

## An XRay Method of Determining Rates of Diffusion in the Solid State

Jesse DuMond and J. Paul Youtz

Citation: [Journal of Applied Physics](#) **11**, 357 (1940); doi: 10.1063/1.1712784

View online: <http://dx.doi.org/10.1063/1.1712784>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/11/5?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Determining thermal diffuse scattering of vanadium with x-ray transmission scattering](#)

Appl. Phys. Lett. **88**, 061903 (2006); 10.1063/1.2170142

[Simple method for estimating and comparing x-ray damage rates](#)

J. Vac. Sci. Technol. A **23**, 1740 (2005); 10.1116/1.2073387

[Atomistic simulation of diffuse x-ray scattering from defects in solids](#)

J. Appl. Phys. **88**, 2278 (2000); 10.1063/1.1287525

[Experimental method to determine the heat production rate, thermal diffusivity, and conductivity of solids](#)

Rev. Sci. Instrum. **55**, 1648 (1984); 10.1063/1.1137634

[A New Method of Determining XRay Intensities](#)

J. Chem. Phys. **16**, 1175 (1948); 10.1063/1.1746782

---



## Re-register for Table of Content Alerts

Create a profile.



Sign up today!



data to within 0.5 percent in nine cases, and to within 1.0 percent in all cases. While the data are not sufficient to show definitely that the method of calculating densities developed in this paper is applicable to these other types of oils, there seems to be good indication that it is.

Two thermodynamic quantities of interest, the isothermal compressibility and the thermal expansivity, can be calculated from the data of this paper. The compressibility can be obtained by differentiation of the density equation at the temperature corresponding to the constants  $a$  and  $b$ , and, if computed at two pressures, shows the normal decrease with increase of pressure. On

the other hand, if the compressibility is calculated at two temperatures, it will be found to increase with temperature. The thermal expansivity can be calculated by applying the density equation at two temperatures at constant pressure. If computations are made at two pressures it will be found that the expansivity decreases also with increase of pressure. In regard to these derived quantities it should be noted that they cannot be calculated to an accuracy claimed for the basic density data. However, this lack of accuracy becomes important only at the lowest pressures where possible inaccuracy in measuring pressure by means of the manganin coil is recognized.

---

## An X-Ray Method of Determining Rates of Diffusion in the Solid State

JESSE DUMOND AND J. PAUL YOUTZ  
*California Institute of Technology, Pasadena, California*  
(Received November 7, 1939)

Gold and copper were simultaneously deposited in vacuum by vaporization on a plate of glass, the copper being deposited at a uniform rate while the gold was deposited in one hundred stratified layers in the copper by alternately raising and lowering the temperature of the molybdenum vaporizing trough containing the boiling gold. The translucent deposit so formed had a total thickness of about 10,000A and hence an average interplanar distance of 100A. In an especially constructed x-ray spectrograph selective diffraction of Mo  $K$  radiation from these stratified films was observed corresponding to the artificially imposed periodicity of the stratification and the intensity of this diffracted image relative to the direct beam was found to fall off with time so as to indicate a "half-life" for the stratified structure of about two days. This suggests a general method for the study of average rates of diffusion and the determination of diffusion coefficients of solids in solids by utilizing the decay of such stratified films. Simple theoretical considerations indicate that such an artificial stratification should, through the

action of diffusion alone, rapidly and automatically lose the higher Fourier harmonics of its periodic density distribution function and retain the fundamental in such a way as to render the determination of the diffusion coefficient quite accurate. The observed behavior of the diffracted maxima seem to support these expectations as does also the absence of any intensity in higher orders than the first. This purification by diffusion probably takes place principally during the depositing process itself while the temperatures are still quite high. Formulae are derived relating the observed rate of decay of the diffracted intensity, the artificial "grating constant" of the strata, and the diffusion coefficient. The method seems especially promising for substances and temperatures where diffusion is so slow as to be otherwise quite unobservable because the diffusion time varies as the square of the distance over which atoms must migrate and in this method these distances are many orders of magnitude smaller than in any other.

