

Small changes of composition apparently have great influence on the catalytic activity and efficiency and it is believed that further investigations in this more restricted field will develop a catalyst which will yield an efficiency of 90 or 95%, or even greater.

Summary.

Due to mechanical difficulties encountered during this investigation the above experimental data are not as extensive or complete as would be desired. It is believed, however, that the way has been cleared for a more comprehensive and exhaustive study of this subject and that in the future, such can be carried out without great difficulty.

Mixtures of especially prepared manganese dioxide containing promoters of copper and silver oxides have been made which possess great catalytic activity for the oxidation of ammonia by air.

Attention is called to the mixture of manganese dioxide and cupric oxide shown in Table, III. This mixture apparently possesses as great efficiency as platinum and during the tests showed no appreciable deterioration after 6 hours continuous run.

A method is indicated for the preparation of manganese alloys relatively free from impurities. Alloys of manganese with silver and copper have been made which serve as catalysts for the oxidation of ammonia, and the approximate composition of an alloy is indicated which should give a high efficiency for this reaction.

Thanks are here expressed to Professor J. C. W. Frazer for advice and suggestions during the course of this investigation.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY. No. 8.]

THE CRYSTAL STRUCTURES OF SODIUM CHLORATE AND SODIUM BROMATE.

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1. Introduction.

Before the present research was undertaken, some X-ray work had already been done on sodium chlorate and bromate. It is mentioned in Bragg's "X-rays and Crystal Structure"¹ that the sodium and chlorine atoms in the chlorate are located approximately as in sodium chloride, but no data are given. Jaeger² published Laue photographs showing that the symmetry of the atomic arrangement of the chlorate is at most

¹ Bragg, "X-Rays and Crystal Structure," G. Belland Sons, Ltd., London, 2nd Ed., p. 173.

² Jaeger, *Verslag akad. Wetenschappen Amsterdam*, **17**, 1 (1915).

no greater than that of pyrite, but he did not attempt to deduce the structure from his results.

Since the completion of the present research in which the X-ray spectrometer was employed, a paper has appeared by Kolkmeijer, Bijvoet, and Karssen,³ who studied the structures of these substances by means of powder photographs. Although their experimental method was different from ours, they arrived at the same type of structure that we had chosen; but the location of the atoms in their structure is not in full agreement with our conclusions. A comparison of their results with ours is given in a later section of this article.

This research was carried on with the aid of a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington, for which we wish to express our indebtedness.

2. Apparatus and Procedure.

The crystals used were prepared either by slow cooling of a saturated aqueous solution in a thermostat, their formation taking place between 40° and 30°, or by the slow evaporation of a solution at room temperature. With the aid of a suitable device the desired faces were ground on the crystals using fine emery on plate glass with carbon tetrachloride as a lubricant. The accuracy of the grinding was better than 15'. Crystal faces thus prepared were set up on a holder which defined vertically the area of crystal presented to the X-ray beam. The crystal face was always chosen sufficiently long horizontally to cover the entire incident beam, even at small angles of reflection. The crystal holder was so constructed that it could be easily removed and accurately replaced on the spectrometer. In order to be able to compare intensities of reflection from various faces, a reference crystal was set up on a second holder interchangeable with the first. The crystals gave sharp reflections and were apparently good specimens.

The source of X-rays was a fine-focus Coolidge tube of the radiator type provided with a molybdenum target set in copper. The filament current was supplied by a 10-volt storage battery; the tube current was measured with a milliammeter and was kept constant with the aid of a variable resistance in the filament circuit. Except for the points mentioned the apparatus was substantially the same as that used previously.⁴

In the measurement of intensities an integration method similar to that described by W. H. Bragg⁵ was employed. The ionization chamber was set on a previously measured angle of maximum reflection; then the crystal was uniformly rotated through an angular range sufficient to give sub-

³ Kolkmeijer, Bijvoet and Karssen, *ibid.*, 23, 644 (1920).

⁴ Dickinson, *THIS JOURNAL*, 42, 85 (1920).

⁵ W. H. Bragg, *Phil. Mag.*, 27, 881 (1914).

stantially all of the peak in question opportunity to reflect, and the total deflection of the electroscope was read. To correct for the general radiation similar integrations were made through equal angular ranges on each side of the peak, and a mean subtracted from the deflection at the peak. The slit defining the incident beam was kept at 0.3 mm. In determining the chamber angles, the chamber slit was 0.5 mm.; but in measuring the intensities the chamber slit was opened to 1.0 mm. to avoid affecting them by any small errors in the chamber angle. In the last step measurements on the reference crystal were alternated with those on the face in question.

