

the main to secondary peroxide decomposition. It is concluded that hydrogen peroxide is the sole product of the reaction significant as regards reaction mechanism.

2. The yield of hydrogen peroxide is unaltered by the presence of water vapor in the gases. As a consequence, the reaction step $H + O_2 + H_2O = H_2O_2 + OH$ cannot be of any importance.

3. The Haber mechanism for the reaction of hydrogen atoms with oxygen molecules does not represent the only course of the reaction at ordinary temperatures. Peroxide formation must occur not only by combination of OH radicals but also by some other reaction.

4. Possible reaction mechanisms consistent with the results have been discussed.

PRINCETON, NEW JERSEY

RECEIVED JULY 19, 1932
PUBLISHED JANUARY 11, 1933

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Effect of Particle Size upon Intensity in x-Ray Spectroscopic Analysis

BY GORDON R. FONDA

In a limited number of elements,¹ a lower intensity of the $L\alpha$ doublet has been observed when the element was in the form of a metallic powder rather than in that of a polished metallic plate or even in that of an oxide. It persisted whether the crystal in the spectroscope was sodium chloride or aluminum oxide. No such difference was observed for the $K\alpha$ doublet. As such irregularities are liable to introduce serious errors in applications of x-ray spectroscopy to quantitative analysis, the subject has been studied further. The conclusion is that they are a consequence of too large particle size which brings about an abnormal absorption of the x-radiation emitted, particularly when it is in the longer wave length range. It is for this reason that it was first noticed in L radiation. The effect has been found to be present likewise in K radiation, though to a much less extent. It occurs under the experimental condition which generally holds—namely, that the emitted x-ray beam be examined at a different angle from that made by the exciting beam of electrons.

x-Radiation is excited throughout a certain depth of material, depending on the penetration of the electrons, and consequently encounters in its emission a corresponding amount of absorption by the material itself. If there are any irregular protrusions in the surface which lie in the path of the beam which is under observation, then the radiation is subjected to additional absorption as it passes through them. Such an effect should

¹ Fonda, *THIS JOURNAL*, 54, 115 (1932).

be presented, for instance, by the surface of a powdered material whose particles are of sufficient size. It can be well demonstrated by examination of the intensity from a grid formed by winding wires closely together with their turns touching. Such a grid was used as a target above the window of the cathode ray tube, placed vertically and operated as before from a regulated dc. circuit at 0.2 ma. and 86 kv. It was held at an angle of 20° to the axis of the tube and the intensity of the α doublet in the radiation given off in a horizontal direction was measured with a Seemann spectroscope placed horizontally. The surface of the crystal in the spectroscope lay in a vertical plane. Measurements were first made with the grid so placed that the turns of wire lay in the axis of the spectroscope, a condition comparable to that of a smooth plate in that the surface irregularities formed by the grid wires were not interposed in the path of the x-ray beam. The intensity was, in fact, found to be the same as for a smooth plate within the limit of error.

The grid was then placed with the turns of wire normal to the axis of the spectroscope. Here the conditions are altogether different as compared with the plate. The x-radiation excited on the side of a grid wire turned away from the spectroscope must pass first through the wire itself and a portion of that formed on the side toward the spectroscope must pass through the adjoining wire. This represents a greater thickness of material than the radiation from a smooth plate is subjected to and the absorption will be correspondingly greater. The loss in intensity will become less only as the size of the wire is decreased, thus lessening the additional absorption, or as x-radiation is chosen of shorter wave length for which the absorption coefficient is consequently lower.

Experiments were made with grids of molybdenum, copper and tungsten. The results are given in Table I. As the interest lies in the intensity from the grid when placed normal to the axis of observation, the value of this term is expressed as the ratio which its intensity bears to that measured when the grid was parallel to the direction of observation. There are geometrical reasons for the increase in the intensity ratio observed for the grid with the larger tungsten wire.

TABLE I
EFFECT OF GRID POSITION ON INTENSITY OF X-RADIATION

	Mo-K α	Cu-K α	W-L α
Wave length x-radiation, Å.	0.708	1.537	1.473
Absorption coeff.	200	540	2700
Intensity ratio—51 μ wire diam.	0.93	0.67	0.41
Intensity ratio—127 μ wire diam.	0.78	..	0.53

These results are in accord with the conclusion that surface irregularities of whatever origin will lead to a loss in intensity by their interposition in the path of the beam. Such a loss was observed, for instance,

in the L radiation of tungsten from a plate which had been roughened by sand blasting or even by etching. It is to be expected likewise from powdered material, in which its effect should increase with particle size and should be more pronounced for L radiation than for K because of the longer wave length of the former and the resulting higher values for the absorption coefficient.

These expectations are supported by examinations of several materials in the powdered form. In all the sample was held at a 20° angle to the axis of the tube. This is important because otherwise the relative value of the absorption factors is changed and a still different order of the intensities will be found in the case of those substances which are affected by these factors. The particle size was determined for each sample in terms of the diameter by examination with the microscope. One hundred or more particles of each lot were measured and a distribution curve plotted. The average diameter was found always to coincide with the peak representing optimum distribution and is therefore the value employed in the tables for the sake of brevity. All of the oxides experimented with had been prepared by chemical precipitation and are consequently so fine in size that no abnormal absorption effects could arise with them. They were frequently used as standards for calibration.

The first group of substances examined included metal powders whose intensities were compared with those from the corresponding oxides in mixtures with a comparison element. The results in terms of normal intensity as unity are given in Table II.