### I. INTRODUCTION

WHEN the experiments here described were started<sup>1</sup> our purpose in trying by con-

<sup>1</sup> See J. DuMond and J. P. Youtz, *Phys. Rev.* **48**, 703 (1935), also for unsuccessful attempts to produce artificial Bragg reflectors see H. Koeppe, *Dissertation Gieszen* 1923, W. Deubner, *Ann. d. Physik* **5**, 261 (1930).

trolled evaporation in vacuum to produce artificially stratified layers of two different substances (gold and copper) was to develop, if possible, a technique of measuring the absolute wave-length of x-rays by a type of diffraction more nearly resembling Bragg reflection than is the case in the

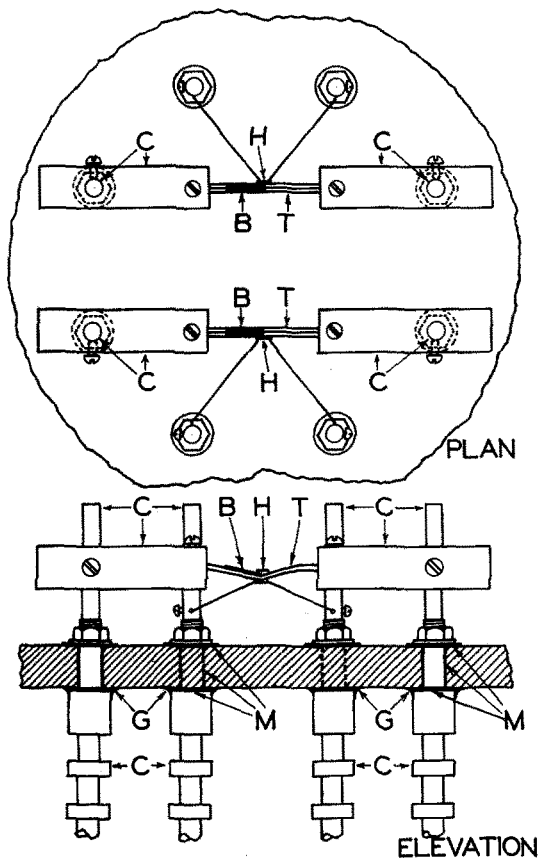


FIG. 1. Showing plan and elevation views of small, V-shaped, molybdenum troughs, *T*, heated by electrical conduction in which gold and copper were vaporized. The thermojunction, *H*, with its heat receiver is shown.

well-known method of grazing incidence on ruled gratings. We had hoped to count the number of artificial strata in process of deposition and to measure the total thickness by optical interference methods in order to ascertain the grating constant in terms of visible light. The many difficulties which one encounters in an effort to get, by evaporation methods, uniformity of layer spacing comparable to the ruling of a good grating have led us to abandon the original project. A by-product of this work, however, may prove to be of some utility in the study of the rate of diffusion at ordinary temperatures of one solid through another. This is suggested by our observation that the x-ray diffraction maxima formed by selective interference in the stratified films gradually diminished in intensity, and fell off to half-value in about two days. This must be

interpreted as meaning that the *amplitude* of the periodic functions representing the distribution of the two components as a function of depth in the deposit fell off with time, and that the one component diffused into the other so as to go from a stratified structure toward an increasingly uniform mixture.

The transfer of atoms of kind *A* will occur by diffusion at every point at a rate jointly proportional to their density gradient and the diffusion coefficient so that information as to the form of the periodic density function is important if the diffusion coefficient is to be determined from the rate of decay of the intensity of the selective reflection. Now by a fortunate circumstance it appears that such stratified films should and do by the simple process of diffusion alone rapidly approach and for a considerable fraction of their lives retain a sinusoidal distribution function. For such a function the calculation of the diffusion coefficient is simple. An attractive feature of this method is the fact that the x-ray diffraction reveals the diffusion process for extremely minute displacements of the diffusing atoms. Thus the process of diffusion can be followed without much delay at much lower temperatures than would otherwise be feasible.

## II. METHOD OF DEPOSITING STRATIFIED FILMS

### The evaporating apparatus

The evaporating apparatus consisted of a flat steel disk 15 inches in diameter supported as a horizontal table on steel legs and provided with a two-stage glass mercury diffusion pump and liquid-air trap below the disk and between the legs. Eight large brass electrical terminals (shown at *C* in Fig. 1) pass through the disk insulated therefrom with mica washers and sleeves *M* and made vacuum tight with glyptal lacquer *G*. Air-cooling fins are provided for these terminals. A glass cylinder 12 inches in diameter closed at the top by a metal disk waxed onto it forms the bell jar for enclosing the work. The lower edge of this cylinder previously lapped flat against a plane steel plate with abrasive stands on the steel disk, the joint being made tight with beeswax.

