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I hereby recommend that the thesis prepared under my supervision by Harold E. Phifer

entitled Diffusion of Nickel Sulphate into Agar Gel.

be accepted as fulfilling this part of the requirements for the degree of Doctor of Philosophy

Approved by:

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DIFFUSION OF NICKEL SULFATE INTO AGAR GEL

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by

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CONTENTS

DIFFUSION OF NICKEL SULFATE INTO AGAR GEL

1. INTRODUCTION

Although the phenomena of solute diffusion are very wide-spread in nature and although a very close analogy exists between the flow of solute and the conduction of heat, the experimental data for diffusion and diffusion coefficients available in the literature are rather meager, widely scattered, and often uncorrelated with theory. In many cases, diffusion coefficients have been determined not for their intrinsic value, but for their utility in calculating other physical constants.

It has seemed to the writer, however, that solute diffusion is in itself so important to physical chemistry that a critical investigation embracing all phases of the subject with the sole purpose of testing the validity of the general theory is badly needed. It is hoped that the work described in this paper has, in its small and restricted way, been a step in this direction.

2. HISTORICAL

Although this paper is specifically concerned only with a particular case of the diffusion of nickel sulfate into agar gel, it seems highly desirable for reference purposes, to preface the discussion of the present problem by a rather comprehensive review of all important studies to date on solute diffusion.

Work of Fourier.

The mathematical foundation for the study of heat conduction, and by anàlogy, of solute diffusion, was given in 1822 by Fourier in his Théorie Analytique de la Chaleur.[1] Many other mathematicians, both contemporaries and successors of Fourier, also helped to perfect the technique of representing arbitrary functions by trigonometric series. D'Alembert, Euler, Daniel Bernoulli, Dirichlet, Riemann, Stokes, Seidel, Weierstrass, Du Bois Raymond, Cantor, and Lebesque can only be mentioned in passing.

Work of Fick.

By exact analogy with the Fourier treatment of heat conduction, Fick[2] in 1855 was able to establish, for solute diffusion, the relation

$$dQ = -KA \frac{dc}{dx} dt, \qquad (1)$$

where dQ is the quantity of solute which flows in time dt between two parallel planes. A is the area of surface exposed to diffusion, and $\frac{dc}{dx}$ is the concentration gradient between the surfaces. K is the "solute conductivity constant" of the medium. This is known as Fick's law. From (1) it can be shown that the following differential equation holds for uni-dimensional flow of solute:

$$\frac{\partial c}{\partial t} = k \frac{\partial^2 c}{\partial x^2} , \qquad (2)$$

where c = concentration of solute, t = time, and x = distance along axis of diffusion. k is the "diffusion coefficient." This is sometimes called the Fourier linear diffusion law. Solutions of (2) of the form

$$c = f(x, t) \qquad (3)$$

for a given set of initial and boundary conditions are usually obtainable only by a Fourier Series expansion. (For further details see Mathematical Section, p. 17).

Experimental tests of Fick's law.

Fick conducted crude experiments with salt solutions in the "steady state" to verify relation (1). Similar work was done by Thomas Graham[3], of gas diffusion fame, in 1861, but most of his experiments were not adapted to numerical discussion. The first real confirmation of Fick's Law was obtained in 1879 by Weber[4], who determined concentra-

tion gradients in the case of zinc sulfate by electromotive force measurements. At about this time Stefan[5], who was studying the diffusion of sodium chloride in aqueous solution, found that the value of the diffusion constant was given by

$$K = \frac{\bar{x}^2}{4ta} \qquad (4)$$

where t is time in days required for diffusant to penetrate a distance $\bar{x}$ into pure solvent, and a is a constant.

J. C. Graham[6] in 1904 showed how to calculate k directly from c, x, and t, in the Fourier expansion of $c = f(x,t)$. Procopiu[7] in 1910, stressing the analogy between heat and solute flow, used the formula

$$K = \frac{\bar{x}^2}{2t} \qquad (5)$$

in calculating diffusion coefficients. His value for copper sulfate was 50×10^{-7}.

Mechanism of diffusion.

The mechanism of diffusion is to be found in the energy of the particles diffusing, whether they be true solute molecules or colloidal particles. Diffusion is related both to osmosis and to Brownian movement.

Nernst[8] sought to identify diffusive force with osmotic pressure, showing that solute diffusion is strictly comparable to diffusion of gases except that it is slowed

up enormously by the internal friction of the solvent.

The work of Svedberg (1906) with Brownian movement and Perrin[9] (1909) with sedimentation equilibria gave quantitative evidence for the relation of diffusion to Brownian movement. On the hypothesis that a suspension of gamboge particles behaves as a perfect gas, Perrin was able to derive an expression for concentration gradient of particles in equilibrium under gravity:

$$\frac{RT}{N} \ln \frac{n_o}{n} = \frac{4}{3} \pi r^3 g (D-\rho) h \qquad (6)$$

where:

R = gas constant

T = absolute temperature

N = avogadro number

n, n_o = no. of grains per unit volume at each of two planes h units apart

r = radius of particle

g = acceleration of gravity

D = density of particle

ρ = density of medium

Here r is readily determined by Stokes' Law

$$v = \frac{2}{9} \frac{D r^2 g}{\eta} , \qquad (7)$$

where

v = velocity of fall of particle

η = viscosity of medium.

Einstein[10] in 1908 derived a relation giving the mean square of the x component of the horizontal displacement for such colloidal particles in Brownian movement:

$$x^2 = \frac{RT}{N} \frac{t}{3\pi r \eta} \qquad (8)$$

By extending (8) to solute particles, Wogau and Einstein obtained the following formula for diffusion coefficients:

$$K = \frac{RT}{6\pi\eta\sqrt[3]{\frac{MN^2}{4\pi D}}}\ ,^{*} \qquad (9)$$

where M = molecular weight of solute. Wogau[11] found equation (9) to hold in the case of various solutes in water. In the absence of a relation connecting M and D, it is difficult to reconcile (9) with the empirical observations of Pissarievski[12] that

$$\frac{K\eta\sqrt{M}}{\alpha} = const. \qquad (10)$$

for electrolytes, where α = degree of dissociation; or with Exner's rule that

$$K\sqrt{M} = const. \qquad (11)$$

---

* It appears that there is a mistake in (9) and that the following is the correct form:

$$K = \frac{RT}{6\pi\eta\sqrt[3]{\frac{3MN^2}{4\pi D}}}\ .$$

for non-electrolytes in the same solvent. Other formulas for rate of diffusion of particles were developed by Sutherland and Einstein, and by Smoluchowski[13] (theory of fluctuations based on probability conceptions). Perhaps the most useful relation of this type is the Stokes - Einstein equation:

$$K = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta r}\right) \tag{12}$$

which follows readily from (8).

Various tests of (12) are possible:

(1) K·r should be constant for different solutes at constant temperature.

