axis at both temperatures; that is, the normal carbonate cannot be precipitated from solutions containing more than a very few per cent. of the bicarbonate. However, the point moves with increasing temperature toward the $KHCO_3$-H_2O axis, which follows from the fact that the solubility of the bicarbonate increases with temperature rise more rapidly than that of the normal carbonate.

Summary

1. Solubility measurements of systems consisting of potassium bicarbonate, potassium carbonate and water have been made at 25° and at 36°.
2. The only solid phases found in equilibrium with saturated solution at these temperatures are the anhydrous bicarbonate and the sesquihydrated carbonate.
3. Solutions at these two temperatures will not precipitate the normal carbonate if the saturated solution contains more than 2.21 and 3.88%, respectively, of the bicarbonate.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED]

STRUCTURE OF A PROTECTIVE COATING OF IRON OXIDES

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Introduction

In 1877, F. S. Barff[1] described a process by which a smooth, adherent rust- and wear-resisting coat of iron oxide or oxides was produced on the surface of iron objects. A few years later the process was improved and developed by G. Bower,[2] and since that time many modifications have been proposed. In preparing the sample used in this investigation, the iron was heated to 730° in an air-tight furnace and brought into contact with steam for about an hour, cooled slightly in the air, reheated to 715° with steam again for another hour and cooled in the air. This method produced a coating 0.1 to 0.3 mm. thick. Chemical analysis of this coating cannot determine definitely the amount of any phase because it cannot determine what phases exist. The x-ray analysis described below, however, cannot only distinguish between the three oxides and give a means for estimating roughly the amounts of each present, but can also determine the position of any phase relative to the other phases

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[1] Barff, *J. Soc. Arts*, **25**, 254 (1877); **27**, 390 (1879).

[2] Bower, *Trans. Soc. Eng.*, **23**, 59 (1883). Thwarte, *Proc. Inst. Civil Eng.*, **74**, 215 (1883). For a description of the original method and its many modifications see Pollitt, "The Causes and Prevention of Corrosion," D. Van Nostrand Co., New York, **1924**, p. 136.

and to the iron on which the coating is formed. This analysis shows that three oxides are present in layers parallel to the surface, and determines the order of these layers and their approximate thicknesses.

Method

To investigate the structure of a coating consisting of layers of iron oxides lying at different distances from the surface, x-rays having different absorption coefficients, but nearly equal wave lengths, were used. This combination was effected by using x-rays whose wave lengths are close to but on opposite sides of a critical-absorption wave length of iron. Iron $K\alpha$ and copper $K\alpha$ radiations have wave lengths about 1.93 and 1.54 Å., respectively, which lie on either side of the critical-absorption wave length for iron, 1.74 Å., and consequently their absorption coefficients in iron oxides differ. In this case the copper radiations are absorbed about four times as strongly as the iron radiations.

X-rays of these two wave lengths of different penetrating power are reflected in turn from the surface of the sample. The resulting powder photographs contain lines which are produced by reflection from the different atom planes of the different phases present. Since the crystal structures of the three oxides of iron, FeO, Fe_3O_4 and Fe_2O_3 (written in the order of increasing oxygen content), have been previously determined,[3] the positions of the lines on a powder photograph due to reflection of x-rays of a given wave length from all atom planes can be determined for every oxide. The oxides present can, therefore, be ascertained from the observed positions of lines on the powder photographs; the relative positions of two layers, each composed of one oxide, can be determined from the relative intensities of lines due to each oxide on photographs taken with iron and copper $K\alpha$ x-rays; the thickness of each layer can be approximately calculated.

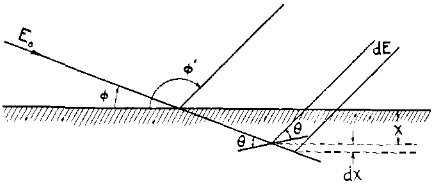

Fig. 1.—Reflection of x-rays from surface of sample.