The glass plate, 2 inches square, on one side of which the stratified deposit was made, was held above the boiling sources of metal vapor in a

small brass frame supported by a fork from the metal top on the glass cylinder. A small vane pivoted to the supporting frame could be swung in a horizontal plane by means of a magnet so as to cover progressively more and more area on one corner of the glass plate. This vane was shifted after every 25 layers had been deposited so as to form a "staircase" in the layered deposit with steps each 25 layers high. Our purpose here was to check by interferometry the uniformity of deposition and also to determine to what extent the phase change of the light reflected by the metal film might be influenced by the varying proximity of the glass backing.

An electrical discharge was maintained while the system was being pumped down to suitable vacuum for evaporation. The discharge from a 15,000-volt transformer occurred between the lower steel plate and the metal frame supporting the glass plate on which the layered deposits were to be made. J. Strong has used this method of the gas discharge which very effectively removes by ion bombardment the last traces of grease, or other organic impurity from the surface to be coated.

### The resistance troughs or boilers

The containers for the boiling metals gave some trouble. The metals gold and copper were chosen originally for the evaporated films because the atoms have much external similarity but widely different atomic numbers and hence very different x-ray scattering power. The melting points of these metals are slightly above  $1000^{\circ}\text{C}$  and they must be made considerably hotter to boil at a sufficient rate in the vacuum. Molybdenum was one of the few substances which we found capable of containing either the boiling gold or copper without amalgamation. The boilers were made by bending a strip 5 mils thick and 0.1 inch wide cut from sheet molybdenum so as to form 90-degree V-shaped troughs each 5 cm long. Each trough ran nearly horizontally between two of the heavy air-cooled current terminals, *C*, (Fig. 1) and was heated by passing an alternating current of 50 amperes through it, furnished by a step-down transformer. At the point where the molten metal lies in the trough the resistance of the conductor is so much diminished that the bulk of the vaporization occurs at the two ends of the melt

adjacent to the hot empty trough. If the trough is nearly horizontal the melt becomes unstable, oscillating back and forth along the length of the trough in an irregular way, impelled apparently by surface tension forces and often breaking into two halves which find their way to the cool regions of the trough at its ends. The consequent heating and cooling of the trough gives a very irregular rate of vaporization which is most undesirable. This we avoided by providing the trough with a definite kink in the middle so that it sloped downward toward this point from either terminal. The metal to be melted, *B*, was placed *on one side only* of this kink. As the vaporization progressed from the hot spot where the lower end of the melt was adjacent to the hot empty trough the metal lost by evaporation would be replaced by fresh metal running slowly down the incline. The rate of evaporation was thus practically constant over a good fraction of the life of the charge. Fig. 1 shows the troughs at *T*.

Chromel-Alumel thermocouples were introduced into the vacuum chamber with heat collectors *H* close to the trough to permit of checking the constancy of the temperature in any given run.

The copper was maintained at as constant a rate of evaporation as possible throughout the run which lasted generally an hour and forty minutes. The periodic vaporization of the gold controlled by a clock mechanism was accomplished by alternately closing and opening a vacuum mercury tilting switch sealed in glass, which short-circuited a resistance in series with the heating current on the boiler containing the gold, increasing the power supply for periods of 28 seconds alternating with periods of reduced power supply of 28 seconds duration. The reduction in power supply was only just enough to inhibit vaporization of the gold. In this manner a total of one hundred spurts of gold would be applied. Distances from boiling metal to the glass plate were varied in different runs from 10 cm to 20 cm. The total deposits were all translucent. They however reflected considerably more visible light than they transmitted.

It is most probable that our technique could be much improved in the matter of boilers by going to more trouble than we have taken. A massive molybdenum boiler heated by electron bom-

bardment and completely enclosed except for a relatively small opening for the vapor jet would give much more uniform results.