In order to compare intensities of reflection from different faces, it was necessary to prepare all faces by grinding in the same manner. Compton⁶ had observed that "if the reflecting surface of a crystal of calcite is roughened by grinding, the reflection coefficient is some three times as great as from a cleavage face." With both sodium chlorate and sodium bromate it was found that with natural faces that had not been cleaved there was a similar effect, and that the increase in intensity on grinding, amounting in some cases to over 100%, was greater the smaller the angle of reflection. By turning the crystal face through 180°, as recommended by W. H. Bragg,⁵ the effect was shown not to be due to inaccurate grinding. W. L. Bragg, James, and Bosanquet⁷ have recently observed the same phenomenon with sodium chloride, using first a cleavage surface. The occurrence of this effect, which is still under investigation in this laboratory, is the rule rather than the exception and seems to indicate that all naturally grown faces, as well as cleavage faces of crystals, are covered by a thin absorbing, but non-reflecting layer.

Another important precaution was found necessary in the present measurements. It is, perhaps, best shown by means of an example. A large (110) face of sodium chlorate was set up not limited vertically by one of the holders described above; the crystal was set with two cube faces vertical and with the other four making angles of 45° with a horizontal plane. The chamber and crystal angles for two reflections were found; with the aid of these, the angles of reflection in the entire region between chamber angles of 2° and 33° were measured, rotating the crystal half as fast as the chamber. In this manner peaks were found at chamber angles of 9° 10', 13° 40', 18° 0', and 27° 0'. If each of these is divided by two and a correction of 11' subtracted from each of the results, the glancing angles 4° 24', 6° 39', 8° 49', and 13° 19' are obtained. These seemed to be the angles of reflection for the second, third, fourth and sixth orders, respectively, consistent with the fundamental equation $n \lambda = 2d \sin \theta$; for on dividing the sines of these angles by 2, 3, 4, and 6, re-

⁶ A. H. Compton, *Phys. Rev.*, **10**, 95 (1917).

⁷ W. L. Bragg, James, and Bosanquet, *Phil. Mag.*, **41**, 316 (1921).

spectively, the numbers 0.0384, 0.0386, 0.0384, 0.0384 are obtained. Yet, if the crystal and slits have moderately large vertical dimensions, reflections from a number of atom planes with different indices, but from the same boundary of the crystal, may enter the ionization chamber; moreover, it can be shown analytically that when the crystal is set with an important zone axis horizontal, as in the above case, these reflections, although coming from planes whose spacings are irrationally related to those of the prepared face, may have crystal and chamber angles very nearly in accord with the sine law and thus appear to come from the prepared face. That this had taken place in the case of the (110) spectra was clearly shown photographically. A photographic plate was set up perpendicularly to the incident beam, and in place of the ionization chamber. The crystal (set up as above) was rotated slowly and uniformly through a region sufficient to include the above lines. The reflections which had been called the 2nd, 4th, and 6th orders appeared as a horizontal row of vertical lines. The reflection which had been called the third order showed as a strong vertical line, which was not, however, in a horizontal row with the others. Another strong line was found directly below and partly overlapping the 2nd order. These last two clearly did not belong to the (110) spectra. Other lines from other faces were also in evidence. If this interpretation is correct, it should follow that when the crystal is moved in such a way that (110) remains vertical but the other faces are rotated, and a photograph taken as before, the real reflections from (110) should persist, but those from other faces undergo alteration. A photograph was made in the same manner as the previous one, but with two cube faces horizontal and four vertical. The lines previously called the 2nd, 4th, and 6th orders were the only ones common to the two photographs. By limiting the crystal face vertically to about 5 mm. by means of the holder, and by setting the crystal with no important zone axis horizontal, it was found possible to isolate these three lines for intensity measurement. Similar precautions were taken in the measurements on other faces. It seems likely that failure to observe this precaution is responsible for confusion that has arisen in the literature and that it accounts for cases where one investigator has reported reflections which the other did not find.

3. The Experimental Data.

An extended series of observations on sodium chlorate and a few on sodium bromate are given in Tables I and II. Since faces of the form (hok) are geometrically indistinguishable from those of the form (ohk) until the directions of the axes have been chosen, the faces (201), (10 $\bar{2}$), (301) and (10 $\bar{3}$) were all cut from the same crystal. The same is true of the two faces (111) and ($\bar{1}\bar{1}\bar{1}$). The tabulated values are, in many cases, means of several determinations.