Let a beam of x-rays of total energy E_0 be incident at angle ϕ upon the surface of the sample as shown in Fig. 1 and let it be reflected by the atom planes of many crystals lying at depths x below the surface, and let the beam so reflected emerge on the same side of the surface and make with it the angle ϕ', the angle of deviation being $\phi' - \phi = 180° - 2\theta$, where θ is the angle between the incident beam and the reflecting plane. The energy dE which is reflected from crystals lying between x and $x + dx$ is $dE = \alpha N S^2 E_0 e^{-\mu x(\csc\phi + \csc\phi')}\, dx$, where α is a factor, the same

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[3] For a summary of work on these structures, see "International Critical Tables," McGraw-Hill Book Co., New York, 1926, vol. 1, p. 342.

for each oxide of iron, S is the structure factor of the form responsible for reflection calculated so that its maximum value (when the x-rays from all atoms are in phase) is unity, N is the number of planes of the form and μ is the linear absorption coefficient of the x-rays.

For three oxides arranged in layers so that for the outer layer $x_1 > x > 0$, for the second layer $x_2 > x > x_1$, and for the third layer $x > x_2$, the energies reflected from these layers are, respectively,

$$E_{\mathrm{I}} = \int_0^{x_1} \mathrm{d}E = \frac{\alpha N_{\mathrm{I}} S_{\mathrm{I}}^2 E_0}{\mu(\csc\phi + \csc\phi')} [1 - e^{-\mu x(\csc\phi + \csc\phi')}]$$

$$E_{\mathrm{II}} = \int_{x_1}^{x_2} \mathrm{d}E = \frac{\alpha N_{\mathrm{II}} S_{\mathrm{II}}^2 E_0}{\mu(\csc\phi + \csc\phi')} [e^{-\mu x_1(\csc\phi + \csc\phi')} - e^{-\mu x_2(\csc\phi + \csc\phi')}]$$

$$E_{\mathrm{III}} = \int_{x_2}^{\infty} \mathrm{d}E = \frac{\alpha N_{\mathrm{III}} S_{\mathrm{III}}^2 E_0}{\mu(\csc\phi + \csc\phi')} e^{-\mu x_2(\csc\phi + \csc\phi\ )}$$

where each Roman subscript is the number of the corresponding layer of oxide and μ is considered to be the same for all layers.

Putting $E_{\mathrm{II}} N_{\mathrm{I}} S_{\mathrm{I}}^2 / E_{\mathrm{I}} N_{\mathrm{II}} S_{\mathrm{II}}^2 = R_1$ and $E_{\mathrm{III}} N_{\mathrm{II}} S_{\mathrm{II}}^2 / E_{\mathrm{II}} N_{\mathrm{III}} S_{\mathrm{III}}^2 = R_2$, and solving for x_1 and x_2, we have

$$x_1 = ln \left[\frac{1 + R_1 + R_1 R_2}{R_1 + R_1 R_2}\right] / \mu(\csc\phi + \csc\phi')$$

$$x_2 = ln \left[\frac{1 + R_1 + R_1 R_2}{R_1 R_2}\right] / \mu(\csc\phi + \csc\phi')$$

The value of ϕ may be set at pleasure. The values of ϕ' for the reflections which are compared in getting R_1 and R_2 must not be too widely different.

The absorption coefficient is calculated from the equation[4] $\mu = C\rho\lambda^3(\Sigma Z^4)/M$, where ρ is the density of the absorbing substance, λ the wave length of the x-rays, Z the atomic number of an atom in the absorber, the summation to be taken for all atoms in the molecule, M is the molecular weight of the absorber, and C is a constant. If ρ is in g./cc.^{3} and λ in Å., C is 0.00186 or 0.0136, depending on whether the wave length of the x-rays is longer or shorter than the K critical-absorption wave length. Calculation shows that for the present purpose it is sufficiently accurate to put $\mu = 440$ for iron $K\alpha$ radiation and $\mu = 1650$ for copper $K\alpha$ radiation for each oxide.