### Control circuit for periodic deposition

The mercury tilting switch for heating and cooling the boiling gold was operated as a relay actuated by a clock pendulum. The appropriate swing of the pendulum was selected by a magnetically driven ratchet wheel. The clock pendu-

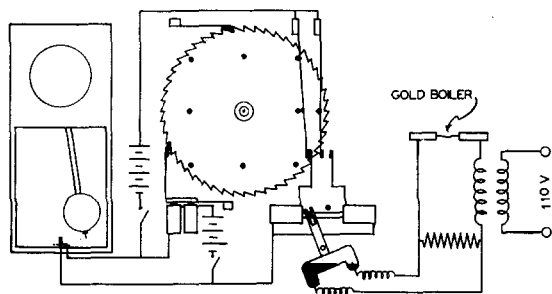


FIG. 2. Control circuits, relays, and ratchet by means of which a pendulum clock was made to control the heating and cooling of the trough containing the gold so as to deposit one hundred approximately uniform layers of that metal in a matrix of copper.

lum which made and broke an electrical contact (on for one second, then open for one second) caused the ratchet wheel to advance one tooth every second by a solenoid actuated ratchet. Pins on this wheel after 28-second intervals closed circuits permitting the next swing of the pendulum alternately to open then 28 seconds later to close the solenoid operated mercury tilting switch. Fig. 2 showing the circuit diagram is self-explanatory.

### III. X-RAY DIFFRACTION STUDIES WITH STRATIFIED FILMS

#### The diffraction camera

It occurred to us that the surface of the polished glass plate on which the layered deposits are made is, from the point of view of x-ray wavelengths, probably very far from flat. As the successive layers of gold are deposited in the matrix of copper it is more than likely that the initial irregularities of the surface may be augmented by the random nature of the vaporization so that the strata higher up in the deposit

may also be very far from plane. X-rays reflected from such surfaces might well give images as blurred as that of the moon seen reflected in a choppy sea. To avoid this difficulty we resorted to the well-known device of Bragg in which the crystal is rocked through a small range of angles, the photographic emulsion and the effective source of x-rays (slit or focal spot of x-ray tube) being stationary and equidistant from the center about which the crystal is rocked (Bragg "focusing" condition). The geometry whereby this focusing condition minimizes the blurring of the diffracted maxima caused by angular distortions of the diffracting planes and emphasizes only the *periodicities* responsible for the selective diffraction is too well known to require repetition here.

We expected our first-order diffraction angle to be very small from a rough estimate of the grating constant made by laying an optically flat glass plate on the stratified film. Interference fringes could be seen presenting discontinuous lateral displacements where they crossed the steps 25 layers high in the stratified deposit which we had made with the movable shielding vane in the process of deposition. We estimated the total thickness of the deposit at roughly 10,000Å and from this the "grating constant" of our artificial strata would be 100Å. For the Mo K x-rays we used whose wave-length is about 0.7Å this calls for a diffraction angle in the first order of about  $\theta=12$  minutes of arc. It seemed interesting however to explore at larger angles for higher orders and to look for diffraction effects from the atomic structure of the deposit if such might exist.

At such small grazing angles as 12 minutes of arc it becomes a problem to prevent fogging of the photographic emulsion by primary radiation transmitted directly past the stratified deposit without reflection therein. To prevent such fogging we provided a lead wedge confronting the stratified deposit supported by a lever mechanism designed to make the opening between the wedge and the deposit increase as the grazing angle of incidence and reflection of the x-rays increased. Fig. 3 shows a plan and an elevation of the spectrograph with the linkage for moving the wedge *W*. This linkage is designed so that over the entire range of angles the opening left by the

wedge permits a little less than the entire surface of the stratified deposit to be illuminated by x-rays. To insure against leakage of direct x-rays past the glass plate on which the stratified deposit was laid, a long pivoted brass paddle, *P*, shown in Fig. 3, was provided. This paddle extended through the pivot *q* to within a few millimeters of the photographic film and the glass plate *S* with its stratified film was supported in a square hole in the paddle so that the reflecting surface was quite accurately in the plane of the paddle. Paddle and crystal were rocked together by means of a cam, *C*, cut on the end of a cylinder, consisting of two equal right- and left-hand helical arcs. The small schema at bottom of Fig. 3 shows the geometry of reflection and shielding for two different angles.

In such a Bragg focusing diffraction camera the width of the source determines the width of the spectral lines. Instead of defining this width of source by a slit we have, as shown in Fig. 3, turned the target surface of the x-ray tube at such an angle as to give effectively a very thin line source situated so as to fulfill the Bragg focusing condition.

