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PRELIMINARY REPORT ON THE DIFFUSION OF SOLIDS.

By C. E. Van Orstrand and F. P. Dewey.[1]

INTRODUCTION.

Although 19 years has elapsed since Roberts-Austen[2] published his classical paper on the diffusion of solid metals, no attempt seems to have been made to verify his important results and conclusions or to extend the investigations to minerals and to the great number of solids in which diffusion may be expected to occur. Progress has been made by means of chemical and electrical methods[3] in the detection of diffusion in a number of metals in the solid state, some progress has been made in explaining the phenomena of diffusion on the basis of osmotic pressure and the kinetic theory, and recent measurements of the vapor pressures[4] of solids have contributed indirectly to the progress of the science, but investigators have not undertaken the difficult and essential task of making definitive determinations of the coefficients of diffusivity at various pressures and temperatures.

The investigation of which this paper is a preliminary note has for its first object the determination of the coefficients of diffusivity over a considerable range of pressures and temperatures for metals and minerals. The investigation was first undertaken in connection with some experiments on the elasticity and plasticity of metals. Although it is believed that the results are essential for the construction of a complete theory of the physical properties of elastic and plastic bodies in the normal state or in a state of isostatic adjustment, it is realized that this is only one of many fields in which the results are of fundamental importance. Roberts-Austen emphasized the importance of diffusion in its relation to the formation of alloys and the more vital problem of the constitution of matter; the importance of the general problem of diffusion in the elucidation of geologic problems has been emphasized by Becker,[5] who also prepared a table for the computation of diffusivities; Elsden[6] and Liesegang[7] give an extended discussion of the subject in their textbooks; Desch[8] has pointed out the possibility of explaining secondary replacements of minerals, the formation of pseudomorphs, schiller inclusions, and other geologic features on the basis of the diffusion of minerals in the solid or molten state; and recently Gillette[9] has discussed a theory of ore deposition in which osmotic pressure is assumed to be one of the fundamental factors.

In their more general aspects the phenomena of diffusion are not confined to the inorganic world. It is well known that diffusive processes play an important part in living matter, and

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[1] Dr. Dewey is assayer to the Bureau of the Mint, United States Treasury Department, and this paper is published with the permission of the Director of that bureau.

[2] Roberts-Austen, W. C., On the diffusion of metals: Roy. Soc. London Philos. Trans., vol. 187 A, pp. 383–415, 1896; On the diffusion of gold into solid lead at the ordinary temperature: Roy. Soc. London Proc., 1900, pp. 435–441; also vol. 67, pp. 101–105.

[3] Guillet, L., and Bernard, V., Local prevention of casehardening and diffusion in solids: Rev. métallurgie, vol. 11, pp. 752–765, July, 1914. Desch, C. H., Report on diffusion in solids: British Assoc. Rept., 1912, pp. 348–372. (As this report contains an excellent summary of the literature of the subject, the references need not be repeated in this paper.)

[4] Hulett, G. A., The distillation of amalgams and the purification of mercury: Phys. Rev., vol. 33, pp. 307–317, 1911. (Hulett made an approximate determination of the vapor pressure of platinum at a temperature of 200° C.) Langmuir, Irving, The vapor pressure of metallic tungsten: Idem, 2d ser., vol. 2, pp. 329–343, 1913. Langmuir, Irving, and Mackay, G. M. J., The vapor pressure of the metals platinum and molybdenum: Idem, 2d ser., vol. 4, pp. 377–387, 1914. Wartenberg, H. von, Über Metalldampfdrucke: Zeitschr. Elektrochemie, vol. 19, p. 482, 1913.

[5] Becker, G. F., Note on computing diffusion: Am. Jour. Sci., 4th ser., vol. 3, pp. 280–286, 1897.

[6] Elsden, J. V., Principles of chemical geology, Whittaker & Co., London, 1910.

[7] Liesegang, R. E., Geologische Diffusionen, Theodor Steinkopff, Dresden and Leipzig, 1913. (An important review of this work is given by Adolph Knopf in Econ. Geology, December, 1913, pp. 803–806.)

[8] Desch, C. H., op. cit.

[9] Gillette, H. P., Osmosis as a factor in ore formation, in Emmons, S. F., Ore deposits, pp. 450–454, Am. Inst. Min. Eng., 1913.

it will be interesting in this connection[1] to quote from the conclusion of the paper by Roberts-Austen, already cited. Referring to Graham's great work on the diffusion of salts into liquids and of liquids into each other, he says:

> His work in experimental physics, more than that of any other investigator, taught the physiologist that tracing the relations of the phenomena of life as revealed in diffusion, transpiration, and osmosis will afford natural history its most precious records.
>
> The evidence gathered by the metallurgist of active atomic movement in fluid and solid metals may sustain the hope of the physiologist that he will ultimately be able to measure the atomic movements upon which vitality and thought depend.

THEORETICAL CONSIDERATIONS.

The phenomenon of diffusion as exemplified by gases, salts, liquids, solids, and certain constituents of organisms is supposed to be a transfer of mass in a given direction due to the continuous haphazard motion of the molecules of which the substances are composed. A simple analogy is that of spheres moving over a smooth horizontal surface bounded on the edges by perfectly elastic walls. We may imagine one system to consist of white and the other of red spheres, and the two systems to be separated from each other by a perfectly elastic partition. If the spheres are set in motion and the air resistance is negligible, they will continue to collide with one another for an indefinite time. The mean kinetic energy of each system, corresponding in our analogy to the temperature of the system, may or may not be the same, but in either case if the partition is removed the red and white spheres begin to collide with one another and to occupy areas previously occupied by spheres of a single color. A strip on each side of the line marking the original position of the partition will thus contain spheres of both colors, the greatest number of mixed colors being in the immediate vicinity of this line. It is conceivable that a very small number of spheres will reach the boundary wall parallel to the partition in a very short time, and that as the process continues spheres of the opposite color will accumulate in this region and there will then be reflection or resultant motion in the direction toward the partition, the tendency being always for a sphere to move away from the region in which the number per unit area of spheres of its particular kind is greatest. Statistical equilibrium in density will be attained when the number of red spheres per unit area is constant throughout the entire area, and similarly for the white spheres. The paths traced out by the spheres are of course very irregular, and even after equilibrium is established the spheres zigzag back and forth across the plane, but always in such a way that the average number of different spheres per unit area remains unchanged. It is evident that equilibrium of this kind implies that the average number of red or white spheres entering any fixed area of the surface over which the spheres are moving is the same as the number leaving the same area in a given interval of time.

