

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

DIFFUSION IN ALKALINE COPPER SYSTEMS¹

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A. Mathematical.—The mathematical theory of heat conduction has been adapted to the study of solute diffusion in the field of physical chemistry. The identity of the theory in the two fields arises from the fundamental assumptions made in each case. In the theory of heat conduction it is assumed that when two parallel faces of a sheet of material are kept at two different temperatures, the equilibrium rate of flow of heat across the sheet is proportional to the difference in temperature between the faces. Similarly in solute diffusion, the rate of flow of solute across a lamina of diffusion medium is assumed proportional to the difference in concentration between the faces. The exact analogy of the two assumptions made leads to identical differential equations, for three-dimensional flow, for both heat conduction and solute diffusion. Thus²

$$\frac{\partial v}{\partial t} = K \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} \right)$$

and

$$\frac{\partial c}{\partial t} = k \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)$$

K , physical constant
 v , temperature
 x, y, z , space coördinates

t , time
 k , diffusion coefficient

are identical differential equations. From this it follows that if $v = F(x, y, z, t)$ satisfies the differential equation above, and certain initial and boundary conditions, then $c = F(x, y, z, t)$ will satisfy the conditions for diffusion, and a mathematically similar set of boundary and initial conditions. The equations of heat conduction and solute diffusion, then, are interchangeable for analogous conditions.

When the concentration function is known, in general, there exists a function which expresses the total quantity of solute within a given boundary. This quantity function is the integral of the concentration function taken throughout the volume in question. The quantity function therefore is obtained almost immediately by integration with appropriate limits of the equations of Carslaw.² The integration for three of the simpler initial and boundary conditions has already been carried out by A. V. Hill.³

¹ The original manuscript which was abbreviated to form this article was received April 13, 1931.

² Carslaw, "Heat Conduction," The Macmillan Co., New York, 1921, pp. 1-8.

³ A. V. Hill, *Proc. Roy. Soc. (London)*, **104**, 39 (1928).

Table I gives the equations expressing concentration, and the corresponding equations for quantity.⁴

B. Alkaline Hydroxy-Organic Copper Systems.—Copper salts have the property of forming deep blue solutions, in the presence of alkali, with certain of the organic compounds which contain the OH group. The common example of this group of compounds is the tartrates (which form the Fehling's solution used in sugar analysis), glycerol, glycol, mannitol,

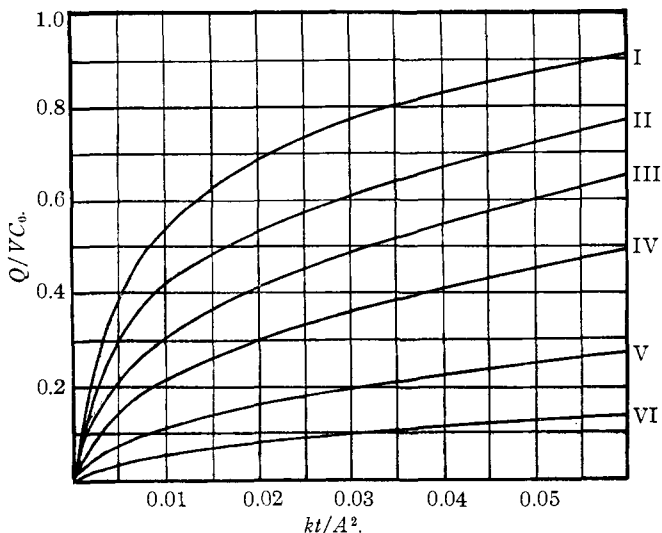


Fig. 1.—I, Cube; II, cylinder, $c = c_0$, $r = a$, $c = c_0$, $z = o, h$; III, sphere; IV, cylinder, $c = c_0$, $r = a$; V, diffusion column, impermeable to solute, $b = 1/2a$; VI, diffusion column, $c = c_0$, $x = 0$.

lactic acid and the sugars. Although these alkaline copper systems are well known, as a class, for their property of yielding cuprous oxide with the reducing sugars, the investigations of the structure of these systems, up to this time, have not even been of a quality to warrant their definite classification as complexes or as colloids. The difficulty seems to lie in the