#### Diffraction photographs and control tests

Throughout the exposures the x-ray tube was operated at 40 kilovolts and 10 milliamperes. For each of the exposures we show here the cam *C* made four revolutions in a time interval of 28 minutes. Only a rough estimate can be made of the fraction of this time effective in reflecting the

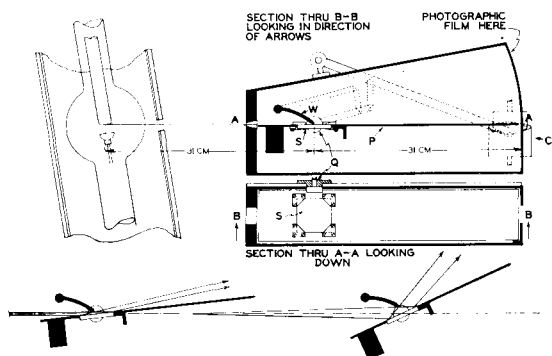


FIG. 3. The x-ray spectrograph used for examining the stratified deposits.

diffracted lines observed on our spectra. From the geometry of the apparatus and the width of the diffracted line this fraction seems to be about

1/100 so that the effective time of reflection for each exposure is apparently about 17 seconds.

While the time and intensity of each exposure was sensibly the same, another factor, the geometry of the alignment of the focal spot in the x-ray tube with the paddle *P* and lead wedge *W*, when these are nearly in contact at one extreme end of their travel, has a strong influence on the width and intensity of the undeflected direct beam and we believe that variations in this geometry account for the greater width of the direct beam in the first and last exposures shown in Fig. 4. This figure is a reproduction of the

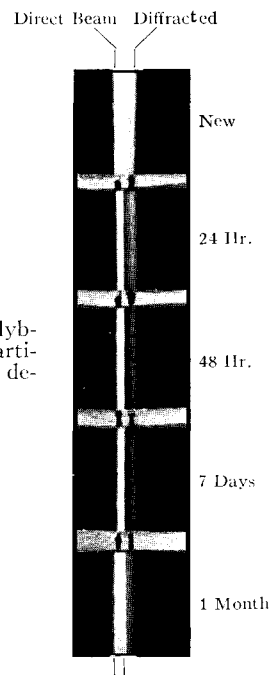


FIG. 4. X-ray spectra of molybdenum *K* radiation made with artificially stratified metal films deposited by evaporation.

spectra we have obtained from one of our best stratified deposits.

The decay in the intensity of the diffracted maximum relative to the directly transmitted intensity with increasing age of the deposit is apparent. This decay, in itself, is strong internal evidence that the observed effect is indeed diffraction from the artificially produced stratification and not some vagary of the glass or metal surface or some imperfection in the camera. To be absolutely sure, however, that we were not mistaken in this interpretation we ran control exposures with the stratified deposit replaced by: (1) clean glass, (2) a pure evaporated copper

deposit on glass, (3) a copper plate, (4) nothing whatever in the square hole in the paddle, (5) a calcite crystal cleavage surface. Nothing resembling the diffraction maxima from the stratified deposit was observed in any of these control exposures.

While the results here shown represent admittedly only very rough qualitative work there is not the slightest doubt as to the reality of the decay of the diffracted intensity with age of the deposit.

#### **Absence of orders of reflection higher than the first and our interpretation thereof**

We were struck by the complete absence of higher order reflection than the first in all the diffraction photographs. The diffraction angle indicated in our photographs checks very well with our estimate of the 100Å "grating constant" for the stratification assuming this to be a first-order reflection. A sinusoidal distribution of the density of gold atoms in the copper (as a function of depth) is the only one incapable of diffracting the x-ray intensity in other orders than the first. Our method of producing the intermittent vaporization of the gold should give layers with more or less diffuse boundaries. Furthermore, since the displacement of the gold into the pure copper regions is proportional to the density gradient of the gold and the time rate of change of the quantity of gold in any region is proportional to the second space derivative of the density function *one would expect the process of diffusion itself to render the density function rounded and sinusoidal* rather than angular and discontinuous. Indeed as we shall show immediately, if the periodic density function be represented by a Fourier series the process of diffusion will obliterate all the higher harmonics so much faster than the fundamental that in a very short time it should become quite strictly a simple harmonic function and no higher order reflections should then be observed. It is this circumstance which in our opinion renders the decay of reflected x-ray intensity from artificially stratified films a promising method of studying diffusion and diffusion coefficients in the solid state for if the concentration function automatically becomes a simple harmonic function it is a very simple matter to compute the diffusion

coefficient from the grating constant and the time rate of decay of the diffracted intensity.