The iron and copper x-rays were produced in a Hadding gas-discharge x-ray tube,[5] in series with a thermionic rectifier. The x-ray beam was most intense for a current of about 10 milliamperes at 40 kv. The voltage across the tube was automatically regulated by the device shown in Fig. 2. Here T is a mercury trap which can be opened and closed by raising and lowering the mercury well W, and C is a laminated iron core attached

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[4] For a discussion of this formula as applied to crystal powders, see Havighurst, *Proc. Nat. Acad. Sci.*, **12**, 477 (1926).

[5] Hadding, *Z. Physik*, **3**, 369 (1920).

to the well W. Both are suspended from a spring about 150 cm. long. H is a solenoid coaxial with C and connected across the primary of the high-tension transformer. The maintenance of proper operating conditions proceeds as follows. If pumping lowers the pressure of the gas in the x-ray tube below the optimum, and the voltage across the tube consequently increases, the voltage across the primary of the transformer and the current in the solenoid also increase, the core C rises and the trap T closes. The gas pressure now increases, due to small leaks or diffusion through the aluminum window. When the voltage across the x-ray tube becomes too low because of the increased gas pressure, the reverse operation takes place and the trap T opens. In actual practice the opening of the trap is not intermittent but the device adjusts itself so that a steady stream of gas flows in at a rate which maintains the voltage constant. Adjustment for different operating voltages can be made by means of the variable resistance *R*.

The focal spot on the target was 3 cm. from the nearest slit (the narrower one, 0.2 mm. wide) and the sample was 13.1 cm. from this slit and the same radial distance from the cylindrical film. The target and body of the tube were water-cooled. The aluminum cathode was cooled by low-pressure air circulated through it.

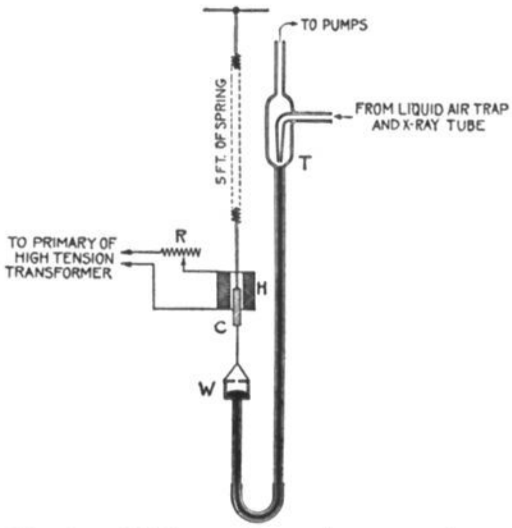

Fig. 2.—High-tension voltage regulator.

The Experimental Data

Powder photographs of different samples were taken as follows. (1) The coating, separated from its iron base by dissolving the iron electrolytically, was ground to a fine powder and placed in a thin paper tube; molybdenum $K\alpha$ x-rays were passed through the sample. (2) The coating was separated from its iron base as in (1); iron $K\alpha$ x-rays were reflected from its inner (iron-side) surface; $\phi = 15°$. (3) The same as (2), except copper $K\alpha$ x-rays. (4) The coating on its iron base; iron $K\alpha$ x-rays reflected from its outer surface; $\phi = 15°$. (5) The same as (4), except copper $K\alpha$ x-rays. (6) Powdered magnetite, Fe_3O_4, with a plane surface; iron $K\alpha$ x-rays; $\phi = 15°$. (7) Powdered ferric oxide, Fe_2O_3, prepared by strongly heating ferric nitrate in a crucible; iron $K\alpha$ x-rays; $\phi = 15°$.

The positions and intensities of the lines to be expected on the powder photographs of magnetite (Fe_3O_4) and ferric oxide (Fe_2O_3) were calculated from the structures of these crystals as already published.[3] Table I shows the calculated distance *s* from the central image to the line due to the nth-order reflection from planes of the form $\{hkl\}$, and shows also

