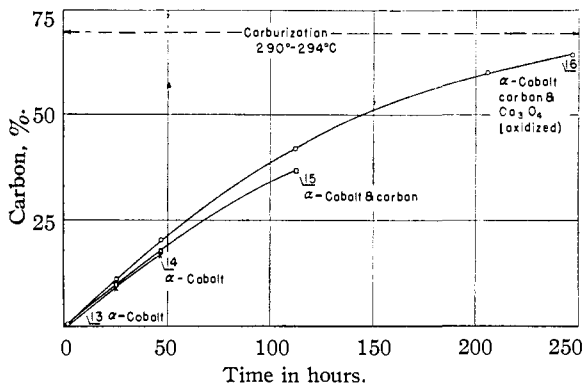


Fig. 4.—Experiment 16.

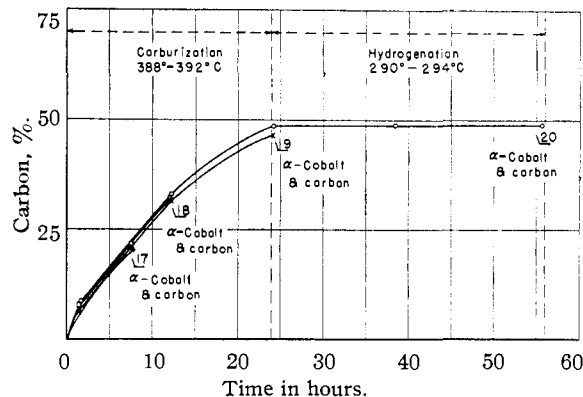


Fig. 5.—Experiment 19.

X-Ray Diffraction Methods.—Due to the pyrophoric nature of the samples, special techniques were employed to prevent their combustion on contact with the atmosphere. The reaction tube was cooled to -80° with solid carbon dioxide-acetone slush, and a stream of carbon dioxide gas was allowed to flow through the tube for about fifteen minutes. While the tube was still cold, the sample was removed under an atmosphere of carbon dioxide. The sample was left in a large battery jar in indirect contact with some pieces of solid carbon dioxide. When all the carbon dioxide was all sublimed and the jar had reached room temperature, the sample could be exposed to air without danger of pyrophoric combustion. Although all the diffraction patterns were made within two days of exposure to air, some of the samples were stored twelve months in a desiccator in contact with air with no deterioration

detectable by X-ray diffraction analysis. A sample of Experiment 11, Tube 4, contained 99.08% cobalt after four months of exposure to air in a desiccator as compared with 99.4% cobalt before exposure. Another sample from Experiment 16, Tube 3, contained 63.7% cobalt after four months of exposure in a desiccator as compared with 63.5% before exposure. These discrepancies lie within experimental error. (The percentage of cobalt prior to exposure is taken as one hundred minus the percentage of carbon from Table I; the percentage of cobalt after exposure was determined by direct analysis.) Any oxide formed by exposure is thus less than a fraction of a per cent. of the total sample and is under the limit detectable by X-ray diffraction analysis.

In order to establish completely the presence of easily hydrogenated carbon in the sample of Experiment 11, Tube 4, at the time the diffraction pattern was taken, another sample, which had been exposed to the atmosphere for twelve months in a desiccator, was loaded in a reaction tube in the usual manner and treated with hydrogen at 240° for twenty-three hours. The tube lost 0.0702 g. in weight; at the same time 0.0184 g. of water equivalent to 0.0163 g. of oxygen was formed. The amount of easily hydrogenated carbon is then 0.0702 - 0.0163 = 0.0538 g. or 6.86%, since the original sample weighed 0.785 g. Assuming this carbon is combined as Co_2C the sample contains 74% Co_2C , as compared with 85% Co_2C before exposure to the atmosphere. Mass spectrographic analysis of the off gas revealed enough methane to account for this amount of carbidic carbon.

The X-ray diffraction patterns were made by the usual powder method. A finely ground sample mixed with colodion was partly extruded from a 3/4-inch length of 19-gage stainless steel tubing of 0.7 mm. inside diameter. All the films were mounted in the Straumanis asymmetric manner. $\text{FeK}\alpha$ radiation filtered with manganese dioxide was used.