TABLE I.
REFLECTION DATA FOR SODIUM CHLORATE.

Plane.	Order. n.	Observed angle of reflection (corrected).	Intensity. ^a	Calculated angle of reflection.
(100)	2	6° 12'	1.00	6° 13'
	4	12 28	0.042	12 30
	6	18 53	0.116	18 57
	8	25 33	0.033	25 39
(110)	1	4 23	0.218	4 23
	2	8 47	0.047	8 48
	3	13 14	0.052	13 16
(111)	1	5 22	0.441	5 23
	2	10 47	0.071	10 48
	3	16 18	0.165	16 20
(111̄)	1	5 21	0.466	5 23
	2	10 45	0.080	10 48
	3	16 16	0.196	16 20
(201)	1	6 56	0.957	6 57
	2	0.00	14 0
(102̄)	1	0.00	6 57
	2	13 56	0.097	14 0
(301)	1	9 44	0.074	9 51
	2	19 58	0.017	20 1
(103)	1	9 47	0.088	9 51
	2	19 53	0.088	20 1

^a Intensities are referred to that of second order of (100) of NaClO₃ taken as unity.

TABLE II.
REFLECTION DATA FOR SODIUM BROMATE.

Plane.	Order. n.	Observed angle of reflection (corrected).	Intensity. ^a	Calculated angle of reflection.
(100)	2	6° 5'	0.284	6° 4'
	4	12 14	0.081	12 13
	6	18 32	0.081	18 31
(111)	1	5 16	0.281	5 16
	2	10 33	0.133	10 33
	3	15 58	0.133	15 57

^a Intensities are referred to that of second order of (100) of NaClO₃ taken as unity.

4. Derivation of the Crystal Structures.

The type of atomic arrangement in these substances is probably most conveniently arrived at by a method which has been described by Wyckoff,⁸ to whom we are also much indebted for personal explanations of the application of the theory of space groups. It is always possible to regard a cubic crystal as built up by the repetition of a unit of structure on a simple cubic lattice; and we can determine the number *m* of molecules (of NaClO₃ or NaBrO₃) in the unit of structure by means of the equation

⁸ Wyckoff, *Am. J. Sci.*, 1, 127, 138 (1920).

$\frac{n^3}{m} = \left(\frac{2 \sin \theta}{\lambda} \right)^3 \frac{M}{N\rho}$. In this equation n denotes the order of reflection (based on the simple cubic lattice); λ , the wave length⁹ of the X-rays used (0.710×10^{-8}); θ , the angle of reflection from a cube face; ρ , the density of the crystal; M the formula-weight of sodium chlorate (or bromate), and N Avogadro's number (6.06×10^{23}). The density has been taken as 2.49 for the chlorate and 3.30 for the bromate.¹⁰ Taking for θ the smallest angle at which reflection was found from the cube face with each substance, and substituting the proper values of the other quantities, we get n^3/m equal to 1.99 for the chlorate and 2.00 for the bromate. If $n = 2$ and $m = 4$, n^3/m is 2; and these are the only possible values of n and m that bring n^3/m into close agreement with the values calculated above. For, if the structure be assumed to contain only one kind of sodium atom and one kind of chlorine (or bromine) atom, and not more than three kinds of oxygen atoms, the value of m can only be 48 or a submultiple of 48; for there are 12 equivalent directions in the cubic tetartohedral point-group, and there may be 1, 2, or 4 lattice points associated with the unit of structure. This shows that the crystal structure may be obtained by the repetition of a unit containing 4 NaClO₃ (or 4 NaBrO₃) on a simple cubic lattice.

The dimensions of the lattices can probably be most accurately obtained from the densities. Thus, the length d_{100} of the side of the unit cube may be calculated by the equation,

$$d_{100} = \left(\frac{4M}{N\rho} \right)^{1/3}$$

This gives for sodium chlorate 6.56×10^{-8} cm., and for sodium bromate 6.71×10^{-8} cm.

The angles at which reflection should occur from any other face having the Miller indices (h k l) may now be calculated with the aid of the expression

$$n \lambda = \frac{2 d_{100} \sin \theta}{\sqrt{h^2 + k^2 + l^2}}$$

With the omission of the odd orders from the cube faces, the angles so calculated are given in Tables I and II along with the observed angles.