(2) K·η should be constant for the same solute in different solvents at constant temperature.

(3) $\frac{K\eta}{T}$ should be constant, for different solvents, if r is independent of temperature.

Experimental evidence indicates that (12) is at least a good first approximation. The most rigid test of the Stokes-Einstein equation was made by Cohen and Bruins[14] in 1922. By a refinement of technique so that concentration was maintained constant throughout an experiment, and by use of a very sensitive water interferometer, an accuracy of 0.3% for diffusion coefficients was made possible. The following table for the diffusion of tetrabromethane into tetrachlorethane shows how well the Einstein equation holds:

Temperature	K (Observed)	K (calculated)	r X 10^8 (Calculated)
0 C	0.300	(0.300)	2.15
10	0.385	0.385	2.15
15	0.429	0.431	2.16
25	0.527	0.531	2.17
35	0.633	0.643	2.18
50	0.811	0.833	2.21

Deviations of diffusion coefficients.

The coefficient of diffusion is not a true constant, but varies both with temperature and concentration of diffusant, as well as with the diffusing medium. "Öholm[15] working with sugar in aqueous solution found the temperature coefficient of k to be about 3.5% per degree, and the variation of k with c to be linear. Optical rotation methods were used to determine concentrations.
The more accurate measurements of Cohen and Bruins[14] indicated similar variations.

Svedberg[16] studied diffusion in an anisotropic medium and showed that k was different in different directions. He attempted to use his results in calculating shape of molecules.

Electrolytes, which in terms of the Arrhenius theory would be expected to diffuse both as ions and as undissociated molecules, do not appear to conform to Fick's law. Since in general the mobilities of ions are different, it might be expected that the more mobile ions would out-

strip the slower ones in diffusion. The tremendous electrostatic field which would thereby be set up, however, overcomes any such tendency, and the two ions diffuse together but at a slower rate than the molecules. On these assumptions Nernst[8] derived his diffusion law for simple electrolytes

$$dQ = -\frac{2UV}{U+V} RT A \frac{dc}{dx} dt , \qquad (13)$$

where U and V are mobilities of cation and anion respectively. Whence $K = \frac{2UV}{U+V} RT$ (14)

It is assumed that the diffusant is so dilute that it may be considered completely ionized.

"Oholm"[15] who made a comprehensive study of diffusion coefficients for salt solutions, has presented the following data in support of the Nernst theory:

Substance	K, 18° (observed)	K, 18° (calculated)
KCl	1.460	1.460
NaCl	1.170	1.173
LiCl	1.000	0.994
HCl	2.324	2.431
KOH	1.903	2.109
NaOH	1.432	1.558
KI	1.460	1.467
CH_3COOH	0.93	1.37

Noyes and Haskell[17] derived a relation similar to (13) for the general case of any electrolyte $A_{v+}^{z+} B_{v-}^{z-}$.

George McPhail Smith[18] introduced the concept of ideal diffusion coefficients, defined by the relation

$I = k/M$. Here, I would represent the diffusion constant for molecules having all properties the same as before, except that their masses are reduced to unity. Smith found $IM^n = \text{const.}$, where $n \doteq 1.50$, which was further evidence in support of Exner's rule.

Dubinin[19] in 1926 pointed out that Fick's Law represents the limiting case for very dilute solutions. The discrepancy between fact and theory for concentrated solutions arises from the existence of attractive forces between the diffusing molecules, and from the fact that $k = f(c)$. Boltzmann's vector differential equation

$$\frac{\partial c}{\partial t} = \text{div} (k \text{ grad } c) \qquad (15)$$

is supposed to hold for any concentration.

Diffusion in gels.

The use of gels in quantitative diffusion work is fairly recent, although Lodge[20] early showed that gelatine in spite of its high viscosity offers practically no retarding influence on the migration of hydrogen ions in an electrostatic field. Voigtlander[21] in 1889, after studying the diffusion of four electrolytes in agar at 20°, came to the conclusion that k was independent of gel concentration. Bechhold and Ziegler[22] in 1906, however, found a

considerable decrease in k with increasing concentration of gel. In 1920 Adair[23], who studied the penetration of electrolytes into gels, applying Fourier's linear diffusion law, found practically the same thing. Moreover Adair was able to correlate the influence of gel concentration with viscosity on the basis of the Einstein relation(12).

Mann[24] was the first to determine k by chemical analysis of slices at various depths. Seven metallic chlorides were studied in 2% agar at 20° and 30° . Fricke[25] perfected a method of microtome slicing and microchemical analysis, studying sodium chloride in agar.

Wo. Ostwald[26] (1925) presented his "diffusion wave" theory to account for formation of Liesegang rings as an interference phenomenon.

Diffusion of nickel salts.

The only record to be found of work done with nickel salts is that of Mario Torre[27] (1915) and Elizabeth Rona[28] (1920). Torre studied aqueous solutions of chlorides, sulfates, and nitrates of chromium, manganese, iron, nickel, and cobalt, in concentrations ranging from 0.01 to 0.1 molar at 30° , 40° , and 50° . For 24 hour runs, it was found that quantity of solute diffused was proportional to concentration and to temperature.

Rona used diffusion coefficients to calculate ionic mobilities of cobalt and nickel at 18°C. Cobalt chloride and nickel nitrate were studied in pure water and in 0.1 N and 0.01 N solutions of the common anion acid. The K's were calculated by Stefan's law (4) and the following values were given for nickel nitrate in aqueous solution:

$Ni(NO_3)_2$ concentration	K at 18°C., t in days
0.068 N	0.802
0.0226	0.711
0.0204	0.692
0.0068	0.577

Ionic mobilities were calculated by means of the Nernst equation (14).

Compilations of data.

Further data on diffusion coefficients, compiled from the work of various investigators is to be found in Thovert's Tabelles Annuelles Internationalles de Constantes[29] (volume 4, p. 746), and in Landolt - Bornstein, Physikalisch-chemische Tabellen[30] (volume 1, p. 68).

Recent work.

This brings us up to very recent work in the field of diffusion. E. L. Lederer[31] in 1928 applied Fourier's partial differential equation to colloid problems. Weaver[32] inaa purely mathematical paper gave a complete and rigorous treatment for the case of a column of gel containing solute at the uniform concentration c_o, and dipped with one face exposed into a finite quantity of pure water.

Hill[33], also in 1928, in connection with his study of diffusion into nerves and muscles, presented a very good mathematical discussion. He showed that the general differential equation for diffusion was completely solvable for only three cases:

1. Infinite plane sheet.
2. Semi-infinite solid.
3. Infinite cylinder.

Hill introduced a powerful new tool into diffusion work by showing that the total quantity of solute absorbed into a given solid can be obtained by integrating the concentration function (e.g. equation (3)) throughout the volume in question. Heretofore in order to determine diffusion constants it had been necessary either to measure small concentration gradients, which was inaccurate, or to determine rate of flow in the steady state, which was cumbersome.