For the determination of the lattice parameters of the hexagonal α -cobalt, a modification of the technique described by Davy⁸ was used. Sodium chloride (A. C. S. specification) was mixed with the specimen as a standard. The diffraction patterns were made as described above. The lines were measured to ± 0.05 mm. at the darkest part of the lines. Error due to film shrinkage was then eliminated by the Straumanis technique. Although the $\alpha_1\alpha_2$ doublet was resolved in the sodium chloride lines in the back angle region, this was not the case for the cobalt lines. The various interplanar spacings producing the sodium chloride reflections were calculated using 5.628 Å. as the lattice parameter of sodium chloride. The difference between the calculated values and the observed values is a measure of the error due to absorption, eccentricity, etc., at each interplanar spacing. Thus the error can be obtained as a function of the interplanar spacing. This function is almost linear in the range of spacings from 1 to 2.5 Å. By applying the proper correction as obtained from the above function to the observed cobalt interplanar spacings the true interplanar spacings are obtained. By using these corrected values, a set of equations of the form

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a_0^2} \right) + \left(\frac{1}{c_0^2} \right)^2$$

can be written, one for each interplanar spacing. By the method of least squares the values for a_0 and c_0 were calculated. This method is particularly useful in evaluating diffraction patterns of noncubic crystals having only few lines in the back angle region. The results are summarized in Table II. The experimental error is less than ± 0.002 Å. in all cases. The interplanar spacings of cobalt carbide were corrected in the same way with sodium chloride.

TABLE II

LATTICE PARAMETERS OF THE COBALT SAMPLES IN EXPERIMENT 11

	a_0 , Å.	a_0 , Å.	c_0/a_0
α -Cobalt (by reduction from oxide)	4.0629 \pm 0.0015	2.5017 \pm 0.0005	1.6239 \pm 0.0002
α -Cobalt (in partly carburized sample)	4.0629 \pm 0.0003	2.5025 \pm 0.0014	1.6239 \pm 0.0015
α -Cobalt (by hydrogenation of carbide)	4.0601 \pm 0.0007	2.5025 \pm 0.0015	1.6119 \pm 0.0005

(8) W. P. Davey, "A Study of Crystal Structure and its Applications," McGraw-Hill Book Company, New York, N. Y., 1934, p. 163.

Results

The percentage of carbon in cobalt carburized at 218° (Fig. 1) approaches a value corresponding approximately to cobalt carbide (9.3%) in accordance with the observations of Bahr and Jessen.⁴ The process is extremely slow, as can be seen in Fig. 1. The carbon so deposited is easily hydrogenated at 218° although the process was accelerated by heating to 290° for 42 hours after 107.5 hours at 216°. The weight changes on carburization and hydrogenation are really due to the deposition and hydrogenation of carbon as demonstrated by the nearly complete lack of water in the off gas. X-Ray diffraction patterns of the uncarburized, partly carburized, completely carburized, and hydrogenated cobalt show that the carburization leads to the formation of a new phase, which reverts on treatment with hydrogen to the original α -cobalt. This new phase can only be a carbide or an allotrope of cobalt. The latter possibility seems unlikely because this phase occurs only when carbon is present. During the carburization no change in color was observed; the fully carburized material had the same metallic gray color as the original α -cobalt.

These results do not agree with those of Meyer,⁵ who found no new crystalline species in samples of cobalt. The discrepancy may be due to a variety of causes. First, Meyer used illuminating gas which contained hydrogen, methane, carbon dioxide, and higher hydrocarbons in addition to carbon monoxide. In all probability it also contained sulfur compounds in traces, which might poison the carburizing reaction. Meyer mentions a yellow coloration which formed on his samples during carburization. This may indicate a side reaction. Second, Meyer states that his samples were made by "hammering and pressing." This would probably result in a large particle size which would impede the reaction. Carburization at 243° (Fig. 2) was considerably more rapid than at 218°. As carburization proceeded the samples became black and this black color remained even after hydrogenation. The percentage of easily hydrogenated (carbidic) carbon was only 5.94% as compared with a total carbon content of 9.14%, so the color probably is due to free carbon. As in the samples carburized at 218° a new phase developed during carburization which reverted to hexagonal cobalt on hydrogenation.