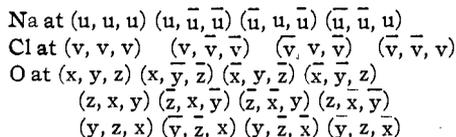
The assumption is made that all of the oxygen atoms occupy equivalent positions in the structure, it is next necessary to consider among the cubic tetartohedral space groups those which give in the most general or in special cases 4, 4, and 12 equivalent positions per unit of structure. There are two space groups which accomplish this, namely, those designated by Schönflies¹¹ T¹ and T⁴.

⁹ See Duane, *Nat. Research Council Bull.*, 1, part 6 (1920).

¹⁰ Groth, "Chemische Krystallographie," Wilhelm Engelmann, Leipzig, 1908, vol. 2, p. 84.

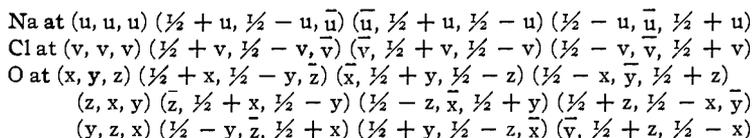
¹¹ Schönflies, "Krystalssysteme u. Krystalstruktur," Teubner, Leipzig, 1891.

The arrangement of atoms is, according to T^1 ,



The parameters appearing in the coördinates are taken as fractions of d_{100} . Since the right- and left-handed varieties of a crystal behave in the same manner toward X-rays,² it is not possible to choose between two enantiomorphously related structures.

The arrangement of atoms is, according to T^4 ,



No odd orders of reflection were found from the cube faces of either of the substances. Now irrespective of the values of u , v , x , y , and z , and of any special assumptions as to the reflecting power of the different atoms, the second arrangement, but not the first, causes all the odd orders of reflection from the cube faces to vanish.

The assumption here made that all the oxygen atoms occupy equivalent positions seems justifiable. For no arrangement with the requisite symmetry and number of sodium chlorate per unit is possible on the assumption that two oxygen atoms are equivalent and the third different; and the assumption that all three oxygen atoms are non-equivalent is improbable. We have therefore adopted the arrangement derived from the space group T^4 .

Completion of the knowledge of the crystal structure requires the determination of the values of the 5 unknown parameters, and this can best be done by a consideration of the intensities of reflection. There seems to be no way of finding the values of these parameters except by trial; and since 5 of them are involved, the number of possibilities is great. In view of the present rather scant knowledge of the mechanism of reflection there is no way of knowing how good agreement to expect between the calculated and observed results. There is, moreover, no assurance that when a satisfactory set of values has been found, another equally good set may not be possible. We have nevertheless determined a set of values of these parameters which leads to a rough agreement between the calculated and observed intensities.

The intensities were calculated with the aid of the expression, $I = f(\theta)(A^2 + B^2)$. In this expression,

$$\begin{aligned}
A = \bar{N}a & \left[\cos 2\pi n (h+k+1)u + \cos 2\pi n \left(\frac{h+k}{2} + (h-k-1)u \right) \right. \\
& \left. + \cos 2\pi n \left(\frac{k+1}{2} + (-h+k-1)u \right) + \cos 2\pi n \left(\frac{h+1}{2} + (-h-k+1)u \right) \right] \\
+ \bar{Cl} & \left[\cos 2\pi n (h+k+1)v + \cos 2\pi n \left(\frac{h+k}{2} + (h-k-1)v \right) \right. \\
& \left. + \cos 2\pi n \left(\frac{k+1}{2} + (-h+k-1)v \right) + \cos 2\pi n \left(\frac{h+1}{2} + (-h-k+1)v \right) \right] \\
+ \bar{O} & \left[\cos 2\pi n (hx+ky+lz) + \cos 2\pi n \left(\frac{h+k}{2} + hx-ky-lz \right) \right. \\
& + \cos 2\pi n \left(\frac{k+1}{2} - hx+ky-lz \right) + \cos 2\pi n \left(\frac{h+1}{2} - hx-ky+lz \right) \\
& + \cos 2\pi n (hz+kx+ly) + \cos 2\pi n \left(\frac{k+1}{2} - hz+kx-ly \right) \\
& + \cos 2\pi n \left(\frac{h+1}{2} - hz-kx+ly \right) + \cos 2\pi n \left(\frac{h+k}{2} + hz-kx-ly \right) \\
& + \cos 2\pi n (hy+kz+lx) + \cos 2\pi n \left(\frac{h+1}{2} - hy-kz+lx \right) \\
& \left. + \cos 2\pi n \left(\frac{h+k}{2} + hy-kz-lx \right) + \cos 2\pi n \left(\frac{k+1}{2} - hy+kz-lx \right) \right]
\end{aligned}$$