Friedman and Kraemer[34] in 1930 applied their dif-

fusion studies with non-electrolytes to the problem of the structure of gelatin and agar gels. The conditions of Weaver[32] were followed, and concentrations were measured by means of refractive index. Unfortunately, Weaver's formula was incorrectly applied (See Ricketts[35]). In the case of 5% sucrose diffusing into 6.91% gelatin at 5°, the mean of ten determinations of k was 0.148×10^{-5} (Average deviation, 3.7%) Linear relations between k and gel % were found to hold. The size of pores was found to be of the order of 5.5 mμ for 5% gelatin, 2.9 mμ for 2% agar, and 0.74 mμ for 5% agar. The relation $k\sqrt{M} = \text{const.}$ (11) was found to hold approximately for a number of non-electrolytes. The effect of manner of preparation of gel, as well as the influence of non-electrolytes on grain size of gel were also studied.

Ricketts and Culbertson[35] (1931) studied diffusion in alkaline copper systems, in an attempt to determine the nature of the copper-glycerol complex. The mathematical case studied is identical with that studied by the writer using nickel sulfate, and discussed at length under Mathematical (p.36). The diffusion coefficient for the complex was found to be 0.29×10^{-5} cm.²/sec., with an average deviation of 5%. This was compared with the k for copper sulfate ($k = 0.25 - 0.6 \times 10^{-5}$).

Newman[36] and Sherwood[37] have applied the laws of diffusion to the drying of materials. Finally a very com-

plete mathematical discussion of the mechanism for the diffusion of electrolytes, in terms of the modern theories of inter-ionic attraction, has been presented by Onsager and Fuoss[38].

3. MATHEMATICAL

Definition of diffusion.

Diffusion in the most general terms can be defined as the spontaneous flow of matter from a region in space of higher pressure, concentration, or activity to one of lower. To restrict this definition to solute flow only, we can say that solute diffusion is the spontaneous flow of solute in solution from a region of higher concentration to one of lower concentration. The substance diffusing is called the "diffusant".

Theory of solute diffusion.

The mechanism for diffusion has been discussed already under Historical (p. 4). We will here only present a brief summary of the facts known. Solute diffusion appears to be related both to osmosis and to Brownian movement. Nernst[8], stressing the analogy between gaseous and solute molecules, worked out a theory in which the force causing diffusion was identified with osmotic pressure. The fact that non-diffusing substances or states of dispersion are common, and that there is a wide variation in the rates of diffusion of different solutes is at variance with the Nernst theory.

By statistical treatment, Einstein[10] and others have derived relations, identifying solute diffusion with

Brownian movement, which apparently hold well, if hydration is assumed. See equations (9) and (12).

The following factors influencing diffusion must therefore be considered:

1. Temperature. On the basis of either theory, K is proportional to T.

2. Medium. Viscosity, grain size if a gel, interfering solutes. From the Einstein formula (12), K is inversely proportional to η for constant T.

3. Size of partical diffusing. The Einstein formula predicts that K is inversely proportional to the radius (r) for constant T. More complicated relations between K and M exist. See formula (9).

Analogy with heat conduction.

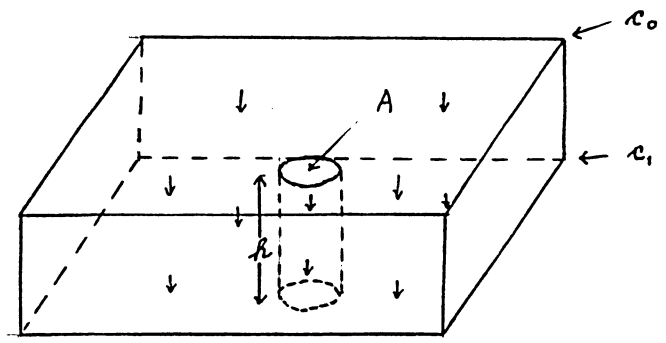
If we put aside for the moment all considerations of the mechanism of diffusion and look upon it, in the light of the general definition, as simply the flow of matter from a higher to a lower potential, we are struck by the similarity between flow of solute on the one hand and conduction of heat (and of electricity) on the other. The "cause" from the standpoint of thermodynamics is the same in each case: it is merely the existence of a potential gradient in space, together with an inherent tendency of all energy to seek a lower level of availability.

The identification of the basic assumptions of the solute problem and the heat problem leads to a complete set of analogous equations. If "temperature" be replaced by "concentration", and "quantity of heat" by "quantity of solute" in any given heat conduction equation, the corresponding solute diffusion equation is obtained. Since the heat problem has been very completely handled by Fourier[1] and by Carslaw[39] itiis often convenient to obtain the solute expressions for any particular case by direct substitution. If these derived expressions meet the test of experiment, the validity of the original assumptions can scarcely be doubted.

Derivation of Fick's law.

For the sake of completeness Fick's law (1) and the Fourier diffusion law (2) will be derived from first principles. The reasoning in every step is completely analogous to that used by Carslaw in his treatise on Heat Conduction.[39] Consider an infinite slab of liquid or gel, assumed homogeneous and isotropic, of thickness h and with plane faces kept at the constant concentrations c_0 and c_1 ($c_0 > c_1$), respectively by contact say with large volumes of well stirred liquids of these concentrations. Suppose that the distribution of concentration does not vary with time. Consider solute flow within a cylinder perpendicular

to the plane surfaces and with area of cross section A.



This case cannot be realized in practicedbut it can be approached as closely as desired. Experiments show that the quantity of a given solute flowing through the cylinder from face 0 to face 1, Q, is directly proportional to A, to $(c_0 - c_1)$, and to time t, and inversely proportional to h.

$$\therefore \quad Q = \frac{K (c_0 - c_1) A t}{h} \tag{16}$$

where K = const.

If we consider a very thin sheet, $h \rightarrow dx$ and $\frac{c_0 - c_1}{h}$ becomes $- \frac{dc}{dx}$, the concentration gradient. The rate of flow of solute is therefore

$$\frac{dQ}{dt} = - K A \frac{dc}{dx} \tag{17}$$

$$\text{or} \quad dQ = - K A \frac{dc}{dx} dt, \tag{1}$$

which is Fick's law. The negative sign indicates that flow of solute is in the direction of decreasing concentration.

K is the solute conductivity constant of the medium, which may be defined by the relation:

$$K = \frac{\frac{dQ}{dt}}{A\,\frac{dc}{dx}} \qquad (18)$$

i.e. it is the rate of flow of solute per unit area per unit time across a unit concentration gradient. If x is in cms., A in cms.^{2} and t in seconds, and if Q and c are in any corresponding units, e.g.: moles and moles /cm^3, or grams and grams/cm^3, then K is in cm.^{2}/sec.

In the case considered it is apparent that the direction of flow of solute is perpendicular to the plan faces of the slab, or to use an analogy with electricity, the "lines of diffusive force" are normal to the faces.