⁴ Of the recently published mathematical work on solute diffusion the paper by Friedman and Kraemer [THIS JOURNAL, 52, 1295 (1930)] contains an equation which is obviously in error. The equation, as given, is

$$v = \frac{1}{2} - \sum \frac{8}{(2n+1)^2 \pi^2} e^{-(2n+1)^2 \frac{\pi^2 T}{4}}$$

t , time; K , diffusion coefficient; $T = Kt/a^2$; a , thickness of gel and of the solution; v , fraction of the solute diffused into the gel when the solute is originally all in the liquid layer. The $v-t$ curve intersects the v axis ($t = 0$) at $-1/2$ instead of zero as required by the physical conditions. Diffusions in which the surface concentration varies cannot be represented in such simple form. The correct form is given in Weaver's original paper [*Phys. Rev.*, 31, 1072 (1928)].

TABLE I
EQUATIONS

Geometrical classification	Boundary and initial condition	Equation for concentration	Equation for quantity
1 Semi-infinite column	$x = 0 \quad c = c_0$ $t = 0 \quad c = 0$	$\frac{c}{c_0} = 1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\xi^2} d\xi$	$\frac{Q}{Ac_0} = 2\sqrt{\frac{kt}{\pi}}$
2 Finite column	$x = 0 \quad c = c_0$ $x = a \quad \left\{ \begin{array}{l} \text{Impermeability} \\ \partial c / \partial x = 0 \end{array} \right.$ $t = 0 \quad c = 0$	$\frac{c}{c_0} = 1 - \sum_{n=0}^{\infty} \frac{4}{(2n+1)\pi} \sin \frac{(2n+1)\pi x}{2a} e^{-kt(2n+1)^2\pi^2 \cdot 4a^2}$	$\frac{Q}{c_0\mathcal{V}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-kt(2n+1)^2\pi^2 \cdot 4a^2}$
3 Circular cylinder	$c = c_0 \quad r = a$ $c = 0 \quad t = 0$	$\frac{c}{c_0} = 1 - \frac{2}{a} \sum \frac{e^{-kt\alpha_n^2}}{\alpha_n} \frac{J_0(\alpha_n r)}{J_1(\alpha_n a)}$ where $J_0(\alpha_n a) = 0$	$\frac{Q}{c_0\mathcal{V}} = 1 - \frac{4}{a^2} \sum \frac{1}{\alpha_n^2} e^{-kt\alpha_n^2}$
4 Cube	$c = c_0 \quad x = 0, a$ $y = 0, a$ $z = 0, a$ $c = 0 \quad t = 0$	$\frac{c}{c_0} = 1 - \left(\frac{4}{\pi}\right)^3 \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} \frac{1}{(2p+1)(2q+1)(2r+1)} \sin \frac{(2p+1)\pi x}{a} \sin \frac{(2q+1)\pi y}{a} \sin \frac{(2r+1)\pi z}{a} e^{-kt\pi^2/a^2} \left\{ \begin{array}{l} (2p+1)^2 \\ (2q+1)^2 \\ (2r+1)^2 \end{array} \right.$	$\frac{Q}{c_0\mathcal{V}} = 1 - \left(\frac{8}{\pi^2}\right)^3 \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} \frac{1}{(2p+1)^2(2q+1)^2(2r+1)^2} e^{-kt\pi^2/a^2} \left\{ \begin{array}{l} (2p+1)^2 \\ (2q+1)^2 \\ (2r+1)^2 \end{array} \right.$

TABLE I (Concluded)