At 266° carburization formed a great deal of free carbon in only 341 hours of treatment as shown by the total carbon content of 41.0% compared with 7.7% carbidic carbon. Here again, as in all the experiments at higher temperatures, carburization produced a black color which hydrogenation did not remove. The new phase also developed as carburization progressed and reverted during hydrogenation to α -cobalt. In this experiment the samples with the high carbon content all exhibited a diffuse line, $d = 3.3$ – 3.4 Å., which is probably due to finely divided carbon.

Carburization at 292° is again faster; the sample from Experiment 16, Tube 1, contained 60.2% carbon after only 205 hours of carburization. The pressure due to the accumulated carbon became sufficiently great to break the tube after a total of about 250 hours and as a result the sample was partly oxidized. This is the cause of the Co_3O_4 pattern in the diffraction pattern from this sample. The X-ray diffraction patterns of the other samples carburized at this temperature revealed only α -cobalt and carbon. No trace of the new phase present in the samples carburized at lower temperatures could be found. Therefore, the new phase is not present at all or its pattern is so diffuse as to be lost in the background. This is to be correlated with the observation of Bahr and Jessen that cobalt carburized at this temperature contained only small amounts of easily hydrogenated carbon as compared with samples carburized at lower temperatures.

A run was also made at 390°. The carbon deposition was most rapid of all and hydrogenation of the carburized sample produced no weight loss. (The tube even gained 1.1 mg. during the process.) As might be expected, the samples in this run contain only α -cobalt and carbon but no trace of the new phase. (This temperature is too low for the formation of the Co_3C phase described by Meyer.)

Throughout these experiments there is a one to one relationship between the presence of easily hydrogenated carbon and the new phase, and this suggests that the easily hydrogenated carbon is combined with cobalt to form a cobalt carbide. The new phase cannot be due to carbon alone because such a phase would not have sufficient diffracting power to register on the photographic film in the same time as metallic cobalt; furthermore, the cobalt phase disappears as the new phase develops, suggesting that the cobalt is converted to a new form.

That the diffraction pattern of this new phase is due to a single phase rather than two or more is indicated by the similarity of the diffraction patterns of all completely carburized samples prepared under a diversity of conditions. Even the diffraction patterns of completely carburized Fischer-Tropsch catalysts of the formula $\text{Co}:\text{ThO}_2:\text{kieselguhr}$, 100:18:100 present the same pattern. In Table III the diffraction data for a completely carburized sample and for α -cobalt are compared. In Fig. 6 the actual diffraction films are reproduced.

To investigate any diffraction lines which might be present at smaller angles than those found with the 71-mm. camera, a 114-mm. camera was used capable of resolving a reflection from an interplanar spacing of 20Å., but no new lines were found. The pattern is relatively simple, but it is definitely noncubic. This very simplicity suggests the pattern is due to a single phase for if it were due to two or more phases, these phases would need to have even simpler patterns and

TABLE III
X-RAY DIFFRACTION DATA FOR COBALT CARBIDE AND α -COBALT

Hexagonal cobalt ^a (Expt. 11, Tube 3, first pattern)		Cobalt carbide ^a (Expt. 11, Tube 4, third pattern)	
I ^b	d/n hkl	I ^b	d/n
		w	2.4137
		vw	2.3287
		w	2.1712
w	2.1645 (100)	vS	2.1127
M	2.0234 (002)	vw	2.0358 (α -Co?)
		S	1.9826
vS	1.9104 (101)	vw	1.9159 (α -Co?)
		M	1.6244
		vw	1.5558
		w	1.4454
		M	1.3166
S	1.2522 (110)	M	1.2469
		w	1.2187
		w	1.2053
		S	1.1680
S	1.1494 (103)	S	1.1267
w	1.0831 (200)	vw	1.0754
S	1.0655 (112)	vw	1.0638
		vw	1.0565
M	1.0469 (201)		
w	1.0149 (004)	M	0.9949
		vw	.9895

^a Values corrected by calibration against NaCl, $a_0 = 5.628 \text{ \AA}$. ^b vS, very strong; S, strong; M, medium; w, weak; vw, very weak.

this would greatly restrict the possibilities. These considerations all lead to the conclusion that easily hydrogenated carbon is combined with cobalt in a distinct crystalline phase whose diffraction pattern is given in Table III. The data on the quantitative carburization and hydrogenation in the Bahr and Jessen paper and in the present paper suggest that the formula of this carbide is Co_2C .