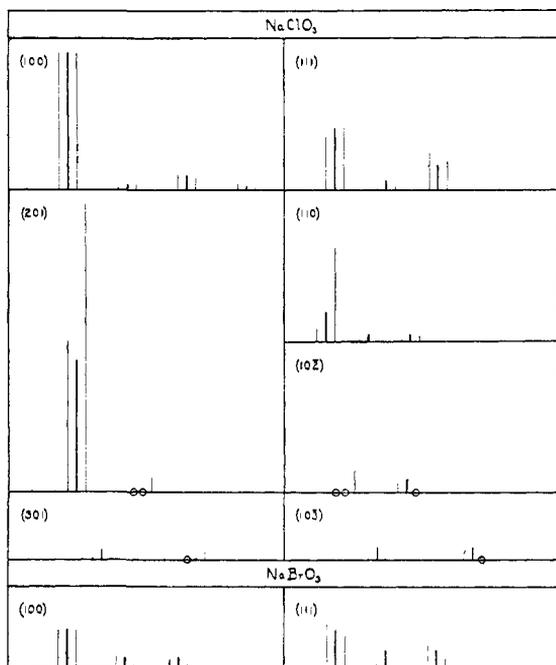


Fig. 1

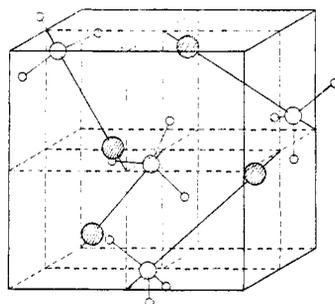
B is a similar expression in sine terms. Here Na, Cl, and O have been taken proportional to the atomic numbers of the respective elements. The relative values of $f(\theta)$ have been estimated by taking 100:20:5 as the normal ratios for the cube face of sodium chloride, plotting these against $\sin \theta$, and drawing an interpolation curve through these points. In order to get a straighter curve, the plot was actually made with the reciprocals of the square roots of the normal intensities against $\sin \theta$.

Tables III and IV contain the results of these calculations. The values of the parameters finally chosen are for the chlorate, $u = 0.08$, $v = 0.43$, $x = 0.30$, $y = 0.59$, $z = 0.47$; for the bromate; $u = 0.09$, $v = 0.41$, $x = 0.30$, $y = 0.60$, $z = 0.47$. The tables show in the fourth column the observed intensities; in the fifth, the intensities calculated using our values of the parameters; in the sixth, the intensities calculated using the parameters $u = \frac{5}{12} = (0.083)$, $v = \frac{5}{12} = (0.417)$, $x = \frac{1}{2} = (0.500)$, $y = \frac{5}{12} = (0.417)$, $z = \frac{11}{36} = (0.306)$, which are those chosen by Kolkmeijer, Bijvoet and Karssen.³ These three sets of intensities are also shown graphically in Fig. 1. The heavy lines represent the observed intensities. The lighter lines to the left represent the intensities calculated with our parameters, while the light lines to the right represent the intensities calculated with the parameters of Kolkmeijer, Bijvoet and Karssen. Their structure gives as good agreement with our data as our own structure except for faces all of whose indices are different. That any disagreement should appear here, if at all, is not surprising, since powder photographs, from which their structure was derived, do not separate reflections due to (hkl) and (khl).

5. Discussion of the Crystal Structures.

Their structure and ours are in substantial agreement as regards the displacement of the sodium and halogen atoms toward each other along diagonals from the positions occupied by these atoms in the sodium halides; and both agree in placing 3 oxygen atoms near a halogen with the halogen nearly in their plane. But their structure orients the oxygen atoms somewhat differently from ours and places them considerably closer to the halogen. Thus the distances between the respective atoms corresponding to their parameters and ours are shown in Table V.