Geometrical classification	Boundary and initial condition	Equation for concentration	Equation for quantity
5 Sphere	$c = c_0 \quad r = a$ $c = 0 \quad t = 0$	$\frac{c}{c_0} = 1 + \sum_1^{\infty} \frac{2a}{n\pi} \frac{(-1)^n}{r} \sin \frac{n\pi r}{a} e^{-kt n^2\pi^2/a^2}$	$\frac{Q}{c_0v} = 1 - \frac{6}{\pi^2} \sum \frac{1}{n^2} e^{-kt n^2\pi^2/a^2}$
6 Circular cylinder Distance axis = r Along axis = z	$c = c_0 \quad r = a$ $c = c_0 \quad z = 0, h$ $c = 0 \quad t = 0$	$\frac{c}{c_0} = 1 - \frac{\sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{8 J_0(\alpha_m r)}{\alpha \alpha_m J_1(\alpha_m a)(2n+1)\pi \sin \frac{(2n+1)\pi z}{h}}}{J_0(\alpha_m a) = 0} e^{-kt(\alpha_m^2 + (2n+1)^2\pi^2/h^2)}$	$\frac{Q}{c_0v} = 1 - \frac{32}{\pi^2} \frac{\sum_{n=0}^{\infty} \sum_{m=1}^{\infty} 1}{a^2 \alpha_m^2 (2n+1)^2 e^{-kt(\alpha_m^2 + (2n+1)^2\pi^2/h^2)}}$
7 Finite column	$x = 0, a \left\{ \begin{array}{l} \text{Impermeability} \\ \partial c / \partial x = 0 \end{array} \right.$ $t = 0 \left\{ \begin{array}{l} c = c_1 \quad 0 < x < b \\ c = 0 \quad b < x < a \end{array} \right.$	$\frac{c}{c_0} = \frac{b}{a} + \sum_1^{\infty} 2 \sin \frac{n\pi b}{a} \cos \frac{n\pi x}{a} e^{-n^2\pi^2 \frac{kt}{a^2}}$	$\frac{Q}{c_0v} = \frac{b(a-b)}{a^2} - \sum \frac{2}{n^2\pi^2} \left(\sin \frac{n\pi b}{a} \right)^2 e^{-n^2\pi^2 \frac{kt}{a^2}}$

MATHEMATICAL SYMBOLS.— c , concentration; t , time (seconds); k , diffusion coefficient (sq. cm./sec.); x, y, z , distances (Cartesian coordinates) (cm.); r , distance (cylindrical or spherical coordinates) (cm.); Q , quantity of solute within a given region; a , radius, length (cm.); h , length of cylinder (cm.); J_0 , Bessel's function first kind, order zero; J_1 , Bessel's function first kind, first order; v , volume (cc.); n, m, p, q, r , positive integers; c_0 , surface concentration (constant).

ease with which the compounds are hydrolyzed to form hydrous cupric oxide. This behavior has led to a somewhat general belief that the solutions contain colloidal cupric oxide protected by the alkali and the organic substances of the solution, and that this colloid flocculates on dialysis due to the removal of the protecting substances. The following quotation from a paper by Sen and Dhar is a typical example of literature favoring the colloid hypothesis.⁵ "It is very difficult to explain the production of the same colour in all these cases on the view of complex formation as the same colour is developed by so many reagents. We have to assume that the positive ion $\text{Cu}(\text{NH}_3)_4^{++}$ in ammoniacal copper solutions, the negative ion $\text{Cu}(\text{OH})_4^-$ in alkaline hydroxide solutions, the copper salt solutions containing alkali and glycerol or sugars, having such different compositions, all have the same blue colour. The real explanation of the existence of the same blue colour in all these different substances seems to lie in the fact that we are probably considering the same structure in all cases, namely, negatively charged $\text{Cu}(\text{OH})_2$ due to the adsorption of hydroxyl ions, which are present in all cases, and the negatively charged colloidal $\text{Cu}(\text{OH})_2$ has the blue colour."

The application of diffusion to the problem of differentiating between complex and colloid is an obvious attack on the problem. The classification of substances as colloids or as crystalloids is a matter of determining relative particle sizes. The well-known Stokes-Einstein equation illustrates the functional relationship between the particle radius r and the diffusion coefficient k .

$$k = \frac{RT}{N} \frac{1}{6\pi\eta r}$$

R , gas constant
 T , absolute temperature

N , Avogadro number
 η , viscosity of solution

The diffusion coefficient is seen to be inversely proportional to the particle radius. In the true colloids the radius is of such magnitude that diffusion of the particles can scarcely be detected.

The study of the diffusion of copper in these systems was simplified by the finding of a gel structure which could be used in the experiments to avoid effects due to the thermal convection currents. Agar gel and silica gel were the only media found which could be used in moderately alkaline solutions. Alkaline tartrate solutions of copper sulfate and alkaline glycerol solutions of copper sulfate when placed upon agar gels produced Liesegang ring precipitation of cuprous oxide which could only be explained on the basis of diffusion. By preliminary treatment of the gel with sodium hypobromite, the reduction of the copper could be prevented, and the gel assumed the deep blue color of the supernatant liquid. Aged silica gels gave similar evidence of diffusion. This is reasonably conclusive

⁵ Sen and Dhar, *J. Phys. Chem.*, **27**, 376 (1923).

evidence for the existence of blue copper complexes of comparatively simple structures.