That the interdiffusion of gases, liquids, and solids and the diffusion of gases into solids and of gases and solids into liquids are mechanical processes analogous to the simple process just described may be inferred from the observations and verifications with theory of the Brownian movements. A study of these phenomena has sufficed to establish Maxwell's fundamental laws for the equipartition of energy and the distribution of velocities about the average velocity for liquids and has thus provided a sound foundation on which the kinetic theory of matter in the three states—solid, liquid, and gaseous—may be constructed. The remarkable theoretical and experimental investigations of Perrin,[2] Einstein, and others leave no doubt as to the reality of molecules and molecular motion in liquids, and it therefore seems reasonable to infer that solids are mechanical systems of the same kind, in which the molecular displacements are much restricted, and in some solids, such as crystals, the law of restriction varies from one form of crystal to another. It is conceivable that molecules possess axes along which the attractive forces vary. In the liquid and gaseous states the molecules are in constant rotation, and the distance between centers is so great that the directional forces are inappreciable, but in the solid crystalline state these forces may predominate to such an extent that the

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[1] See also, for example, Livingston, B. E., The rôle of diffusion and osmotic pressure in plants, Univ. Chicago Press, 1903.

[2] Perrin, Jean, Brownian movement and molecular reality, by F. Soddy, Taylor & Francis, London, 1910.

strictly random rotations and displacements do not occur. The number of degrees of freedom of the system has been diminished.

Attempts have been made to explain diffusion and osmotic pressure on the basis of chemical affinity, the formation of loose chemical compounds, and the influence of surface tension.[1] Chemical affinity, however, is merely the potential energy of a dynamic system; the formation of loose compounds is simply aggregation and dissociation, and surface tension has long been known to be due to unequal molecular attractions. Each explanation is in reality the application of a special feature of dynamic theory, although it was apparently intended by the advocates of these hypotheses to obtain an explanation of the phenomenon which would be independent of mechanical systems. The fact that there is an observed transportation of matter would seem in itself to be a sufficient justification for the assumption that the system is mechanical, but the additional fact that solids possess a vapor pressure would seem to leave little doubt in regard to the validity of the hypothesis that solids[2] are composed of discrete particles in a state of rapid oscillation, although restricted somewhat in their movements.

In the consideration of the migration of the particles in the diffusion process, one of the simplest methods of procedure is to adopt a certain average value or constant which corresponds to a certain type and state of molecular activity of the given substances. The quantity selected, the coefficient of diffusivity (k), may be defined by considering the exchange of molecules between two cylinders of different substances when the ends are placed in contact with each other and the entire system is maintained at constant temperature. The principle of sufficient reason suffices to show that the molecular transfer will take place in such a manner that the concentration, the mass of dissolving substance per unit volume of solution, is constant throughout a layer of infinitesimal thickness perpendicular to the common axis of the cylinders. The simplest assumption that can be made in regard to the interdiffusion of the two substances is to assume that the amount of diffusing substance which passes any plane perpendicular to the axis of the cylinder is proportional to the time, the area of cross section, and the rate of change of concentration per unit length, measured in the direction in which the solute is moving into the solvent. Expressed in the form of an equation, the assumption may be written

$$m=ka\frac{(v_1-v_2)\,t}{\Delta x} \tag{1}$$

wherein

m = mass of solute
k = coefficient of diffusion
a = area
t = time
Δx = distance between two planes at which the concentrations are v_1 and v_2.

Now put a, t, Δx, and (v_1-v_2) each equal to unity; then k is the mass of solute passing through a unit cube of the solvent in unit time when the difference between the concentrations at the opposite faces of the cube is equal to unity. It will be noted that equation (1) represents also the quantity of heat flowing through a plate of cross-sectional area a, thickness Δx, in time t, when the temperatures of the respective surfaces are v_1 and v_2. The quantity k is here called the thermal conductivity of the substance.

With this definition of the coefficient of diffusivity as a basis, we now proceed to find the amount of solute in any given volume of the solution whose center is at distance x from the plane of contact, after a given time interval t has elapsed. If we imagine the two parallel planes which are perpendicular to the direction of flow of the solute to approach each other, we have in the limit, when the time interval also is infinitesimal,

$$dm=ka\frac{\partial v}{\partial x}dt$$

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[1] For a discussion of these and other explanations, see Whetham, W. C. D., Theory of solution, Cambridge Univ. Press, 1902; Findlay, Alexander, Osmotic pressure, Longmans, Green & Co., 1913.

[2] See also Nernst, Walther, The theory of the solid state, Univ. London Press, 1914. Bragg, W. H. and W. L., X rays and crystal structure, G. Bell, London, 1915. Magie, W. F., Relation of osmotic pressure to temperature: Phys. Rev., October, 1912, pp. 272–275.

Here again it is evident that our assumption is the simplest possible, for it would not be unreasonable to assume that dm is a function of the higher powers of $\partial v/\partial x$. Our equation merely amounts to stating that

$$f_x = k\frac{\partial v}{\partial x} \tag{2}$$

is the rate per unit time at which the solute flows through unit area of a plane which is perpendicular to the axis of the cylinder and at distance x from the plane of contact. The term flow is here used to designate the resultant motion of the solute in a given direction and is merely the summation in a given direction of the very irregular displacements of the molecules. The resultant at right angles to the direction of flow is zero, on account of reflection at the surface, but there is always a small resultant displacement of the particles in the direction from higher to lower concentration.