TABLE I

POWDER-PHOTOGRAPHIC DATA FOR IRON OXIDES, IRON $K\alpha$ X-RAYS

	Fe_3O_4 (6)					Fe_2O_3 (7)					FeO		
n\{hkl\}	s	N	S	I	n\{hkl\}	s	N	S	I	n\{hkl\}	s	N	S
\{111\}	5.2	4	0.06	1	\{110\}	6.9	3	0.22	4	\{111\}	10.4	4	0.53
2\{110\}	8.6	6	.24	4	\{211\}	9.5	3	.55	10	2\{100\}	12.2	3	1.00
\{311\}	10.2	12	.41	10	$\{\bar{1}10\}$	10.2	3	.54	8	2\{110\}	17.9	6	1.00
2\{111\}	10.7	4	.18	1	2\{111\}	11.4	1	.15	0	\{311\}	21.9	12	0.53
4\{100\}	12.5	3	.52	7	\{210\}	11.8	6	.26	5	2\{111\}	23.3	4	1.00
\{331\}	13.7	12	.09	0	2\{100\}	12.6	3	.09	0				
2\{211\}	15.6	12	.24	2	2\{110\}	14.4	3	.68	6				
3\{111\}	16.7	4	.08	5	\{321\}	15.8	6	.61	7				
\{511\}	16.7	12	.37		$\{\bar{2}10\}$	16.5	6	.12	1				
4\{110\}	18.5	6	.85	5	$\{2\bar{1}1\}$	16.8	6	.13	2				
\{531\}	19.5	24	.06	0	\{332\}	16.9	.3	.42					
2\{221\}	19.9	12	.01	0	\{310\}	18.4	6	.64	4				
2\{310\}	21.3	12	.24	0.5	$\{\bar{2}11\}$	18.9	3	.94	4				
\{533\}	22.4	12	.41	2	\{320\}	19.6	6	.12	0				
2\{311\}	22.7	12	.76	2	2\{211\}	20.8	3	.29	0.5				
					\{432\}	21.7	6	.26	2				
					\{421\}	22.7	6	.12	1				
					$2\{\bar{1}10\}$	22.8	3	.55					
					\{330\}	23.6	3	.21	0				
					\{411\}	23.6	3	.21					

N and S and the relative intensity I, identified with reflections calculated for these photographs (6, 7). The positions of the lines were not determined with great accuracy, but they all coincide closely with calculated positions. In every case where there was any ambiguity in regard to the origin of a line, all possible origins have been indicated in the tables. Reflections produced by $K\beta$ or $K\gamma$ radiation did not cause any ambiguity.

Tables II to IV give the data obtained from the photographs (2,3,4,5) of the Bower-Barff coating. In these tables s is now the observed distance of the line from the central image. The photograph (1) of powdered coating shows only the presence of ferrous oxide and this indicates that if magnetite or ferric oxide is present, neither constitutes more than about 10% of the coating. The photographs (2,3) for which the x-rays were reflected from the inner side of the coating show five lines arising from the presence of ferrous oxide, but one line (probably from magnetite) appears faintly, indicating that a very thin film of magnetite covers the inner

TABLE II

POWDERED COATING (1), MOLYBDENUM $K\alpha$ X-RAYS; FILM RADIUS, 20.4 CM.

s	n\{hkl\}	I	s	n\{hkl\}	I
5.8	\{111\}	2	17.0	2\{211\}	5
6.8	2\{100\}	7	18.1	3\{111\} \{511\}	2
9.6	2\{110\}	10			
11.3	\{311\}	5	19.8	4\{110\}	1
11.8	2\{111\}	4	20.8	\{531\}	2
13.7	4\{100\}	3	21.1	2\{221\} 6\{100\}	2
15.0	\{331\}	3			
15.4	2\{210\}	5	22.4	2\{310\}	1

All lines are due to reflections from ferrous oxide crystals.