Derivation of Fourier diffusion law.

Now let us consider diffusion through a medium of any shape. The concentration will in general vary from point to point, and will vary with time at the same point, so that we can say

$$c = f(x, y, z, t) \qquad (19)$$

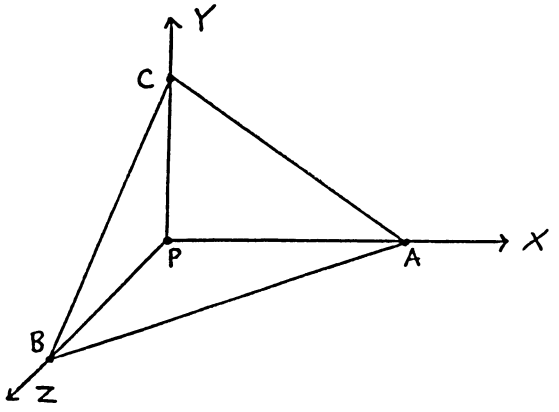
Construct an equi-concentration surface through the medium, having a concentration c_o. Such a surface separates points at a higher concentration from those at a lower. Construct

an entire series of such shells of equal concentration, The flow of solute must, by definition of an equi-concentration surface, be normal to it.

The rate at which solute crosses from inside to outside of an equi-concentration surface per unit area per unit time is equal to $$- K \frac{\partial c}{\partial n} \qquad (20)$$

where $\frac{\partial}{\partial n}$ denotes differentiation along the outward drawn normal to the surface. This is true because by taking the surface area small enough this case approaches that already considered under <u>Fick's law</u>. (P.-18).

Now consider the case of flow across any surface, not necessarily of equal concentration. Since a limiting process is to be used, we can make this surface a plane A B C with direction cosines of normal, λ , μ, ν



Let f = rate of flow of solute across triangular face A B C.

f_x = rate of flow across P B C

f_y = " " " " P A B

f_3 = rate of flow across P A C

Let Δ = area of face A B C

p = perpendicular distance from P to A B C.

Then area P B C = $\lambda \Delta$ (21)

" P A B = $\mu \Delta$

" P A C = $\nu \Delta$

Ultimately the tetrahedron gains solute at the rate:

$$f_x \lambda \Delta + f_y \mu \Delta + f_z \nu \Delta - f \Delta \qquad (22)$$

Let s = quantity of solute required to increase the concentration of one gram of the medium by one unit. (one gram per cc, or 1 mole per cc). This is the "solute capacity" of the medium. Let ρ = density of medium. Then $s\rho$ = quantity of solute required to raise one cc of medium, one concentration unit. (The product $s\rho$ would be unity, if there were no volume effect attending the process of solution). The rate of gain of solute, therefore, is given also by:

$$\frac{1}{3} p \Delta s\rho \frac{\partial a}{\partial t} \qquad (23)$$

Let the tetrahedron shrink down to a point (i.e., $p \to 0$) Then the relation

$$f = \lambda f_x + \mu f_y + \nu f_z \qquad (24)$$

holds. Assume that P is on an equi-concentration surface, the normal to which is the Z - axis,

Then $$f_x = f_y = 0 \tag{25}$$

$$\therefore \quad f = v f_z = - K v \frac{\partial c}{\partial z} \tag{26}$$

$$\therefore \quad f = - K \frac{\partial c}{\partial \ell} \tag{27}$$

where $\frac{\partial}{\partial \ell}$ denotes differentiation in the direction (λ, μ, ν).

(Since $$\frac{\partial c}{\partial \ell} = \lambda \frac{\partial c}{\partial x} + \mu \frac{\partial c}{\partial y} + \nu \frac{\partial c}{\partial z} \tag{28}$$

and $$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial y} = 0 \;) \tag{29}$$

Thus we have generalized our previous concept of flow of solute, and can now say that the rate of flow of solute at a point across <u>any</u> surface from the inside to the outside per unit area per unit time is

$$- K \frac{\partial c}{\partial n}$$

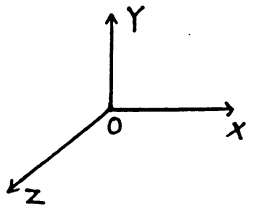
where $\frac{\partial}{\partial n}$ denotes differentiation along the outwardly drawn normal to the surface at this point.

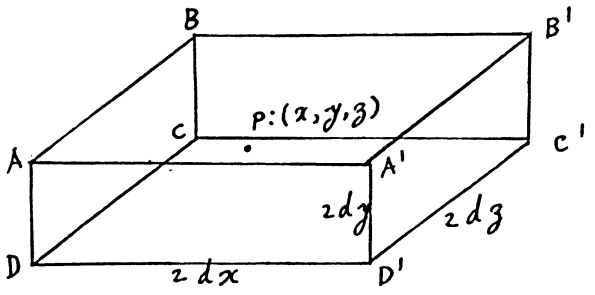
Therefore the quantity of solute flowing across one of these equi-potential surfaces is given by

$$d^2 Q = - K \frac{\partial c}{\partial n} \, dA \, dt \tag{30}$$

This is a generalization of Fick's law (equation (1)).

Consider now the rectangular parallelopiped with center at (x, y, z).





Ultimately, the flow across A B C D

$$= 4\,dy\,dz\,\left(f_x - \frac{\partial f_x}{\partial x}\,dx\right) \tag{31}$$

and the flow across A' B' C' D'

$$= 4\,dy\,dz\,\left(f_x + \frac{\partial f_x}{\partial x}\,dx\right) \tag{32}$$

$\therefore$ Rate at which solute is accumulating inside the solid, due to the two faces considered is

$$-8\,dy\,dz\,\frac{\partial f_x}{\partial x}\,dx \tag{33}$$

Similarly for the other two sets of faces, we have:

$$-8\,dx\,dz\,\frac{\partial f_y}{\partial y}\,dy \tag{34}$$

and

$$-8\,dx\,dy\,\frac{\partial f_z}{\partial z}\,dz \tag{35}$$

$\therefore$ The total rate of gain of solute is

$$-8\,dx\,dy\,dz\left(\frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z}\right) \tag{36}$$

which is equal to

$$8\,dx\,dy\,dz\;s\rho\,\frac{\partial c}{\partial t} \tag{37}$$

$$\therefore\quad \frac{\partial c}{\partial t} = -\frac{1}{s\rho}\left(\frac{\partial f_x}{\partial x} + \frac{\partial f_y}{\partial y} + \frac{\partial f_z}{\partial z}\right) \tag{38}$$

But

$$\left.\begin{aligned} f_x &= -K\,\frac{\partial c}{\partial x} \\ f_y &= -K\,\frac{\partial c}{\partial y} \\ f_z &= -K\,\frac{\partial c}{\partial z} \end{aligned}\right\} \tag{39}$$

Substituting these values, we have:

$$\frac{\partial c}{\partial t} = \frac{K}{s\rho}\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \qquad (40)$$

or $$\frac{\partial c}{\partial t} = k\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \qquad (41)$$

where $k = \frac{K}{s\rho} \equiv$ the "diffusivity", (42)

or the coefficient of diffusion. Since $s\rho$ is a pure number, the units of k are the same as those of K, namely cm^2/sec.