Now imagine a parallelepiped whose edges are $2dx$, $2dy$, $2dz$, and whose center is at distance x from the plane of contact. The change in concentration per unit volume at x in time dt is $(\partial v/\partial t)\,dt$ and the increment in the mass of the solute in this elementary volume is therefore represented by the equation

$$\text{volume} \times \text{change in concentration} = 8\,dxdydz\frac{\partial v}{\partial t}dt \tag{3}$$

We can obtain another expression for the same quantity, for the rate at which the solute is flowing into the parallelepiped across the plane nearest to the plane of contact is

$$4\,dydz\left(f_x + \frac{\partial f_x}{\partial x}\right)dx$$

Similarly the rate of outflow across the plane farthest from the plane of contact is

$$4\,dydz\left(f_x - \frac{\partial f_x}{\partial x}\right)dx$$

and the total gain to the parallelepiped in time dt is therefore

$$8\,dxdydz\,\frac{\partial f_x}{\partial x}dt$$

Equating this expression to (3) and making use of (2) we get the result

$$\frac{\partial v}{\partial t} = \frac{\partial f_x}{\partial x} = k\frac{\partial^2 v}{\partial x^2} \tag{4}$$

An integral of (4) is

$$v = v_0\left[1 - \frac{2}{\sqrt{\pi}}\int_0^q e^{-q^2}dq\right] \tag{5}$$

in which

$$v_0 = \text{constant}$$
$$q = x/2\sqrt{kt}$$

This result may be established by expressing the integral as a function of the limits of integration and performing the necessary differentiations.[1]

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[1] For other methods of integration, see, for example, Carslaw, H. S., Fourier's series and integrals, Macmillan & Co., 1906; Ingersoll, L. R., and Zobel, O. J., Mathematical theory of heat conduction, Ginn & Co., 1913; Byerly, W. E., Fourier's series and spherical harmonics, Ginn & Co., 1895; Woodward, R. S., A new method of integrating one of the differential equations of the theory of heat diffusion: Phys. Rev., vol. 16, pp. 176–177, 1903; On the free cooling of a homogeneous sphere: Annals Math., vol. 3, pp. 75–88, 1887

If k is replaced by

$$\kappa = \frac{h}{\rho c}$$

where ρ, h, and c are respectively density, conductivity, and specific heat of the substance, equation (5) will then represent the distribution of temperature in an insulated bar of great length, initially at a uniform temperature of 0° throughout the mass, and subjected at one end to a constant temperature v_0 for the time interval t. Similarly, equation (5) represents the distribution of concentration in a cylinder of initially pure substance in the solid or liquid state when a layer of constant concentration v_0 is maintained at the base of the cylinder for a time t. When $t=0$, equation (5) gives $v=0$ for all values of x, thus expressing the fact that at the beginning of the experiment the cylindrical mass contained no solute. For all finite values of t other than zero, equation (5) gives $v=v_0$ for $x=0$, which agrees with the condition that constant concentration is maintained at the plane of contact; and for other values of x, v diminishes as x increases until for $x=\infty$, $v=0$. These results agree with the general form of the observed curve indicated in figure 32 (p. 94). As time proceeds, the curves continue to rise, and when an infinite time has elapsed, $v=v_0$ for all values of x. In other words, constant concentration is attained in a cylinder of infinite length in an infinite time. Stefan [1] assumed that reflection occurs at the ends of a cylinder of finite length and that the concentration at any point is the sum of the concentrations at corresponding points in a cylinder of great length, the long cylinder being supposed to be cut into lengths equal to that of the short cylinder and then folded backward and forward upon itself until the extreme portion containing solute is contained within the short length. The correctness of the assumption has been abundantly verified by the experiments of Roberts-Austen on molten metals.

EXPERIMENTAL METHODS.

Roberts-Austen determined the coefficients of diffusion of solid gold into solid lead at temperatures of 100°, 165°, 200°, and approximately 18° C. In some experiments a gold plate was fused to the end of the lead cylinder; in others a gold plate or a 5 per cent alloy of gold and lead was pressed against the surfaced end of the lead cylinder by means of binding screws. The specimens were maintained at constant temperatures for various time intervals ranging from 10 to 41 days for the high temperatures and 4 years for the ordinary temperature, after which they were sliced and the gold content of each section determined to a high degree of precision by means of a careful assay.

We have conducted similar experiments at temperatures of 100°, 150°, 180°, and 197° C., using for some of the specimens 0.5-millimeter gold plates clamped to the ends of the lead cylinders, and for others a gold electroplate on one or both ends of the lead cylinder, in accordance with a suggestion of Dr. N. E. Dorsey, of the Bureau of Standards. After the specimens were heated for a number of days in an air thermostat controlled by a mercury regulator, they were cut into sections by means of a sharp bevel-edged wheel attached to a turning lathe.

The distances from the planes of contact to the boundary planes of the section were first determined with a micrometer attached to the lathe, but this method proved to be unsatisfactory on account of the necessity of shifting the specimen in the lathe chuck. A more satisfactory method consisted in marking the beginning and end of each section with a dividing engine. A slight error results from inaccuracy in setting the cutting tool, but such errors are accidental and are therefore not of a serious character. The method of determining the lengths from the densities will be used in connection with the preceding method for determinations of the very highest precision.

As the edges of the electroplate must be turned off to obtain a perfect cylinder, the plates frequently tend to curl, and it is therefore necessary to clamp the ends lightly in order to insure perfect contact throughout the plane surface. None of the electroplated specimens failed to show

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[1] Stefan, J., Über die Diffusion der Flussigkeiten: K. Akad. Wiss. Sitzungsb., Band 79, Abt. 2, pp. 161–214, 1879.

diffusion when heated to a temperature above the normal, but in some of our trials with 0.5-millimeter gold plates only 20 per cent of the specimens showed diffusion at temperatures of 100° and 180° C. In another experiment, however, in which five pairs of gold and lead were heated to a temperature of 150° C., each specimen was found to contain a sufficient quantity of gold for the determination of the coefficient of diffusion (k). We have no explanation to offer for the cause of failure other than the possibility of oxidation and imperfect mechanical treatment. The ends of the lead cylinders were carefully surfaced on a lathe. Oil was used in the surfacing process and afterward removed by the use of caustic soda and a 10 per cent solution of nitric acid. The 0.5-millimeter gold plates (20 millimeters in diameter) require no preparation other than cleansing in dilute nitric acid and distilled water.