TABLE III

X-RAYS REFLECTED FROM INSIDE OF COATING

	Iron $K\alpha$ x-rays (2)				Copper $K\alpha$ x-rays (3)		
s	Oxide	$n\{hkl\}$	I	s	Oxide	$n\{hkl\}$	I
10.2	Fe_3O_4 Fe_2O_3	$\{311\}$ $\{\bar{1}10\}$	0.5[a]	8.1	Fe_3O_4 Fe_2O_3	$\{311\}$ $\{\bar{1}10\}$	0.5[a]
10.4	FeO	$\{111\}$	4	8.2	FeO	$\{111\}$	6
12.2	FeO	$2\{100\}$	10	9.5	FeO	$2\{100\}$	10
17.9	FeO	$2\{110\}$	7	13.8	FeO	$2\{110\}$	8
21.9	FeO	$\{311\}$	3	16.6	FeO	$\{311\}$	3
23.3	FeO	$2\{111\}$	3	17.4	FeO	$2\{111\}$	3

[a] This reflection is probably due to Fe_3O_4 $\{311\}$. If it were due to Fe_2O_3 $\{\bar{1}10\}$, the line Fe_2O_3 $\{211\}$ would be expected to appear also.

TABLE IV

X-RAY REFLECTED FROM OUTSIDE OF COATING

	Iron $K\alpha$ x-rays (4)				Copper $K\alpha$ x-rays (5)		
s	Oxide	$n\{hkl\}$	I	s	Oxide	$n\{hkl\}$	I
6.9	Fe_2O_3	$\{110\}$	0.5	6.8	Fe_3O_4	$2\{110\}$	1
8.6	Fe_3O_4	$2\{110\}$	1	7.5	Fe_2O_3	$\{211\}$	2
9.5	Fe_2O_3	$\{211\}$	1	8.1	Fe_3O_4 Fe_2O_3	$\{311\}$ $\{\bar{1}10\}$	6
10.2	Fe_3O_4 Fe_2O_3	$\{311\}$ $\{\bar{1}10\}$	10	9.5	FeO	$2\{100\}$	2
10.4	FeO	$\{111\}$	0.5	9.8	Fe_3O_4	$4\{100\}$	7
11.8	Fe_2O_3	$\{210\}$	0	11.2	Fe_2O_3	$2\{110\}$	1
12.2	FeO	$2\{100\}$	8	12.3	Fe_2O_3	$\{321\}$	1
12.5	Fe_3O_4	$4\{100\}$	3	13.0	Fe_3O_4 Fe_3O_4 Fe_2O_3 Fe_2O_3	$3\{111\}$ $\{511\}$ $\{2\bar{1}1\}$ $\{332\}$	4
16.7	Fe_3O_4 Fe_3O_4	$3\{111\}$ $\{511\}$	2	14.2	Fe_2O_3 Fe_3O_4	$\{310\}$ $4\{110\}$	2
17.9	FeO	$2\{110\}$	2				
18.4	Fe_2O_3 Fe_3O_4	$\{310\}$ $4\{110\}$	2				

surface of the coating. This magnetite was probably formed by exposure to the air after the coating was separated from the iron base. The photographs (4,5) taken with x-rays reflected from the original outer surface of the coating each show two lines from magnetite, but when iron x-rays were used (4) there were two lines from ferric oxide and three from ferrous oxide, whereas, when copper x-rays were used (5) there were four lines from ferric oxide and only one from ferrous oxide. This shows that outside of the layer of ferrous oxide there is a layer of magnetite, and outside of this again a layer of ferric oxide. Beginning at the iron side of the coating then, the layers are in the order of increasing oxidation of iron.

The order of magnitude of the thicknesses of these layers may be calculated by the formulas derived in the last section. Table V presents the data on which the calculation is based. The thickness, x_1, of the ferric oxide layer is calculated to be 2×10^{-5} cm. (0.01 mil) and the thickness of the magnetite layer 2×10^{-4} cm. (0.1 mil). The total thickness of

TABLE V

THE THICKNESSES OF THE OXIDE LAYERS

Photograph with Iron $K\alpha$ x-rays (4)

						Depths	
Oxide	n {hkl}	s	I	R_1	R_2	x_1	x_2
Fe_2O_3	{210}	11.8	<0.5			$<10^{-4}$ cm.	
				>3.0			
Fe_3O_4	4{100}	12.5	3				$<5 \times 10^{-4}$ cm.
					0.73		
FeO	2{100}	12.2	8				
Photograph with Copper $K\alpha$ x-rays (5)							
Fe_2O_3	{211}	7.5	2			2×10^{-5} cm.	
				3.9			
Fe_3O_4	4{100}	9.8	7				2×10^{-4} cm.
					0.08		
FeO	2{100}	9.5	2				