Quantitative experiments were made to estimate the magnitude of the diffusion coefficient of the copper-glycerol complex. The method consisted in suspending a cylinder of agar gel in a large volume of stirred solution (two liters) so as to maintain an approximately constant surface concentration. The gel was removed, blotted dry and the outer edges cut away to eliminate diffusion from the sides of the cylinder. Samples were removed for analysis by means of a mold. The agar was melted by warming in a moderately concentrated solution of acetic acid, the solution was cooled, and the copper was estimated iodimetrically by addition of potassium iodide and titration with sodium thiosulfate.

Special attention was paid to the preparation of the gels. The agar solutions were partly cooled and a few droplets of bromine were added. The agar was decanted and tested for adsorption of the iodine and sodium thiosulfate. If a poor grade of agar is obtained it may not be possible to obtain gels which will not adsorb iodine even after the preliminary bromine treatment. The bromine bleaches the gel and makes it gel less easily.

The copper-glycerol solutions used in the experiment were from a stock solution. They had the following composition

Copper sulfate, 0.3 molal (hydrated salt)	KOH, 2 molal Glycerol, molal
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The solutions were maintained at 25° during the period of the diffusion. Stirring of the supernatant liquid was fairly rapid so as to maintain as nearly as possible a constant concentration at the surface of the gel. The following are the results obtained from two runs, using two liters of solution each time. A small correction was applied for the dilution of the supernatant solution. There was no evidence of hydrolysis of the complex in the gel during the experiments.

TABLE II

Q , quantity; c_0 , concentration of solution; t , time (seconds); k , diffusion coefficient (sq. cm./sec.); A , area of sample taken (sq. cm.); Q and c_0 in arbitrary units of standard solution.

Q	A	$4.838 c_0$	t	$\frac{2\% \text{ Agar gel}}{k \times 10^5}$
10.29	6.41	26.84	5400	0.309
10.23				.306
9.80				.280
9.89				.285
9.76				.277
			Mean	.29

The gels were thick enough so that the copper did not reach the center in the time allowed for the diffusion. Calculations could, therefore, be

made from the quantity-time equation for the semi-infinite diffusion column with surface maintained at constant concentration; that is

$$\frac{Q}{Ac_0} = 2 \sqrt{kt/\pi}$$

The quantity Q above is divided by two in the calculations, since the solution is diffusing into two surfaces. The diffusion coefficient obtained, 0.29×10^{-5} , may be considered an approximation to that which would be obtained from diffusion into the solvent alone.⁶ Its magnitude is one which favors a comparatively simple structure for the copper-glycerol complex. From the comparison of this coefficient with that of copper sulfate ($k = 0.25 - 0.6 \times 10^{-5}$) the rate of diffusion of the copper is seen to have undergone a relatively small change in the transformation from the positive ion to the negative complex ion.

These experiments do not disprove the presence of colloidal cupric oxide. Since the alkaline glycerol-copper sulfate system precipitates hydrous cupric oxide on sufficient dilution with water, it seems certain that this colloid will exist during the first stages of hydrolysis. The characteristic blue component, however, is diffusible, and must therefore be considered a complex anion.

Summary

1. The concept of quantity in diffusion is discussed, and equations are developed expressing the relationship between quantity and time for certain boundary conditions.

2. The theory has been applied to the problem of distinguishing between colloids and complexes in certain alkaline hydroxy-organo copper systems. In particular, experiments dealing with the diffusion of the glycerol-copper complex into agar gels indicate a diffusion coefficient of about 0.3×10^{-5} . This is of the same order of magnitude as those of many of the crystalline salts.

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⁶ The work of Friedman would seem to indicate that the retarding influence of dilute agar gels was somewhat larger than was formerly supposed [THIS JOURNAL, 52, 1311 (1930)]. The conclusions of this paper, however, are based only on the assumption that the magnitude of the diffusion coefficient is at least as large in the pure solvent as in the agar gel.