#### **Behavior of the images with time**

Beside the absence of higher order reflections we think our spectra, shown in Fig. 4, exhibit other slight evidences of this tendency for the density distribution function to become and remain for some time a simple harmonic grating. In the spectrum from a so called "new" deposit in Fig. 4, the width of the direct beam prevents a satisfactory estimate of the structure of the diffracted image for this case but judging from the exposure of a deposit 24 hours old compared to those for two and for seven days there seems to be a little sharpening of the diffracted image with time. The time required to remove the plates from the vaporization machine, load them in the x-ray diffraction camera and take the x-ray exposures would prevent any of our observations from being made on strictly "new" deposits. The rate of decay of the higher harmonics in the distribution function will be especially rapid during the deposition itself and for a short time thereafter because of the much higher initial temperature of the deposit, exposed as it is to radiation from the molten metal and to the hot metal vapor condensing on its surface. The diffraction from so called "new" deposits must therefore be regarded as coming from strata which already have passed through a substantial portion of the diffusion process whereby the higher harmonics are suppressed.

After very long times one expects the fundamental simple harmonic distribution function itself to disappear from one or both of two causes. First, the so called fundamental period made by the intermittent vaporization of the gold may be superposed on weaker subharmonics of longer period caused by mal-functioning of the vaporization technique. Just as the fundamental should persist much longer than any of the higher harmonics so such subharmonics should persist long after the fundamental has become negligible by comparison. Second, given a perfect simple harmonic distribution function decaying in amplitude with time this amplitude will eventually reach a value of the same order as the accidental fluctuations in density to be expected in a "uniform" mixture of gold and copper upon

statistical fluctuation theory. The artificial periodicity will then be completely submerged and obliterated. The diffraction exposure of a stratified deposit one month old seems to show that either or both of the last two processes may have occurred.

#### IV. THEORETICAL RELATIONS BETWEEN RATE OF DECAY OF THE DIFFRACTED LINE, GRATING CONSTANT AND DIFFUSION COEFFICIENT

We shall confine our theory so as to agree with the following simplifying assumptions.

In a binary mixture of components  $A$  and  $B$  (gold and copper in our case) we assume that over the range of concentrations obtaining in the stratified deposit the average volume per atom of a given kind is sensibly constant independent of the relative concentration of the two components.<sup>2</sup> We also assume that, save for the artificially imposed stratification, no structure exists (such as a crystal structure characteristic of the components) and that the mixture is free from voids.

Let  $\rho_A(x,t)$  represent the mass of atoms of kind  $A$  per unit volume of the mixture,  $\rho_B$  being the corresponding quantity for  $B$  atoms. We shall frequently refer to these as the density distribution functions for atoms of kinds  $A$  or  $B$ . They are of course not to be confused with the densities characteristic of  $A$  or  $B$  atoms in the pure solid state.

The number  $n_A$  of atoms  $A$  per unit volume of mixture will be proportional to  $\rho_A$ ;  $n_A = \rho_A/\mu_A$ ;  $n_B = \rho_B/\mu_B$  where  $\mu_A$  is the mass of an atom  $A$ ,  $\mu_B$  the mass of an atom  $B$ .

Let  $V_A = 1/\rho_{0A}$  represent the net volume (a constant) occupied in the mixture by unit mass of atoms of kind  $A$  with a corresponding definition for  $V_B$ . Evidently  $\rho_{0A}$  would be the density of the pure, void-free, amorphous solid  $A$  if, even in the complete absence of  $B$ , the atomic volume remained unchanged.

Now  $V_A \rho_A$  is the volume of atoms of kind  $A$  in unit volume of mixture with corresponding sig-

nificance for  $V_B \rho_B$  and hence

$$V_A \rho_A(x,t) + V_B \rho_B(x,t) = 1; \quad (1)$$

$$\rho_A(x,t)/\rho_{0A} + \rho_B(x,t)/\rho_{0B} = 1.$$

It is clear then that  $\rho_A(x,t)$  is a linear function of  $\rho_B(x,t)$ . Also  $n_A(x,t)$  and  $n_B(x,t)$  are linearly related to each other and to the preceding two functions.