Pure gold was obtained from Mr. Jacob B. Eckfeldt, of the United States Mint at Philadelphia. Lead was obtained from the Pennsylvania Smelting Co., Pittsburgh, in the form of bars 1 by 3 by 6 inches. It was found to be free from gold and silver but contained a trace of copper.

The thermostat is provided with two heating coils, one consisting of insulated resistance tape attached to a cylinder of coarse wire screen and placed just within the inside wall, and the other consisting of 20 nickel coils wound on soapstone cylinders (2 by 3½ inches) and placed on the bottom of the thermostat. The insulation powder (Silox) was obtained from the General Electric Co.

Temperatures were measured with standardized mercury thermometers placed at various points. The temperature gradients were found to be so slight that no errors could have arisen from this source.

METHODS OF EVALUATION OF CONSTANTS.

In the evaluation of the coefficient k, investigators frequently use Stefan's tables,[1] which are very convenient when an alloy or concentrated solution of known height and concentration diffuses into pure solvent. In order to apply the tables it is necessary to make the height of the section selected for analysis equal to one-half the height of the alloy or solution from which diffusion emanates. Such tables are not adapted to our needs, and we have used instead some manuscript tables of the probability integral which have been prepared especially for the computation of diffusivities.

The observed concentrations require no correction for the differences in density of the two metals, but the observed distances (x') from the plane of contact must be corrected for the expansion of the solvent over the temperature interval ($T-T_0$) where T_0 is the temperature at which the specimen is sliced and T is the temperature at which diffusion takes place. If α is the coefficient of expansion of the solvent, the value of x to be used in the formula for q is

$$x=x'\,[1+\alpha(T-T_0)].$$

With q as an argument the values of the probability integral are taken from the special tables for points which correspond to the upper, middle, and lower planes of the section, and in accordance with the approximate formula of Cotes, the average value of the integral for the entire section may be taken to be

$$\frac{1}{6}[\text{sum of end ordinates}+4\times\text{middle ordinate}].$$

Designating the difference between unity and this value of the integral by i, equation (5) may be written

$$v=v_0 i \qquad (6)$$

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[1] Stefan, J., op. cit.

Equation (5) contains two unknown constants, v_0 and k. Numerous solutions may be obtained by adopting different methods of procedure or by assigning different weights to the observation equations. As the different methods lead to slightly different values of the constants, it is essential that the method adopted should be theoretically correct.

For the data of this paper the maximum error in the determination of the gold content of each section is of the order of magnitude of 0.005 milligram. The probable error of a single determination is of course less than this quantity, and there is no reason for assuming it to vary for the different sections. The weight of each point on the concentration curve is therefore equal to unity for sections of normal height and one-fourth for sections of one-half the normal height.

Roberts-Austen determined the value of v_0 by extending the concentration curve backward until it intersected the axis of ordinates. This method is not entirely satisfactory on account of the rapid changes in curvature of the concentration curve in the vicinity of the origin. For this reason we have adopted the linear equation

$$idv_0 + qe^{-q^2}\frac{v_0}{\sqrt{\pi k}}dk = dv \text{ - (7)}$$

or

$$idv_0 + qe^{-q^2}dk' = dv \text{ - (8)}$$

which enables us by the method of least squares to determine both constants at the same time. The approximate values necessary for the computation of dv were determined by selecting at least three values of k at equal intervals apart and over a sufficient range to include the correct value. Substituting each value of k in (6) and solving in the form

$$v_0 = \frac{\Sigma piv}{\Sigma pi^2} \text{ - (9)}$$

wherein weights are designated by p, we obtain the corresponding weighted values of v_0. The sum of the weighted squares of the residuals was then computed in the usual manner and plotted with the values of k as abscissas. The value of k which corresponds to a minimum value of the sum of the weighted squares of the residuals was ascertained by drawing a tangent to the curve parallel to the k axis. The corresponding value of v_0 was determined by interpolation, using k as an argument. A rough check on the computation consists in plotting the sum of the weighted squares of the residuals for the new values of v_0 and k on the original diagram. The new point should of course fall at the vertex of the curve. A more satisfactory check is obtained by solving equations (7) and (8). The coefficients and absolute terms of the observation equations are computed from one of the original pairs of values of v_0 and k that are adjacent to but do not coincide with the minimum point of the curve which represents the sum of the weighted squares of the residuals.

In order to show the influence which the data from the various sections exert in fixing the final values of the constants, and at the same time to illustrate the method of computation, the observation equations for the data of Table 1 are tabulated below.

$$\begin{array}{rrl}
0.68722\ dv_0 & +0.14949\ dk' & =+0.00059 \\
.44324 & .27868 & \quad -\ .00005 \\
.26730 & .37185 & \quad -\ .00037 \\
.15024 & .42083 & \quad -\ .00053 \\
.07850 & .42608 & \quad -\ .00040 \\
.03802 & .39519 & \quad +\ .00009 \\
.01704 & .34005 & \quad +\ .00015 \\
.00706 & .27351 & \quad +\ .00014 \\
.00269 & .20665 & \quad +\ .00009 \\
.00095 & .14715 & \quad +\ .00008 \\
.00031 & .09899 & \quad -\ .00023 \\
.00009 & .06302 & \quad -\ .00006
\end{array}$$

The normal equations are

$$1.69266\,dv_0 + 0.94621\,dk' = -0.0000016$$
$$0.94621\,dv_0 + 1.02166\,dk' = -0.0003281$$

from which we obtain

$$dk' = -0.000664$$
$$dv_0 = +0.00037$$

As

$$\frac{v_0}{\sqrt{\pi k}} = 1.54386$$

we have

$$dk = -0.00043$$

and

$$k = 0.0080 - 0.0004 = 0.0076$$
$$v_0 = 0.02189 + 0.00037 = 0.02226$$

The approximate values

$$k = 0.0080$$
$$v_0 = 0.02189$$

were determined as explained above from the following quantities:

k	v_0	$\Sigma(\text{residuals})^2$
0.0070	0.02283	126
.0075	.02234	84
.0080	.02189	105