Hägg⁹ has shown that the borides, nitrides, and carbides of the transition elements of the periodic table occur in face centered cubic, close packed hexagonal, or again face centered cubic structures depending on whether the approximate composition is M_4X , M_2X , or MX , respectively, provided that the ratio of the radius of the metalloid atom to that of metal atom be less than 0.59. (These structures refer only to the arrangement of the metal atoms; the metalloid atoms are thought to be distributed among the metal atoms.) These compounds are characterized by great stability, although the stability falls off for compounds in which the ratio approaches 0.59. When the ratio is greater than 0.59 compounds of unusual crystal structure are formed. For the carbides of iron, cobalt and nickel the ratio varies from 0.61 to 0.62.

(9) G. Hägg, *Z. physik. Chem.*, **B12**, 33 (1931).

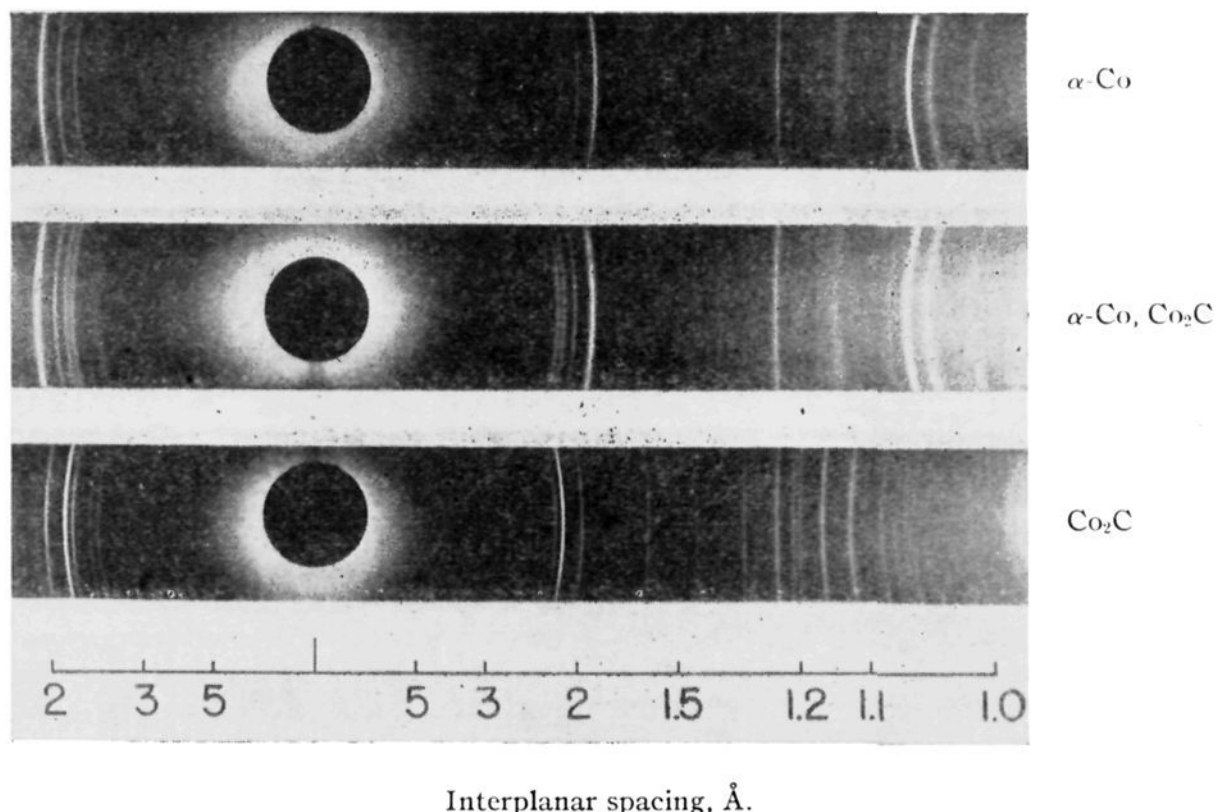


Fig. 6.—Diffraction patterns of cobalt metal, partly carburized cobalt metal, and cobalt carbide as obtained in Experiment 11.