We now assume that the diffusion equation

$$\partial \rho_A / \partial t = K \partial^2 \rho_A / \partial x^2 \quad (2)$$

holds; with  $K$  a constant independent of  $\rho_A$ <sup>3</sup> over the range<sup>2</sup> obtaining in the stratified deposit. On account of the linear relationship expressed by Eq. (1) it is evident that a diffusion equation of the same type as (2) with the same numerical

<sup>3</sup> It is a well-known fact that the diffusion coefficient for solids is not in all cases a constant but is in fact a function of the concentration. In this more general case the diffusion equation must be written

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( K \frac{\partial c}{\partial x} \right)$$

or

$$\frac{\partial c}{\partial t} = \frac{dK}{dc} \left( \frac{\partial c}{\partial x} \right)^2 + K \frac{\partial^2 c}{\partial x^2}.$$

Matano has shown, Jap. J. of Phys. 8, 109 (1933) how to obtain a solution to this equation for the special boundary conditions obtaining at an initially sharp interface. The solution for the periodic case here discussed is difficult when the amplitude of the concentration is large but such a case is perhaps not very significant. Both Matano in the above reference and R. F. Mehl, J. App. Phys. 8, 174 (1937) adduce evidence by Matano's method for variation of  $K$  with concentration, the former for diffusion of copper in nickel, the latter for copper in aluminum. The diffusion coefficient increases, they find, in the first case with increasing proportions of copper and in the second case with increasing proportions of aluminum. Over a considerable range of concentrations, however,  $K$  can be treated as a constant. This variation of the diffusion coefficient with concentration is of considerable interest and we believe it might be studied by the x-ray observations of the decay of artificially stratified films. In order that the considerations here set forth shall apply to the case where  $K$  depends on concentration it is only necessary to wait until the amplitude of the periodic concentration function shall have decayed to a point such that the total range of variation of concentration embraced in the periodic part of the distribution shall correspond to a negligible variation in  $K$ . The concentration distribution function can be made to consist of a periodic component superposed upon a uniform mixture with the latter in any desired proportions, by proper control of the evaporation ratio. By preparing a number of samples with different average proportions of the components and taking the rate of decay toward the end of the life of the stratification it should be possible to study the variation of  $K$  with concentration. An approximate curve of  $K(c)$  and from this of  $dK/dc$  coming from the experiment itself could be used to decide whether the appropriate smallness of concentration amplitude had been realized or whether a correction would be required.

<sup>2</sup> The justification for this assumption will increase as the amplitude of the periodic density distribution becomes small compared to the constant term in the later stages of decay of the stratified deposit.



coefficient  $K$  will characterize the diffusion of  $\rho_B$  and obviously this same equation will also hold with  $n_A$  or  $n_B$  as the dependent variable.

In Fowler's *Statistical Mechanics*<sup>4</sup> (1936) that author following Einstein derives a diffusion equation of the type of Eq. (2) (with the number density as the dependent variable) from statistical considerations alone without regard to the state of the diffusing atoms. Fowler's principal assumption for this purpose is that the chance of an atom migrating from a point  $x$  at a time  $t$  to a point  $x'$  at a time  $t'$  depends on the intervals  $(x' - x)$  and  $(t' - t)$  and nothing else. This seems to be tantamount to the assumption of constant  $K$ .

We further assume that the density distribution functions  $\rho_A(x, t)$ ,  $\rho_B(x, t)$  can be represented with sufficient accuracy by a terminating Fourier series periodic in  $x$  with period " $d$ " whose coefficients (save for the constant terms which we shall call  $\rho_A'$  and  $\rho_B'$ ) are exponentially decaying functions of the time. These series terminate with harmonics  $N'$  of wave-length large compared to the statistical fluctuations of density arising from the atomic nature of the deposit so that the series represents only the *artificially imposed* periodicities. Let  $\rho_A^*$  denote the fluctuating part of  $\rho_A$  so that  $\rho_A = \rho_A^* + \rho_A'$  and

$$\int_x^{x+d} \rho_A^* dx = 0.$$

Since the series is finite we may safely differentiate it term by term without examining the convergence of the derivatives. The series is

$$\rho_A(x, t) = \sum_{n=0}^{N'} S_n e^{-\sigma_n t} \sin 2\pi n x / d + C_n e^{-\gamma_n t} \cos 2\pi n x / d. \quad (3)$$

in which  $\sigma_n$  and  $\gamma_n$  are to be determined while the  $C_n$  and  $S_n$  characterize the shape of the periodic fluctuations of the distribution profile. On substitution into Eq. (1) this solution is justified and the resulting identities give

$$\sigma_n = \gamma_n = 4\pi^2 n^2 K / d^2 \quad (4)$$

or

$$K = \sigma_n d^2 / (4\pi^2 n^2) = \gamma_n d^2 / (4\pi^2 n^2).$$

<sup>4</sup> Fowler, *Statistical Mechanics* (Cambridge, second edition, 1936), p. 770.