If the medium considered is isotropic but not homogeneous, we must write:

$$s\rho \frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(K \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(K \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(K \frac{\partial c}{\partial z}\right) \qquad (43)$$

where K is a function of x, y, and z.

If the medium is homogeneous but not isotropic:

$$s\rho \frac{\partial c}{\partial t} = K_x \frac{\partial^2 c}{\partial x^2} + K_y \frac{\partial^2 c}{\partial y^2} + K_z \frac{\partial^2 c}{\partial z^2} \qquad (44)$$

It has been assumed of course all through the derivation that solute is lost or gained only by diffusion through the six faces. If there is a "source" or "sink" of solute inside the volume considered, such that quantity A of solute is contributed or removed per unit volume per unit time, equation (40) becomes

$$s\rho \frac{\partial c}{\partial t} = K\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) + A \qquad (45)$$

Equation (41) is often abbreviated to

$$\frac{\partial c}{\partial t} = k \nabla^2 c \qquad (46)$$

where $\nabla^2 c$ means the Laplacian function $\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$.

The Concentration Function.

The general solution for (41) (illegible)

which would be of the form

$$c = f(x, y, z, t) \tag{19}$$

is impossible to obtain. Solutions for specified initial and boundary conditions can be obtained in many cases, however, by means of Fourier series, spherical harmonics, zonal harmonics, and similar series developments.

Linear Diffusion.

If the diffusion of solute is known to be unidimensional the problem is enormously simplified. This means that the equi-concentration surfaces are all parallet planes, perpendicular to the line of flow, say along the x - axis. Then

$$\frac{\partial c}{\partial y} = \frac{\partial c}{\partial z} = 0 \tag{47}$$

and equation (41) becomes

$$\frac{\partial c}{\partial t} = k \frac{\partial^2 c}{\partial x^2} \tag{2}$$

Solutions of (2) for specified initial and boundary conditions will be of the form

$$c = f(x, t). \tag{3}$$

Here again the concentration function can usually only be determined by a Fourier series expansion.

The Steady State.

Two trivial cases, however, are immediately solvable:

(a) If the concentration does not change with distance,

$$\frac{\partial c}{\partial x} = 0 \quad ; \quad \therefore \frac{\partial^2 c}{\partial x^2} = 0 \tag{48}$$

$$\therefore \quad \frac{\partial c}{\partial t} = 0 \tag{49}$$

and

$$c = \text{const.}, \tag{50}$$

for all times and distances.

(b) If the concentration at any point does not change with time. This is the "steady state" which is mentioned so often in the literature, and which has been used for most of the earlier determinations of diffusion coefficients.

If

$$\frac{\partial c}{\partial t} = 0 \tag{49}$$

then

$$k \frac{\partial^2 c}{\partial x^2} = 0 \tag{51}$$

$$\frac{\partial c}{\partial x} = A \tag{52}$$

$$c = \int A \, dx = Ax + B \tag{53}$$

where A and B are constants of integration. For the boundary conditions:

$$\left.\begin{aligned} c &= c_0 \text{ , when } x = 0 \\ c &= c_1 \text{ , when } x = h \end{aligned}\right\} \tag{54}$$

equation (53) becomes

$$c = \frac{c_1 - c_0}{l} x + c_0 \qquad (55)$$

See Derivation of Fick's law (P. 18).

The Quantity Function.

When the form of the concentration function (19) is known, the quantity function, expressing total quantity of solute within a given boundary can usually be obtained by integrating (19) over the volume considered:

$$\bar{Q} = \bar{G}(x, y, z, t) = \rho s \int_{z_1}^{z_2} \int_{y_1}^{y_2} \int_{x_1}^{x_2} f(x, y, z, t)\, dx\, dy\, dz \quad * \qquad (56)$$

For the case of linear diffusion, the quantity function is given by:

$$\bar{Q} = \bar{G}(x, t) = \rho s \int_{x_1}^{x_2} A\, f(x, t)\, dx \quad * \qquad (57)$$

These quantity functions have been obtained for three of the simpler cases by Hill.[33]

For the case of linear flow in the steady state, already considered (P. 28), the quantity of solute contained in a volume h A, is given by

$$\bar{Q} = A \rho s \int_0^l \left(\frac{c_1 - c_0}{l} x + c_0 \right) dx$$

$$= \rho s A\, l\, \frac{(c_1 + c_0)}{2} \qquad (58)$$

The quantity of solute contained within a given

* If initial concentration was everywhere zero.

boundary ($\bar{Q}$) must not be confused with the quantity (Q) flowing through the boundary, although sometimes these two functions are identical. In general,

$$\sum_{t=0}^{t} \sum^{\text{over entire surface}} Q = \bar{Q} \tag{59}$$

For any given time interval, in the steady state

$$\sum_{t=t_1}^{t=t_2} \Sigma Q \neq \bar{Q} \tag{60}$$

for $\sum_{t=t_1}^{t_2} \Sigma Q = 0$, and $\bar{Q}$ is a (61)

definite positive constant (e.g., by (58).

The function Q can be obtained by integrating the generalized Fick's law expression:

$$d^2 Q = -K \frac{\partial c}{\partial n} \, dA \, dt \tag{30}$$

$$Q = G(x,y,z,t) = -K \int_{t_1}^{t_2} \int^{\text{over } A} \frac{\partial c}{\partial n} \, dt \, dA \tag{62}$$

For the case of linear diffusion

$$Q = G(x,t) = -K \iint \frac{\partial c}{\partial x} \, dt \, dA \tag{63}$$

In the particular case of linear flow in the steady state, the quantity flowing past one of the equi-concentration surfaces is given by

$$Q = \int_0^t \int^{\text{over } A} -K \frac{\partial c}{\partial x} \, dt \, dA$$

$$= K \frac{(c_0 - c_1)}{L} A t \tag{16}$$

This is the original form of Fick's law.

Fourier series.

Since Fourier series are very frequently useful in obtaining the concentration functions (19), (3), and since in particular, the Fourier integral was used by us in developing the concentration equation for the case studied experimentally, it seems advisable to summarize at this point the chief facts relating to Fourier series. No attempt at proof or mathematical completeness is intended. These points are well taken care of by Carslow[39] and Byerly.[40]

A trigonometric series is any infinite series of the form

$$\frac{1}{2} a_0 + \sum_{n=1}^{\infty} (a_n \cos nx + b_n \sin nx) \qquad (64)$$

where the coefficients, a and b, are either constants or functions of x. If such a series converges in the interval $a \leq x \leq 2\pi + a$, it determines a definite function there. Moreover, if it converges for an interval of 2π, it converges for all values of x, due to the periodicity of the trigonometric functions. The question naturally arises as to whether an arbitrary function $f(x)$ can be

represented by a trigonometric series expansion.