The numbers tabulated in the third column are the first two or three digits only of the actual sums. If these numbers are plotted with the values of k as abscissas, it will be found that the minimum point of the curve falls at $k = 0.0076$. With this value of k as argument, the corresponding value of v_0 is found by interpolation to be $v_0 = 0.02230$. These values agree almost identically with those just found by solving the above system of observation equations. The number found for $\Sigma(\text{residuals})^2$ is 82, which is practically the same as the value found by the graphic method. As the coefficients and absolute terms of the normal equations are summations of squares and products of coefficients and products of coefficients and absolute terms of the observation equations, it is evident that the equations at the bottom of the list exert but little influence in the determination of the constants. The final values would remain practically unchanged if the last two or three equations were omitted. The weights of v_0 and k are each finite and may be determined in the usual manner. The respective weights of these quantities resulting from the use of equation (9) are Σpi^2 and ∞. Another solution consists in assigning an infinite weight to v_0, and then taking the weighted mean of the resulting values of k. It is thus evident that the relative weights of v_0 and k must be taken into account, as well as the relative weights of the observation equations. These distinctions may be of practical importance when the deviations from the theoretical curve are of considerable magnitude.

COMPARISON OF OBSERVATION WITH THEORY.

The data on the diffusion of gold into solid lead under atmospheric pressure are presented in Tables 1 to 11 inclusive. The values in the first columns are the observed distances at temperature T_0 from the plane of contact to the center of the section. The 1-millimeter section adjacent to the plane of contact was always rejected. Column 6 gives the percentage of gold computed from the weight of the alloy and the weight of the gold contained in the alloy as tabulated in columns 2 and 3 respectively. Columns 4 and 7 contain the computed theoretical values, and columns 5 and 8 contain the residuals or the differences between the observed and computed values. It will be noted that in each case equation (5) represents the observed facts to a high degree of precision.

TABLE 1.

Distance (x') from plane of contact (centimeters). 1	Weight of alloy (grams). 2	Weight of gold (milligrams).			Percentage of gold (v).			Constants.
		Observed. 3	Computed. 4	Observed — computed. 5	Observed. 6	Computed. 7	Observed — computed. 8	
0.2	6.7250	1.26	1.23	+0.03	0.0187	0.0184	+0.0003	
.4	6.6105	.96	.97	− .01	.0145	.0146	− .0001	
.6	6.6680	.73	.75	− .02	.0109	.0113	− .0004	
.8	6.6600	.53	.56	− .03	.0080	.0084	− .0004	$\alpha=0.0000293$.
1.0	6.6310	.38	.40	− .02	.0057	.0060	− .0003	T=197° C.
1.2	6.6535	.29	.27	+ .02	.0044	.0041	+ .0003	$t=53.92$ days.
1.4	6.6510	.20	.18	+ .02	.0030	.0027	+ .0003	$v_0=0.02226$.
1.6	6.5785	.13	.11	+ .02	.0020	.0017	+ .0003	$k=0.0076$.
1.8	7.3140	.09	.08	+ .01	.0012	.0010	+ .0002	
2.0	6.6850	.05	.04	+ .01	.0008	.0006	+ .0002	
2.2	6.7030	.01	.02	− .01	.0002	.0003	− .0001	
2.4	6.5480	.01	.01	.00	.0001	.0002	− .0001	

TABLE 2.

0.2	5.5255	0.71	0.70	+0.01	0.0129	0.0127	+0.0002	
.4	5.4750	.53	.53	.00	.0097	.0097	.0000	
.6	5.4775	.37	.39	− .02	.0068	.0070	− .0002	
.8	5.5130	.25	.27	− .02	.0045	.0049	− .0004	
1.0	5.4940	.18	.18	.00	.0033	.0032	+ .0001	T=197° C.
1.2	5.4935	.12	.11	+ .01	.0022	.0020	+ .0002	$t=53.92$ days.
1.4	5.5250	.08	.06	+ .02	.0015	.0012	+ .0003	$v_0=0.01587$.
1.6	5.4880	.04	.04	.00	.0007	.0007	.0000	$k=0.0057$.
1.8	5.4590	.02	.02	.00	.0004	.0003	+ .0001	
2.0	4.8595	.02	.01	+ .01	.0004	.0002	+ .0002	
2.2	5.5080	Trace.	.004	....	....	.0001	....	
2.4	5.4915	Trace.	.002	....	....	.0000	....	

TABLE 3.

0.2	5.5980	0.80	0.79	+0.01	0.0143	0.0141	+0.0002	
.4	5.5200	.59	.60	− .01	.0107	.0109	− .0002	
.6	5.5645	.44	.45	− .01	.0079	.0081	− .0002	
.8	5.5695	.31	.32	− .01	.0056	.0057	− .0001	
1.0	5.4845	.22	.21	+ .01	.0040	.0039	+ .0001	T=197°C.
1.2	5.5590	.15	.14	+ .01	.0027	.0025	+ .0002	$t=53.92$ days.
1.4	5.5120	.10	.08	+ .02	.0018	.0015	+ .0003	$v_0=0.01739$.
1.6	5.6080	.04	.05	− .01	.0007	.0009	− .0002	$k=0.0063$.
1.8	5.5655	.03	.03	.00	.0005	.0005	.0000	
2.0	5.5620	.02	.01	+ .01	.0004	.0003	+ .0001	
2.2	5.8775	Trace.	.008	....	....	.0001	....	
2.4	5.5470	Trace.	.003	....	....	.0001	....	

TABLE 4.

0.2	7.8865	1.03	1.00	+0.03	0.0131	0.0127	+0.0004	
.4	7.8200	.74	.76	− .02	.0095	.0098	− .0003	
.6	7.8140	.54	.56	− .02	.0069	.0072	− .0003	
.8	7.8295	.39	.39	.00	.0050	.0050	.0000	
1.0	7.8225	.26	.26	.00	.0033	.0033	.0000	T=197° C.
1.2	7.8310	.17	.16	+ .01	.0022	.0021	+ .0001	$t=53.92$ days.
1.4	7.6505	.11	.10	+ .01	.0014	.0013	+ .0001	$v_0=0.01588$.
1.6	7.8265	.07	.05	+ .02	.0009	.0007	+ .0002	$k=0.0059$.
1.8	7.8235	.05	.03	+ .02	.0006	.0004	+ .0002	
2.0	7.7865	.01	.01	.00	.0001	.0002	− .0001	
2.2	7.8535	.01	.01	.00	.0001	.0001	.0000	
2.4	7.7580	.01	.003	+ .007	.0001	.0000	+ .0001	

TABLE 5.