Now the important thing to notice is that the decay constants of various harmonic components of the films are proportional to  $n^2$  the square of the ordinal number of the harmonic.

Thus if the ratio of the amplitude of the *fundamental* at some time  $t = \tau$  to the amplitude at  $t = 0$  is

$$R_1 = e^{-(4\pi^2 K / d^2) \tau}.$$

then the corresponding ratio representing the decay of the second harmonic in the same time will be

$$R_2 = e^{-(4\pi^2 \cdot 4K / d^2) \tau} = R_1^4.$$

while for the third harmonic it will be  $R_1^9$  etc. Thus when the fundamental has decayed to one-tenth of its initial value the second harmonic will have only one-ten-thousandth of its initial amplitude, the third harmonic only one-billionth of its initial amplitude and so on with all the higher harmonics decaying to infinitesimals of higher order. This purifying process continues with time until the fundamental amplitude has decayed to a value comparable with the accidental statistical fluctuations of density caused by the atomic nature of the film.

The diffracted x-ray intensity to be expected from such a stratified deposit will be proportional to the square of the amplitude of the periodically varying part of the electron density function. Let  $Z_A$  and  $Z_B$  be the atomic numbers of the components,  $W_A$  and  $W_B$  their atomic weights,  $N$  Avogadro's number, and  $n$  the number density of electrons per unit volume which consists of the sum of a periodic term  $n^*$  and a constant term  $n'$  so that

$$n = n^* + n'.$$

Then evidently

$$n = \rho_A Z_A N / W_A + \rho_B Z_B N / W_B$$

and since from Eq. (1)

$$\rho_B = \rho_{0B} - (\rho_{0B} / \rho_{0A}) \rho_A.$$

it follows that

$$n = \rho_A [Z_A N / W_A - (\rho_{0B} / \rho_{0A}) Z_B N / W_B] + \rho_{0B} Z_B N / W_B. \quad (5)$$

The last term of this expression is constant and

contributes nothing to  $n^*$  the fluctuating part of  $n$ . Denoting by  $\rho_A^*$  the periodic part of  $\rho_A$  we have

$$(n^*)^2 = (\rho_A^*)^2 [Z_A N / W_A - (\rho_{0B} / \rho_{0A}) Z_B N / W_B]^2. \quad (6)$$

The diffracted x-ray intensities will therefore be jointly proportional to the square of the amplitude of the density fluctuations and to the square of the difference in the parenthesis in (6). Since  $Z_A N / W_A$  is practically constant, materials of very different densities will give the strongest reflections as might be expected.

The intensities reflected in the different orders will be proportional to the squares of the amplitudes of the various Fourier harmonics of the density distribution function and it is obvious that all orders above the first will also decay very rapidly in the same way as described above for the amplitudes of the density distribution.

#### Determination of the diffusion coefficient $K$

Assuming that the function  $\rho^*(x, t)$  has by the diffusion process purified itself to a simple harmonic function of  $x$  we observe the ratio  $R_{21}$  of the intensities  $I_2$  and  $I_1$  of the diffracted radiation for a time  $t_1$  and for a later time  $t_2$

$$R_{21} = I_2 / I_1 = e^{-(8\pi^2 K / d^2)(t_2 - t_1)}.$$

Solving this for  $K$  we obtain an expression for the diffusion coefficient entirely in terms of measurable quantities

$$K = -\frac{d^2 \log_e I_2 / I_1}{8\pi^2(t_2 - t_1)}. \quad (7)$$

The value of  $d$  may be measured directly from the diffraction angle and the wave-length of the x-rays used or it may be obtained by measuring the total thickness of the film by interferometry and dividing this by the number of layers. Our present rough results indicate  $K = 5 \times 10^{-20}$  cm<sup>2</sup> sec.<sup>-1</sup> for the diffusion coefficient of gold through copper at room temperature.

It is worth noting that for reasonable time intervals ( $t_2 - t_1$ ) because of the factor  $d^2$  in Eq. (7) values of  $K$  many orders of magnitude smaller can be measured by this method than by methods requiring diffusion over macroscopic distances  $d$ . The time for observable diffusion over a distance of  $\frac{1}{10}$  mm is a hundred million times as great as it is for the 100Å involved in this experiment.

#### ACKNOWLEDGMENTS

We wish gratefully to acknowledge our indebtedness to Dr. Leon L. Watters of New York City for the funds which have supported this work.