In accordance with Hägg's rule, cementite, Fe₃C, belongs to the orthorhombic system, and another carbide of iron, Fe₂C,¹⁰ has an unknown structure but the structure is neither face centered cubic nor hexagonal close packed. In the case of cobalt carbides Hägg's rule again seems to hold; Meyer⁵ has reported one carbide apparently isomorphous with cementite, and the present paper describes another of unknown structure. However, in the case of nickel, carburization with carbon monoxide leads to a product, Ni₃C, in which the nickel atoms have the close-packed hexagonal arrangement, according to Jacobsen and Westgren.¹¹ This arrangement was supported by the studies of Schmidt and Osswald,¹² and Le Clerc and Michel,¹³ although the latter believed himself to be dealing with a new allotrope of nickel. According to Jacobsen and Westgren, the Hägg rule does not exclude the existence of a close-packed hexagonal structure for compounds where the ratio of the radius of the metalloid atom to that of the metal atom is greater than 0.59, but the rule merely demands that such phases shall be highly unstable. Kohlhaas and Meyer,¹⁴ however, conclude that the carbide is really an isomorph of cementite. But if nickel carbide really has a close-packed hexagonal structure, cobalt carbide would be expected to have the same structure, because all the factors are favorable except that of the atom radius ratio. First, the Hägg rule

(10) G. Hägg, *Z. Krist.*, **89**, 92 (1934).

(11) B. Jacobsen and A. Westgren, *Z. physik. Chem.*, **20B**, 361 (1933).

(12) J. Schmidt and E. Osswald, *Z. anorg. allgem. Chem.*, **216**, 85 (1933).

(13) G. Le Clerc and A. Michel, *Compt. rend.*, **208**, 1583 (1939).

(14) R. Kohlhaas and W. Fr. Meyer, *Metallwirtschaft*, **17**, 786 (1938).

favors the hexagonal close-packed structure for compounds of the formulas M₂X-M₃X. Second, in order to form this structure the arrangement of the metal atoms in α -cobalt need not be changed, since it is already in the close-packed hexagonal structure. For these reasons α -cobalt may be expected to hold a good deal of carbon in solid solution.

In order to study this possibility a study of the lattice parameters of the cobalt metal was made. For this purpose α -cobalt as produced by the reduction of Co₃O₄ (Experiment 11, Tube 1), α -cobalt as it exists in a partly carburized sample (Experiment 11, Tube 2), and α -cobalt as produced by the hydrogenation of Co₂C were used. The results (Table II) show that the lattice parameters of the different samples are identical within experimental error. Therefore, either α -cobalt can contain only small amounts of carbon (probably less than 1%) or the solid solution decomposes into cobalt carbide as rapidly as it is formed. The lattice parameters are in good agreement with those of Neuberger.¹⁵

Acknowledgment.—The authors wish to thank Stuart R. Brinkley, Jr., for his aid in developing the method used for calculating lattice parameters.

Summary

1. The easily hydrogenated carbon produced by the action of carbon monoxide on finely divided cobalt metal is shown to be combined with cobalt to form a new crystalline species, Co₂C, whose structure is distinct from either α - or β -cobalt.

2. X-Ray diffraction data indicate that the difficultly hydrogenated carbon is in the form of finely divided carbon crystallites.

(15) M. C. Neuberger, *Z. Krist.*, **93**, 1 (1936).

3. Lattice parameter measurements of α -cobalt give no evidence of any solid solution of

carbon in α -cobalt in a partly carburized sample.
PITTSBURGH, PA. RECEIVED NOVEMBER 25, 1946

[COMMUNICATION FROM THE RESEARCH LABORATORIES, OF THE BUFFALO ELECTRO-CHEMICAL COMPANY, INC.]