Distance (x') from plane of contact (centimeters).	Weight of alloy (grams).	Weight of gold (milligrams).			Percentage of gold (v).			Constants.
1	2	Observed. 3	Computed. 4	Observed—computed. 5	Observed. 6	Computed. 7	Observed—computed. 8	
0.2	7.9530	1.04	1.02	+0.02	0.0131	0.0128	+0.0003	T=197° C. t=53.92 days. v_0=0.01580. k=0.0064.
.4	7.8310	.76	.78	− .02	.0097	.0099	− .0002	
.6	7.8025	.55	.58	− .03	.0071	.0074	− .0003	
.8	7.8530	.41	.41	.00	.0052	.0053	− .0001	
1.0	7.8180	.29	.28	+ .01	.0037	.0036	+ .0001	
1.2	7.7710	.19	.18	+ .01	.0024	.0023	+ .0001	
1.4	7.7970	.13	.11	+ .02	.0017	.0014	+ .0003	
1.6	7.7950	.07	.07	.00	.0009	.0008	+ .0001	
1.8	7.7780	.04	.04	.00	.0005	.0005	.0000	
2.0	7.8805	.01	.02	− .01	.0001	.0003	− .0002	
2.2	7.7940	Trace.	.010	....	....	.0001	....	
2.4	8.0590	.01	.005	+ .005	.0001	.0001	.0000	
2.6	7.6385	Trace.	....	....	....	....	....	

TABLE 6.

0.2	7.8095	0.99	0.98	+0.01	0.0127	0.0125	+0.0002	T=197° C. t=53.92 days. v_0=0.01554. k=0.0058.
.4	7.8490	.74	.75	− .01	.0094	.0095	− .0001	
.6	7.8385	.51	.54	− .03	.0065	.0069	− .0004	
.8	7.8175	.38	.38	.00	.0049	.0048	+ .0001	
1.0	7.7950	.25	.25	.00	.0032	.0032	.0000	
1.2	7.8280	.17	.16	+ .01	.0022	.0020	+ .0002	
1.4	7.7425	.11	.09	+ .02	.0014	.0012	+ .0002	
1.6	7.8155	.06	.05	+ .01	.0008	.0007	+ .0001	
1.8	7.8160	.03	.03	.00	.0004	.0003	+ .0001	
2.0	7.8210	.01	.01	.00	.0001	.0002	− .0001	
2.2	9.2530	.01	.01	.00	.0001	.0001	.0000	
2.4	7.8790	Trace.	.003	....	....	....	....	
2.6	7.8350	Trace.	....	....	....	....	....	

TABLE 7.

0.15	3.7347	0.29	0.28	+0.01	0.0078	0.0074	+0.0004	T=150° C. t=63.29 days. v_0=0.00878. k=0.0043.
.3	7.7415	.46	.47	− .01	.0059	.0060	− .0001	
.5	7.8412	.33	.34	− .01	.0042	.0044	− .0002	
.7	7.8305	....	.24	....	....	.0030	....	
.9	7.9955	.18	.16	+ .02	.0023	.0019	+ .0004	
1.1	7.9550	.09	.09	.00	.0011	.0012	− .0001	
1.3	8.0085	.05	.05	.00	.0006	.0007	− .0001	
1.5	7.9655	.03	.03	.00	.0004	.0004	.0000	
1.7	8.0165	.005	.02	.015	.0001	.0002	− .0001	
1.9	8.0818	Trace.	.007	....	....	.0001	....	

TABLE 8.

0.15	4.0910	0.46	0.42	+0.04	0.0112	0.0103	+0.0009	T=150° C. t=63.29 days. v_0=0.01223. k=0.0044.
.3	7.7562	.63	.65	− .02	.0081	.0084	− .0003	
.5	7.7805	.46	.48	− .02	.0059	.0061	− .0002	
.7	7.8545	.34	.33	+ .01	.0043	.0043	.0000	
.9	7.9800	.24	.22	+ .02	.0030	.0028	+ .0002	
1.1	8.0210	.14	.14	.00	.0017	.0017	.0000	
1.3	8.0762	.09	.08	+ .01	.0011	.0010	+ .0001	
1.5	7.9545	.02	.04	− .02	.0003	.0005	− .0002	
1.7	8.0075	.01	.02	− .01	.0001	.0003	− .0002	
1.9	7.9967	.01−	.01	.00	....	.0001	....	

TABLE 9.

Distance (x') from plane of contact (centimeters).	Weight of alloy (grams).	Weight of gold (milligrams).			Percentage of gold (v).			Constants.
		Observed.	Computed.	Observed − computed.	Observed.	Computed.	Observed − computed.	
1	2	3	4	5	6	7	8	
0. 15	3. 7090	0. 22	0. 23	−0. 01	0. 0059	0. 0062	−0. 0003	
. 3	7. 7700	. 40	. 39	+ . 01	. 0051	. 0051	. 0000	
. 5	7. 8110	. 29	. 29	. 00	. 0037	. 0037	. 0000	
. 7	7. 8028	. 21	. 20	+ . 01	. 0027	. 0026	+ . 0001	T=150° C.
. 9	7. 8800	. 13	. 13	. 00	. 0017	. 0017	. 0000	t=63.29 days.
1. 1	7. 9560	. 09	. 08	+ . 01	. 0011	. 0010	+ . 0001	v_0=0.00738.
1. 3	7. 8985	. 04	. 05	− . 01	. 0005	. 0006	− . 0001	k=0.0044.
1. 5	7. 7985	. 02	. 03	− . 01	. 0003	. 0003	. 0000	
1. 7	7. 8360	. 01	. 01	. 00	. 0001	. 0002	− . 0001	
1. 9	7. 7175	. 005	. 006	− . 001	. 0001	. 0001	. 0000	

TABLE 10.