In the last column are shown the distances derived by Bragg's contact-sphere



● Sodium, ○ Halogen, ○ Oxygen

Fig. 2.

principle using his values for the atomic radii.¹² As already pointed out by Kolkmeijer, Bijvoet, and Karssen, their values for the distances between halogen and oxygen are much less than those to which Bragg's atomic radii lead. The difference is seen to be much less in the case of our values, which for the chlorate were deduced before Bragg's paper appeared.

TABLE III.

CALCULATED INTENSITIES OF REFLECTION FOR SODIUM CHLORATE.

Plane.	Order.	$f(\theta)$.	Observed intensity.	Calculated intensity. Parameters of D. and G.	Calculated intensity. Parameters of K. B. and K.
(100)	2	135	1.00	(1.00)	(1.00)
	4	30	0.042	0.012	0.043
	6	9.1	0.116	0.117	0.097
	8	3.1	0.033	0.047	0.017
(110)	1	280	0.218	0.096	0.68
	2	66	0.047	0.022	0.004
	3	25	0.052	0.016	0.055
(111)	1	183	0.454	0.383	0.46
(111)	2	42	0.075	0.011	0.036
	3	14	0.181	0.270	0.21
(201)	1	106	0.957	1.10	2.1
	2	22	0.00	0.006	0.11
(10 $\bar{2}$)	1	106	0.00	0.000	0.16
	2	22	0.097	0.062	0.001
(301)	1	53	0.074	0.017	0.016
	2	7.5	0.017	0.004	0.095
(10 $\bar{3}$)	1	53	0.088	0.024	0.016
	2	7.5	0.088	0.074	0.000

TABLE IV.

CALCULATED INTENSITIES OF REFLECTION FOR SODIUM BROMATE.

Plane.	Order.	$f(\theta)$.	Observed intensity.	Calculated intensity. Parameters of D. and G.	Calculated intensity. Parameters of K. B. and K.
(100)	2	138	0.284	(0.284)	(0.284)
	4	31	0.081	0.093	0.022
	6	9.4	0.081	0.069	0.038
(111)	1	188	0.281	0.321	0.236
	2	44.5	0.133	0.030	0.026
	3	15	0.133	0.163	0.073

TABLE V.

ATOM DISTANCES.

Distance in 10^{-8} cm.

Substance.	Atoms.	K. B. and K.	D. and G.	Bragg's radii.
NaClO ₃	Cl to O	0.93	1.43	1.70
	Na to O	2.63	2.41	2.42
NaBrO ₃	Br to O	0.95	1.54	1.84
	Na to O	2.69	2.36	2.42

¹² W. L. Bragg, *Phil. Mag.*, 40, 180 (1920).

The arrangement of the atoms in the unit of structure using our chlorate parameters is shown in Fig. 2.

Summary.

1. Considerable X-ray spectrometer data for sodium chlorate and a smaller amount for sodium bromate have been collected and tabulated.
2. In agreement with other observers, it has been found that the nature of the crystal surface has a considerable effect on both the absolute and relative intensities of reflection.
3. The ease with which reflections from one face may be mistaken for those from another, and the necessity of precautions to avoid this have been pointed out.
4. It has been shown that the atoms in sodium chlorate and sodium bromate are very probably arranged with the symmetry of the space-group T^4 , all oxygen atoms being equivalent.
5. Sets of locations of the atoms in the unit of structure, only slightly different for the chlorate and bromate, have been suggested.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY.]

CATALYSIS IN THE INTERACTION OF CARBON WITH STEAM AND WITH CARBON DIOXIDE.

BY HUGH STOTT TAYLOR AND HARVEY A. NEVILLE.

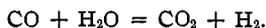
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Introduction.

The interaction of carbon and steam yields, in the first stage of the process, carbon monoxide and hydrogen, according to the equation



In presence of an excess of steam, and especially with suitable catalytic agents, the primary stage may be succeeded by the following reaction.



The first equation represents the desired reaction in the steaming phase of blue water-gas preparation. The second occurs to a certain extent, especially as the temperature of the fuel bed is lowered, the ash content of the coke acting as catalytic agent.¹ In the absence of catalytic agents as, for example, with carbon obtained by the thermal decomposition of hydrocarbons, and therefore ash-free, the first reaction takes place practically exclusively. It is evidently, therefore, a faster reaction than the water-gas reaction in the absence of catalytic agents. The second reaction is the principal reaction in the catalytic process for the manufacture of hydrogen from water-gas and steam. Iron oxide is an important con-

¹ Gwosdz, *Z. angew. Chem.*, **31**, 137 (1918).