If we assume for the moment that it can, we find that the coefficients of the series are given by Euler's formulas:

$$a_n = \frac{1}{\pi} \int_0^{2\pi} f(\alpha) \cos n\alpha \, d\alpha \tag{65}$$

$$b_n = \frac{1}{\pi} \int_0^{2\pi} f(\alpha) \sin n\alpha \, d\alpha \tag{66}$$

$\frac{1}{2} a_0$ instead of a_0 was used as the "constant" term so that it could be included under the general formula for a_n. Such a trigonometric series in which the coefficients have the values given by the Euler formulas is known as the Fourier series expansion of $f(x)$. If $f(x)$ is finite and integrable, a_0, a_n, and b_n exist. This is no guarantee that the Fourier series converges, or if it does, that it converges to $f(x)$. However, it can be shown that if series (64) converges <u>uniformly</u> in $0 \leqq x \leqq 2\pi$, it is the unique Fourier series expansion of the function represented by it.

The sum of the first n terms of a Fourier series, for a particular value of $x = x_0$, is given by the Dirichlet integral:

$$S_n(x_0) = \frac{2}{\pi} \int_0^{\frac{\pi}{2}} \frac{f(x_0+2t) + f(x_0-2t)}{2} \frac{\sin(2n+1)t}{\sin t} dt \tag{67}$$

In order that the Fourier series generated by a function $f(x)$, integrable and periodic with period 2π may converge

at the point x_0 , it is necessary and sufficient that the Dirichlet integral approach a finite limit as n becomes infinite. This limit is the sum of the Fourier series at x_0.

This statement can be further specialized into the Dirichlet conditions for the convergence of Fourier series: If $f(x)$ is periodic, of period 2π , and if $f(x+0)$ and $f(x-0)$ exist, and if $\int_0^{2\pi} |f(x)|\,dx$ converges, and if furthermore both

$$\left.\begin{aligned} &\int_0^{\ell} \frac{|f(x+\alpha) - f(x+0)|}{\alpha}\,d\alpha \\ \text{and}\quad &\int_0^{\ell} \frac{|f(x-\alpha) - f(x-0)|}{\alpha}\,d\alpha \end{aligned}\right\} \qquad (68)$$

($\ell > 0$) converge, then the Fourier series for $f(x)$ converges at the point x to the value

$$\frac{1}{2}\left[f(x+0) + f(x-0)\right] \qquad (69)$$

for $0 < x < 2\pi$. For $x = 0$, or $x = 2\pi$ it converges to

$$\frac{1}{2}\left[f(+0) + f(2\pi - 0)\right] \qquad (70)$$

If $f(x)$ is defined only in the interval $0 < x < 2\pi$, its definition can readily be extended outside, by saying that it is periodic of period 2π.

The fundamental interval of convergence of a Fourier series can readily be shifted, e.g. to $-\pi < x < \pi$ in which case Euler's integrals become

$$a_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(\alpha)\cos n\alpha\, d\alpha \qquad (71)$$

$$b_n = \frac{1}{\pi}\int_{-\pi}^{\pi} f(\alpha)\sin n\alpha\, d\alpha \qquad (72)$$

The fundamental interval of convergence can also be extended by the following transformation

$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty}\left(a_n\cos\frac{n\pi x}{l} + b_n\sin\frac{n\pi x}{l}\right) \qquad (73)$$

$(0 < x < 2l)$ $(l = \text{any const.} > 0)$

$$a_n = \frac{1}{l}\int_0^{2l} f(\alpha)\cos\frac{n\pi\alpha}{l}\, d\alpha \qquad (74)$$

$$b_n = \frac{1}{l}\int_0^{2l} f(\alpha)\sin\frac{n\pi\alpha}{l}\, d\alpha \qquad (75)$$

If the last series is shifted to the interval $(-l < x < +l)$, Euler's formulas for it become

$$a_n = \frac{1}{l}\int_{-l}^{+l} f(\alpha)\cos\frac{n\pi\alpha}{l}\, d\alpha \qquad (76)$$

$$b_n = \frac{1}{l}\int_{-l}^{+l} f(\alpha)\sin\frac{n\pi\alpha}{l}\, d\alpha \qquad (77)$$

If we define f(x) to be even or odd, we need consider only the interval $(0 < x < l)$. If even, a cosine series only is needed, i.e.

$$f(x) = \frac{1}{2}a_0 + \sum_{n=1}^{\infty} a_n\cos\frac{n\pi x}{l} \qquad (78)$$

$$a_n = \frac{2}{l}\int_0^{l} f(\alpha)\cos\frac{n\pi\alpha}{l}\, d\alpha \qquad (79)$$

If odd, a sine series only is needed, i.e.:

$$f(x) = \sum_{n=1}^{\infty} b_n \sin \frac{n\pi x}{\ell} \tag{80}$$

$$b_n = \frac{2}{\ell} \int_0^{\ell} f(\alpha) \sin \frac{n\pi\alpha}{\ell} \, d\alpha \tag{81}$$

Perhaps the following example will make these last statements clearer. The cosine and sine developments of f(x) = x are:

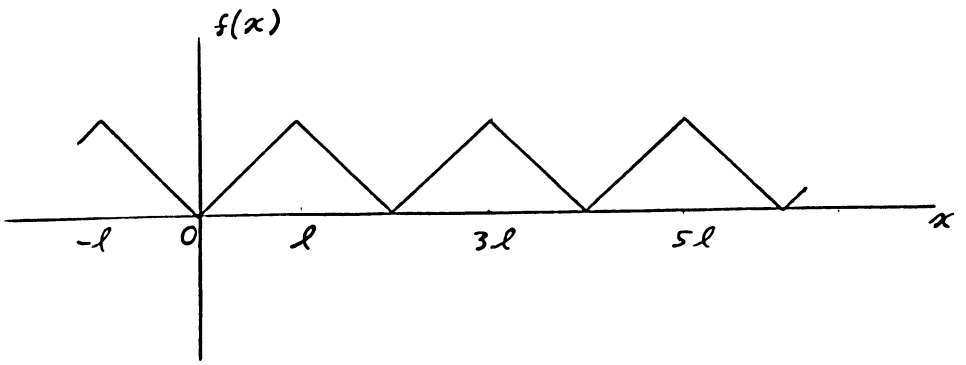
$$f(x) = \frac{\ell}{2} - \frac{4\ell}{\pi^2}\left[\cos\frac{\pi x}{\ell} + \frac{1}{3^2}\cos\frac{3\pi x}{\ell} + \frac{1}{5^2}\cos\frac{5\pi x}{\ell} + \cdots\right]$$