0. 15	4. 0060	0. 45	0. 41	+0. 04	0. 0112	0. 0103	+0. 0009	
. 3	7. 7520	. 63	. 65	− . 02	. 0081	. 0084	− . 0003	
. 5	7. 7710	. 46	. 47	− . 01	. 0059	. 0061	− . 0002	
. 7	7. 8545	. 33	. 33	. 00	. 0042	. 0041	+ . 0001	T=150° C.
. 9	7. 9950	. 23	. 21	+ . 02	. 0029	. 0027	+ . 0002	t=63.29 days.
1. 1	8. 1765	. 15	. 13	+ . 02	. 0018	. 0016	+ . 0002	v_0=0.01231.
1. 3	7. 9370	. 06	. 07	− . 01	. 0008	. 0009	− . 0001	k=0.0042.
1. 5	7. 8960	. 03	. 04	− . 01	. 0004	. 0005	− . 0001	
1. 7	7. 8355	. 02	. 02	. 00	. 0003	. 0002	+ . 0001	
1. 9	7. 8320	. 01	. 01	. 00	. 0001	. 0001	. 0000	

TABLE 11.

0. 15	3. 9050	0. 04	0. 04	0. 00	0. 0010	0. 0011	−0. 0001	T=100° C.
. 3	8. 1800	. 03	. 03	. 00	. 0004	. 0004	. 0000	t=103.43 days.
. 5	8. 0000	. 01	. 00	+ . 01	. 0001	. 0000	+ . 0001	v_0=0.0023.
. 7	8. 1380	. 01−	. 002	....	. 0001−	. 0000	....	k=0.0002+.

The agreement of theory with observation is further shown in figure 32, in which the heavy line represents the theoretical and the dotted line the observed concentrations of Table 1. The short vertical lines drawn perpendicular to the x axis mark the points at which the lead cylinder was sliced. The remarkable agreement between the different determinations of k is shown in Table 12.

TABLE 12.

Temperature. (° C.).	Time (days).	v_0 (per cent).	k	Mean.	Remarks.
197	53. 92	0. 0223	0. 0076	0. 0076	Gold cylinder.
197	53. 92	. 0159	. 0057	....	Electroplate.
197	53. 92	. 0174	. 0063	....	Do.
197	53. 92	. 0159	. 0059	....	Do.
197	53. 92	. 0158	. 0064	....	Do
197	53. 92	. 0155	. 0058	0. 0060	Do.
150	63. 29	. 0088	. 0043	....	0.5-millimeter gold plate.
150	63. 29	. 0122	. 0044	....	Do.
150	63. 29	. 0074	. 0044	....	Do.
150	63. 29	. 0123	. 0042	0. 0043	Do.
100	103. 43	. 0023	. 0002+	0. 0002+	Do.

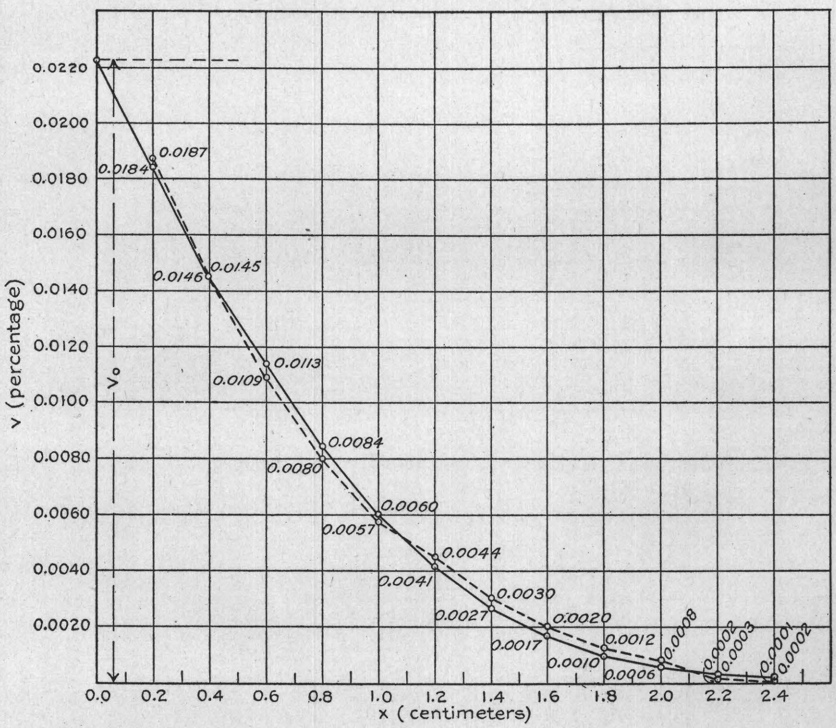

FIGURE 32.—Comparison of observed and theoretical concentrations in experiments on diffusion of solids. The latter are represented by the continuous line; the former by the dotted line.

The value $k=0.0076$ at 197° agrees well with Roberts-Austen's values 0.007 and 0.008 at 200°. The fact that all the values determined from electroplates are low is suggestive, but the deviation of the highest value (0.0076) from the mean of the entire set is less than five times the probable error of a single observation, consequently it must be inferred that the distribution of values is accidental. The value $k=$ 0.0043 at 150° is in close agreement with Roberts-Austen's values 0.004 and 0.005 at 165°, but our value 0.0002+ at 100° is ten times his value at the same temperature.

VARIATION OF THE COEFFICIENT OF DIFFUSIVITY WITH PRESSURE.