Sensitized Catalysis. I. The Fundamental Facts

BY HUGO J. KAUFFMANN

The catalytic oxidation of an acid *indigo carmine* solution by hydrogen peroxide shows peculiarities that are not met with other dyes. The indigo carmine is known as a readily oxidizable substance, and just this property is the cause of its exceptional behavior, giving us, as the following investigations demonstrate, new and significant information about catalysis.

Oxidation turns the color from blue to yellow, the latter color not being intense. By using very dilute dye solutions, about 10^{-5} molar, the yellow color is no longer detectable. Such dilute solutions were used for the photometric study of the kinetics. For the qualitative investigations, more concentrated solutions were taken, the duration of the fading, until the last blue or green shade had disappeared, being a measure of the bleaching time. The dye is no longer detectable in concentration of approximately 1×10^{-7} molar. The dye used was water soluble sodium indigo disulfonate, hereafter simply referred to as indigo.

As in the case of other organic compounds, iron salts are the best catalysts and the reaction rate is slower with higher hydrogen ion concentration. The choice of the acid is important; any unnecessary interference in the oxidation process should be avoided. Difficulties are to be expected, if the acid has a high tendency for forming complex iron salts or if the acid is oxidizable. For that reason, the solutions used were generally not buffered and any detrimental change in the pH was prevented by application of a large excess of acid. Most investigations were made with solutions of ferric sulfate in sulfuric acid and with ferric perchlorate in perchloric acid. The hydrogen peroxide was present in every case in very large excess.

The Accelerators

The First Facts.—Bubbling illuminating gas through an acid indigo solution containing ferric ion and hydrogen peroxide greatly accelerates the bleaching rate of the dye. The velocity of the gas stream is without appreciable influence on the rate, provided care is taken to maintain a constant temperature. Table I shows the effects with different concentrations of the acid.

Washing the gas with permanganate solution did not remove the accelerating substance. Experiments with methane showed a rate acceleration similar to that found for illuminating gas.

The same results occurred when shaking the indigo solution with hydrocarbons, *i. e.*, petroleum

TABLE I
10⁻⁴ mole of indigo, 0.1 mole of H₂O₂ and 10⁻⁵ g. atom of Fe per liter at 25°.

No.	H ₂ SO ₄ , N	Bleaching time, min. in air	min. in gas
1	0.01	63	35
2	.02	114	52
3	.03	160	68

ether, heptane, cyclohexane, benzene, toluene, xylene and naphthalene.

The most effective of these substances was benzene which, although only very little soluble in water, showed a bleaching time of four, six and eight minutes, respectively, when substituted for illuminating gas in Table I. For that reason, benzene was chosen for further investigation.

Naphthalene was found to be less effective and very sensitive to the operating temperature. It worked slowly below 25°. Raising the temperature eliminated the acceleration.

Since hydrocarbons are only slightly soluble in water, their sulfonates were prepared and tested. Commercial sulfonates often contain iron and are usable only after careful purification. The normal salt effect; as tested with sodium sulfate, nitrate or perchlorate, was negative. With the sulfonates, on the other hand, the salt effect was strongly positive. Sodium benzene- and *p*-toluenesulfonate were found to be good accelerators, also dipotassium *p,p'*-diphenyldisulfonate.

Magnesium sulfonates, likewise, were suitable and advantageous in those cases where the purification of the magnesium salts was easier and where the ionic strength of the indigo solution was increased by addition of magnesium sulfate or perchlorate. An example is magnesium *p*-dichlorobenzenesulfonate which shows that chlorine compounds can also be accelerators. Inorganic chlorine compounds, such as sodium or magnesium chloride, retard the catalytic indigo oxidation.

The ability of a sulfonate to accelerate depends upon its constitution, being very evident in naphthalene derivatives. The sodium naphthalene- β -sulfonate is only a weak accelerator, whereas the disodium naphthalene-1,5-disulfonate is a powerful one, suited for further experimental studies.

Other Organic Compounds.—Like the hydrocarbons and their sulfonates, many other organic compounds are powerful accelerators. Their efficiency is a matter of constitution, but not bound to a specific structure, because represen-