In the case of tungsten some direct intensity measurements also were made. In them the intensity from powder whose particles were of 1μ size was found to be the same as that from a polished plate. Larger size particles gave reduced intensities. All the sizes investigated gave reproducible intensities denoting that even for the largest size a sufficient number of particles was involved to maintain the same average orientation under different distribution. For still larger sizes it is to be presumed that the intensity would become irregular depending upon the chance

TABLE II
INTENSITY FROM METAL POWDER AS DEPENDENT ON DIAMETER AND ABSORPTION COEFFICIENT

Metal	Radiation, Å.	Abs. coeff.	Intensity for particle sizes of					
			28 μ	12 μ	8 μ	4 μ	2 μ	1 μ
Sn	K α -0.489	93					1.00	
Mo	K α -0.708	200				1.00		
Cu	K α -1.537	540			1.00			
Co	K α -1.785	560				1.00		
Fe	K α -1.932	590					1.00	
Pb	L α -1.172	1380		0.70				
W	L α -1.473	2710	0.41			0.60		1.00
Sn	L α -3.592	ca. 14000					0.60	

orientation of those particles which were within the area subjected to cathode ray bombardment.

The second group comprised some crystalline sulfides whose brittleness allowed them to be ground up and graded by screening into different sizes. Intensity measurements were made directly under comparable conditions and Table III gives a comparison in terms of the intensity from the smooth face of a large, single crystal as unity.

TABLE III
EFFECT OF PARTICLE SIZE ON INTENSITY OF SULFIDES

Substance	Radiation, Å.	Abs. coeff.	Intensity at particle sizes of						
			520 μ	310 μ	220 μ	160 μ	51 μ	4 μ	2 μ
FeS	K α -1.932	550	0.32	0.52	0.64	0.76	0.76	1.00	1.00
PbS	L α -1.172	1380	.50	.32	.48	.48	.50	0.74	0.80

This serves to demonstrate that the effect may become equally pronounced in the case of K radiation if the particles are of sufficient size. As the average particle size of powders that have been ground for analysis is generally below 4 μ , it is apparent that irregularities are not apt to be encountered in K radiation but only in L. This was demonstrated further by the examination of some carbides. Columbium carbide at an average diameter of 5 μ gave an intensity of the K α doublet at 0.744 Å. that was normal for its columbium content. Tungsten carbide, however, at an average size of 2 μ gave an intensity of its L α doublet at 1.473 Å. that was only 81% normal.

Finally a more complex case was examined of a tantalite containing a small percentage of columbium. A definite analysis was obtained by fusing the ore first and finally obtaining by a precipitation method a pure mixture of tantalum and columbium oxides which was complete and which proved from gravimetric measurements to comprise 66.4% of the ore. Spectroscopic analysis of the oxide, which was so finely divided as to be capable of avoiding error due to particle size, gave values of 93.8% Ta₂O₅ and 7.1% Cb₂O₅ corresponding to a content in the original ore of 62.3% Ta₂O₅ and 4.7% Cb₂O₅. From these values it was possible to calculate what the normal intensity of tantalum and columbium radiation should be from the ore. Table IV gives values for the observed intensity as determined from spectroscopic analysis of the ore at different particle sizes in terms of the normal intensity. In the case of tantalum, correction is made for the small absorption due to the presence of iron and manganese.

TABLE IV
EFFECT OF PARTICLE SIZE ON INTENSITY MEASUREMENTS FROM A TANTALITE ORE

Particle size	Percentage of normal intensity	
	Ta-L α , %	Cb-K α , %
9.5 μ	44.1	62.0
4.2	86.6	...
2.5	98.6	100.0

Conclusion

The intensity of a diffracted x-ray beam has been found to be decreased by surface irregularities of the target in proportion to their magnitude and to the coefficient of absorption of the target material for the wave length involved. This effect was studied for grids of various size and powdered particles of metals and compounds of various diameter. For accuracy in quantitative chemical analysis based on x-ray spectroscopy attention must therefore be given to the fineness of the powdered samples, more especially when $\text{L}\alpha$ radiation is involved.

SCHENECTADY, NEW YORK

RECEIVED JULY 20, 1932
PUBLISHED JANUARY 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Sodium-Lead Alloys. The Structure of the Compound Known as Na_4Pb

BY CHARLES W. STILLWELL AND WALTER K. ROBINSON

A number of recent investigations have shown that when copper, silver or gold is alloyed with cadmium, zinc, tin or aluminum, the same types of crystal structures often occur in each binary alloy even though the empirical formulas of the compounds differ. The type structure of any specific compound seems to depend upon the ratio between the number of atoms and the number of valence electrons in the molecule.¹

The behavior of binary alloys of these three metals is fairly consistent and it is of considerable interest to know whether similar relations hold for alloys in which the first group metal is an alkali metal. The only x-ray study of such alloys which has been reported is that for the lead rich end of the sodium-lead system, up to 32 atomic per cent. of sodium.² An extension of the data for this system is therefore desirable. The present paper presents an analysis of the crystal structure of the compound usually designated as Na_4Pb .

Experimental Part

The alloy was prepared by melting together in an iron crucible the theoretical quantities of sodium and lead, making due allowance for the evaporation of some sodium. Cooling curves showed the initial break at the melting point of the compound Na_4Pb indicated in the equilibrium diagram.³ The alloy was annealed for sixty hours at 280-300° in an atmosphere of argon.

A Mueller tube and $\text{CuK}\alpha$ radiation were used for obtaining the diffraction patterns. The camera was essentially the Debye-Scherrer type tipped on edge so that it rested on the curved surface instead of on the base of the cylinder. With this arrangement the specimen may be mounted at the center of curvature and kept covered with mineral oil

(1) Westgren and Phragmen, *Trans. Faraday Soc.*, **25**, 379 (1929).

(2) Zintl and Harder, *Z. physik. Chem.*, **154**, 79 (1931).

(3) Calingaert and Boesch, *THIS JOURNAL*, **45**, 1901 (1923).