Thickness of Fe_2O_3 layer, 2×10^{-4} cm.; thickness of Fe_3O_4 layer, 2×10^{-5} cm.

the coating examined was 10^{-2} cm. (3 mils). It must be emphasized that the calculation of the thicknesses of the different oxide layers is not very precise. The mean thickness of a layer may be different from that calculated if it is markedly uneven. The estimated thickness may also be in error if the crystals in any layer are not oriented at random. This may be why the 2{110} and 4{100} magnetite reflections have different intensity ratios in the photographs of pure magnetite (6, Table I) and of the coating (2,3, Table IV). In general, however, the intensities of the different reflections from the coating are nearly those to be expected from a consideration of the observed reflections due to each oxide alone, and agree well with calculated structure factors.

Barff attributed[1] to magnetite the resisting qualities of the coating, and apparently believed this oxide was the only one present. The large proportion of ferrous oxide actually present may be necessary to bind the resisting layer of magnetite to the iron so that it cannot be chipped off by mechanical shock.

There is no indication of the formation of any solid solutions, for the lines on the better photographs are too sharp to be consistent with a range in atomic spacing greater than 0.5%. It is barely possible, however, that solid solutions exist between magnetite and ferrous oxide, and that the atomic spacings remain constant within 0.5% as the proportions of the two constituents change.

I wish to express my indebtedness to F. E. Haworth, for taking most of the x-ray photographs, and to J. B. Johnson and H. W. Weinhart, for designing and constructing the thermionic rectifier used with the x-ray tube. The possibility of analyzing this coating by means of x-rays was suggested by H. H. Lowry.

Summary

It is shown that the Bower-Barff protective coating, produced by the action of steam on iron at about 700° with subsequent cooling in air, is built up of layers of ferrous oxide, magnetite and ferric oxide, arranged in this order (the order of oxidation) upon the iron base. The thicknesses of these layers are estimated to be of the order of 10^{-2}, 2×10^{-4} and 2×10^{-5} cm., respectively. The data on which the above conclusions are based are the positions and intensities of lines on powder photographs taken with molybdenum, iron and copper $K\alpha$ x-rays. The iron and copper $K\alpha$ x-rays penetrate the coating to different depths and give information about different parts of its structure because their wave lengths are, respectively, a little greater and a little less than the critical-absorption wave length of the iron which forms the greater part of the coating.

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[Contribution from the Chemical Laboratory of Princeton University]

THE ACTION OF LIGHT ON THE FERROUS-FERRIC: IODINE-IODIDE EQUILIBRIUM

By George B. Kistiakowsky[1]

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Sime time ago, in a paper with the same title, Rideal and Williams[2] described measurements of the quantum yield of the reaction $2Fe^{++} + I_3^- \longrightarrow 2Fe^{+++} + 3I^-$ occurring in light of wave length 5790 Å. A dark equilibrium mixture was used, being about 0.016 N with respect to iodine. The rate of change of the iodine titer in light was approximately unimolecular and the authors, calculating accordingly the initial velocity of the photochemical reaction and measuring the absorbed light energy, came to the conclusion that one molecule of iodine reacted on the absorption of one quantum of green light by the complex I_3^- ion. The spectral sensitivity of the reaction was studied by means of different light filters as light sources, an incandescent and a mercury lamp being used. A distinct maximum of sensitivity for the reaction was observed in the region 6500–5000 Å., no reaction occurring in the light 4000–5000 Å. The authors connected these facts with the known critical potential of the iodine molecule, 2.34 v., corresponding to a wave length of 5300 Å. This supposed pronounced maximum of sensitivity is, however, rather improbable, as the continuous absorption of the tri-iodide ion extends increasingly from red far into the ultraviolet region of the spectrum. The writer has, therefore, repeated and extended the experiments of Rideal and Williams, obtaining different results.

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[1] International Research Fellow.

[2] Rideal and Williams, *J. Chem. Soc.*, **127**, 258 (1925).