$$(0 < x < \ell) \tag{82}$$

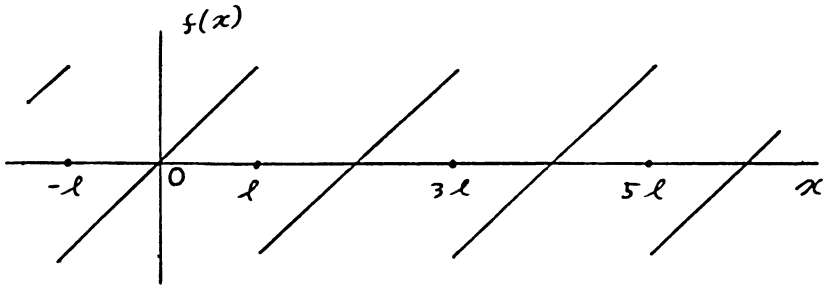
$$f(x) = \frac{2\ell}{\pi}\left[\sin\frac{\pi x}{\ell} - \frac{1}{2}\sin\frac{2\pi x}{\ell} + \frac{1}{3}\sin\frac{3\pi x}{\ell} - + \cdots\right]$$

$$(-\ell < x < +\ell) \tag{83}$$

The curves for each of these are drawn below:



(82)



(83)

If, for a Fourier series, convergent in the interval $(-\ell < x < +\ell)$, it were possible to find the limit of the sum of the series as $\ell \to \infty$, this limiting expression should be equal to the f(x) for all values of x. Fourier's integral is just such a limiting expression: If f(x), arbitrary and defined for all values of x, satisfies Dirichlet's conditions in any infinite interval, and if $\int_{-\infty}^{+\infty} f(x)\,dx$ is absolutely convergent, then

$$\frac{1}{\pi}\int_0^{\infty} d\alpha \int_{-\infty}^{+\infty} f(\lambda)\cos\alpha(\lambda - x)\,d\lambda$$

$$= \frac{1}{2}\left[f(x+0) + f(x-0)\right] \tag{84}$$

at every point where f (x +0) and f(x - 0) exist.

If the function is even, i.e. f(x) = f(- x), Fourier's integral becomes

$$f(x) = \frac{2}{\pi}\int_0^\infty d\alpha \int_0^\infty f(\lambda)\cos\alpha\lambda\cos\alpha x\, d\lambda \qquad (85)$$

If the function is odd, i.e. $f(x) = -f(-x)$, the integral becomes

$$f(x) = \frac{2}{\pi}\int_0^\infty d\alpha \int_0^\infty f(\lambda)\sin\alpha\lambda\sin\alpha x\, d\lambda \qquad (86)$$

If the function is defined for positive values of x only, either (85) or (86) may be used.

Application to the case studied.

The case studied experimentally was the diffusion of nickel sulfate into a finite rectangular parallelopiped of 1% agar gel, with one end open, and all other faces impermeable. The solute was never allowed to reach the opposite end of the column so that it could be treated as of infinite depth. The concentration at the exposed face was kept constant, and the initial concentration of the gel was zero.

The concentration function and the quantity function $\overline{Q}$, have been derived by Hill[33] for the semi-infinite column, of which this is a special case. Since the method he used is not quite clear from his article it is deemed advisable to repeat the derivation here.

On the assumption of straight line flow in the column with no "reflection" or fanning out of the "lines of diffusive force" at the containing walls, the simplified uni-dimensional equations should hold. Either a modified Fourier series expansion, or the Fourier integral could be used to determine the concentration function. Since the latter leads to a neater expression, it only was used by the writer.

Our problem is this: to find a solution of the differential equation

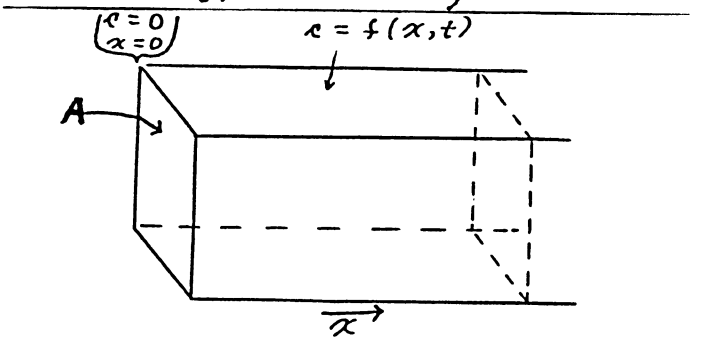
$$\frac{\partial c}{\partial t} = k \frac{\partial^2 c}{\partial x^2} \tag{2}$$

of the form

$$c = f(x,t) \tag{3}$$

subject to the initial and boundary conditions:

$$\left.\begin{aligned} c &= o, \quad \text{when } t = 0 \\ c &= c_o, \quad \text{when } x = 0 \end{aligned}\right\} \tag{87}$$



Since we are concerned only with positive values of x, we may use the form

$$f(x) = \frac{2}{\pi} \int_0^\infty d\alpha \int_0^\infty f(\lambda) \sin \alpha \lambda \sin \alpha x \, d\lambda \tag{86}$$

Since equation (2) is linear with constant coefficients we can obtain a particular solution by the following device:

$$\text{Let } c = e^{\beta t + \alpha x} \tag{88}$$

$$\text{Then } \frac{\partial c}{\partial t} = \beta e^{\beta t + \alpha x} \tag{89}$$

$$\text{and } \frac{\partial^2 c}{\partial x^2} = \alpha^2 e^{\beta t + \alpha x} \tag{90}$$

Substitute in (2) and obtain $\beta = k \alpha^2$. (91)

This is the only relation that need hold between β and α.

Hence $$c = e^{\alpha x + k \alpha^2 t} = e^{k \alpha^2 t} \cdot e^{\alpha x} \tag{92}$$

is a solution of (2), no matter what value is given to α.

To get a trigonometric form replace α by αi in (92). Then

$$c = e^{-k \alpha^2 t} e^{\alpha x i} \tag{93}$$

If we replace α by $-\alpha i$ in (92), we get

$$c = e^{-k \alpha^2 t} e^{-\alpha x i} \tag{94}$$

Subtract the value of c in (94) from the value in (93) and divide by 2 i.

Then

$$c = e^{-k \alpha^2 t} \sin \alpha x \tag{95}$$

is also a solution of (2). Similarly by adding the two values of c in (93) and (94) and dividing by 2, we have

$$c = e^{-k\alpha^2 t} \cos \alpha x \tag{96}$$

(95) and (96) are particular solutions of (2); α is entirely unrestricted.