Only a few preliminary attempts have been made to determine the effect of pressure on the diffusion process. The lead cylinders used for this purpose were about 20 millimeters in diameter and 5 or 6 centimeters in length. The ends of each cylinder were electroplated with gold. A small hole was drilled from one end to the center of the cylinder for the insertion of a thermo-element. Pressures were applied by means of oil. The observations and the constants obtained from them are summarized in Table 13. The data are barely sufficient for the determination of the two constants, as in most of the experiments there were only two observed values. The results obtained from A and C are quite as trustworthy as those obtained from B. The latter shows a very large increase in the rate of diffusion; the former practically none at all. Each end of specimen D was melted during the progress of the experiment. This may have been due to a slight variation in the temperature gradient within the bomb, or to some other accidental irregularity of which we have no knowledge. Specimens E and F were subjected to high pressures at ordinary temperature. No gold was found in either of these specimens. Figure 33 is a photograph of specimen F. The double system of fractures was probably produced by differential stresses resulting from the increased viscosity of the oil at high pressures. A small portion only of the total number of lines on the surface of the lead cylinder

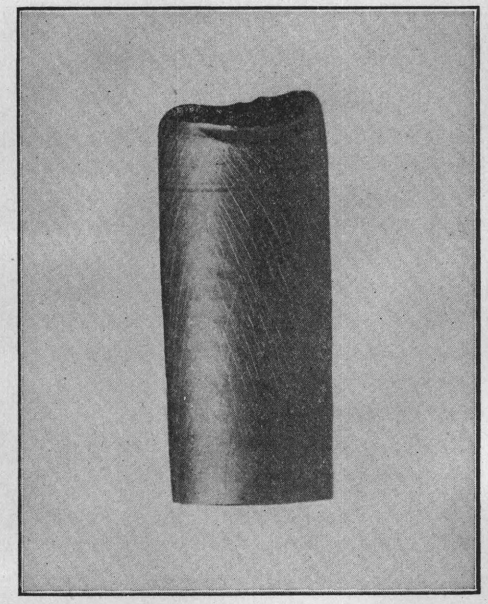

FIGURE 33.—Lead fractured by small differential stresses when subjected to a hydrostatic pressure of 10,200 atmospheres to the square inch.

was reproduced in the photograph. Markings of a somewhat similar character are known as Luder's lines.[1]

TABLE 13.

Specimen.	Distance (x') from plane of contact (centimeter).	Weight of alloy (grams).	Weight of gold (milligrams).	Percentage of gold.	Pressure (atmospheres per square inch).	Temperature (° C.).	Time (days).	Constants.
A....	0.15	4.7125	0.09	0.00191	1,000	150	2.00	v_0=0.006 k=0.006
	.25	3.4570	.02	.00058				
	.35	3.0780	Trace.	....				
	.15	4.9690	.09	.00181	1,000	150	2.00	v_0=0.007 k=0.004
	.25	3.6800	.01	.00027				
	.35	3.2115	Trace.	....				
B....	.2	6.8120	.19	.00279	1,650	150	1.229	v_0=0.012 k=0.010
	.4	6.3735	.01	.00016				
	.6	6.3985	None.	....				
	.2	6.8725	.18	.00262	1,650	150	1.229	v_0=0.010 k=0.013
	.4	6.8900	.02	.00029				
	.6	6.8970	None.	....				
C....	.15	3.2125	.07	.00218	1,900	150	2.00	v_0=0.006 k=0.007
	.25	4.3400	.03	.00069				
	.35	3.8350	Trace.	....				
	.45	3.6270	Trace.	....				
	.15	3.5480	.09	.00254	1,900	150	2.00	v_0=0.008 k=0.005
	.25	3.6375	.02	.00055				
	.35	4.1900	Trace.	....				
	.45	3.0655	Trace.	....				
D....	.05	5.2525	147.04	....	1,650	190	1.250	v_0=0.079 k=0.022
	.15	3.4670	1.40	.04038				
	.30	7.1680	1.19	.01660				
	.50	7.1479	.26	.00364				
	.70	7.1808	.02	.00028				
	.90	7.1964	None.	....				
	.05	3.1250	93.14	....	1,650	190	....	v_0=0.079 k=0.023
	.15	3.6390	1.54	.04232				
	.30	7.1850	1.19	.01656				
	.50	7.4616	.22	.00295				
	.70	7.4728	.01	.00013				
	.90	7.5469	None.	....				
E....	.15	3.8075	None.	....	7,200	20	2.825	....
	.30	7.2725	None.	....				
	.50	7.1885	None.	....				
	.70	7.1700	None.	....				
F....	.2	8.5932	None.	....	10,200	17	2.94	....
	.4	8.3433	None.	....				
	.6	8.4005	None.	....				
	.8	8.3940	None.	....				

CONCLUSIONS AND INFERENCES.

Roberts-Austen's values of the coefficients of diffusion of gold into solid lead are practically correct except for the value at 100° C., which is probably too small. The close agreement of the values of the coefficients obtained from specimens subjected to the same temperature indicate that a higher degree of precision may be attained in their determination. The value of the coefficients probably increases with pressure.

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[1] Mason, W., The Luder's lines on mild steel: Phys. Soc. London Proc., vol. 23, pp. 305-333, 1911.

The observed values tabulated in Table 1 and shown graphically in figure 32 represent the diffusion into lead from a gold cylinder 20 millimeters in diameter and 10 millimeters in height. A very sensitive test failed to detect the diffusion of the lead into the gold at depths greater than 0.2 millimeter, but the methods of detecting lead under these conditions are far less precise than those for detecting gold in lead.

The tendency of molecules to diffuse must always exist when there is a heterogeneous distribution of concentration and the temperature of the masses is above the absolute zero. Considered as a dynamic system operative at all times, the transportation of matter by diffusion in the solid crust of the earth may be very extensive. The possible effects of these persistent motions may be indicated by considering the migration of gold into pure lead at a temperature of 200° C. If we accept the lower value of the coefficient $k=0.007$ and put the initial concentration $v_0=0.02$ per cent, particles of gold would have passed through 6.4 centimeters (2.5 inches) of lead in one year and 64 centimeters (25 inches) of lead in 100 years in sufficient quantities to have produced a concentration of 0.0001 per cent at these points.

If a portion of the materials constituting the crust of the earth are capable of diffusing into one another under pressure, it would seem that the argument for isostatic adjustment is greatly strengthened, for a substance in which the particles glide over one another possesses one of the essential characteristics of a liquid and may therefore be expected to yield slowly when subjected to small stresses operating during geologic epochs.

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