From these solutions we must build up a function which will reduce to

$$c = f(x) = 0 \tag{97}$$

when $t = 0$, and $f(x)$ is to be given by

$$f(x) = \frac{2}{\pi} \int_0^\infty d\alpha \int_0^\infty f(\lambda) \sin \alpha x \sin \alpha \lambda \, d\lambda \tag{86}$$

We shall now build up a function for c which reduces to (86) when $t = 0$. If we multiply (95) by $\sin \alpha \lambda$ the result is still a solution of (2), i.e.:

$$c = e^{-k\alpha^2 t} \sin \alpha x \sin \alpha \lambda \tag{98}$$

Multiply by $f(\lambda)\, d\lambda$, and have

$$c = e^{-k\alpha^2 t} f(\lambda) \sin \alpha x \sin \alpha \lambda \, d\lambda , \tag{99}$$

which is still a solution of (2).

Then

$$c = \int_0^\infty e^{-k\alpha^2 t} f(\lambda) \sin \alpha x \sin \alpha \lambda \, d\lambda \tag{100}$$

is <u>still</u> a solution of (2), since it is the limit of the

sum of terms (99) as λ ranges from 0 to ∞.

Then we have reason to think that

$$v = \frac{2}{\pi} \int_0^\infty d\alpha \int_0^\infty e^{-k\alpha^2 t} f(\lambda) \sin \alpha x \frac{\sin \alpha \lambda}{d\lambda} \quad (101)$$

is also a solution of (2), since it is $\frac{2}{\pi}$ multiplied by the limit of the sum of terms formed by multiplying the second member of (100) by $d\alpha$, and allowing α to range from 0 to ∞. Function (101) reduces to f(x), i.e. to (86) when t = 0.

Equation (101) may be considerably reduced:

$$v = \frac{1}{\pi} \int_0^\infty f(\lambda) d\lambda \int_0^\infty e^{-k\alpha^2 t} \left[\cos \alpha (\lambda - x) - \cos \alpha (\lambda + x) \right] d\alpha \quad (102)$$

or

$$v = \frac{1}{2\sqrt{\pi k t}} \int_0^\infty f(\lambda) \left[e^{-\frac{(\lambda - x)^2}{4kt}} - e^{-\frac{(\lambda + x)^2}{4kt}} \right] d\lambda \quad (103)$$

$$\left(\text{since} \quad \int_0^\infty e^{-px^2} \cos qx \, dx = \frac{\sqrt{\pi}}{2\sqrt{p}} e^{-\frac{q^2}{4p}} \right) \quad (104)$$

Equation (103) may be written:

$$v = \frac{1}{2\sqrt{\pi k t}} \left[\int_0^\infty f(\lambda) e^{-\frac{(\lambda - x)^2}{4kt}} d\lambda - \int_0^\infty f(\lambda) e^{-\frac{(\lambda + x)^2}{4kt}} d\lambda \right] \quad (105)$$

For the first integral,

let $\beta = \frac{\lambda - x}{2\sqrt{kt}}$

then $\lambda = x + 2\sqrt{kt}\, \beta$

$$d\beta = \frac{d\lambda}{2\sqrt{kt}}$$

For the second integral,

$$\text{let } \beta = \frac{\lambda + x}{2\sqrt{kt}}$$

$$\text{then } \lambda = -x + 2\sqrt{kt}\ \beta$$

$$d\beta = \frac{d\lambda}{2\sqrt{kt}}$$

Then equation (105) becomes:

$$c = \frac{1}{\sqrt{\pi}}\left[\int_{-\frac{x}{2\sqrt{kt}}}^{\infty} e^{-\beta^2} f(x + 2\sqrt{kt}\,\beta)\,d\beta - \int_{\frac{x}{2\sqrt{kt}}}^{\infty} e^{-\beta^2} f(-x + 2\sqrt{kt}\,\beta)\,d\beta\right] \tag{106}$$

Case I. : Let the initial concentration be constant and equal to c_o (i.e., when $t = 0$). Then $f(x + 2\sqrt{kt}\ )$ and $f(-x + 2\sqrt{kt}\ )$ are each constant snd equal to c_o, since $f(x)$ in (105) $= c_o$. Hence

$$c = \frac{c_o}{\sqrt{\pi}}\left[\int_{-\frac{x}{2\sqrt{kt}}}^{\infty} e^{-\beta^2} d\beta - \int_{\frac{x}{2\sqrt{kt}}}^{\infty} e^{-\beta^2} d\beta\right] \tag{107}$$

or

$$c = \frac{2c_o}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \tag{108}$$

Case II. : Let the initial concentration be constant and equal to $-c_o$. Then

$$c = -\frac{2c_o}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \qquad (109)$$

Case III. : Let the initial concentration be constant and equal to zero, and let concentration at the plane face, $x=0$, be c_o. This is our case. Then we need only add c_o to the second member of the (109) :

$$c = c_o - \frac{2c_o}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \qquad (110)$$

The second member of (110) $= -c_o$ when $t=0$, and hence $c=0$ when $t=0$. Also the second member $= 0$ when $x=0$, so that $c = c_o$ when $x=0$. We are permitted to add c_o in (110) because c_o is also a solution of (2)

Therefore the concentration function for the case studied experimentally is:

$$c = c_o \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta\right] \qquad (111)$$

This agrees with Hill's[33] result.

It must be remembered that k, the coefficient of diffusion, is related to K, the solute conductivity constant of the medium, in the following way:

$$k = \frac{K}{s\rho} \qquad (42)$$

In the derivation of Fick's law (P. 19), K was an expirical constant of proportionality. In the above derivation of the concentration function, k was assumed to be a constant independent of concentration. If it should turn out that k is a function of concentration, either by virtue of the fact that s and ρ are functions of the concentration, or because K itself is such a function, then to that extent equation (III) would be in error. It is believed, however, that for relatively small variations in concentration, at least, equation (III) is a close approximation to the truth. It is unlikely that the entirely general case of k as a function of c could be solved at all, and if it could be, the solution would certainly be too complicated to be useful.

The portion of equation (III):

$$\frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta$$

is the probability integral, which may be abbreviated to

$$P\left(\frac{x}{2\sqrt{kt}}\right) \tag{112}$$

and which means in words the probability that the function $\frac{x}{2\sqrt{kt}}$ has a value, lying between zero and $\frac{x}{2\sqrt{kt}}$. Since x and t are independent variables, this function can have any value between zero and infinity. Equation (111) can now be written

$$c = c_o\left[1 - P\left(\frac{x}{2\sqrt{kt}}\right)\right] \tag{113}$$

Values of c for given values of c_o, x, and t may be found by means of probability tables, or by expaning $P\left(\frac{x}{2\sqrt{kt}}\right)$ into infinite series:

$$P(\varphi) = \frac{2}{\sqrt{\pi}}\left(\varphi - \frac{\varphi^3}{3.1!} + \frac{\varphi^5}{5.2!} - \frac{\varphi^7}{7.3!} + \cdots\right) \tag{114}$$

Derivation of quantity function.

We have already seen that the quantity of solute inclosed in a given boundary is given by

$$\bar{Q} = \bar{G}(x,t) = \rho s \int_{x_1}^{x_2} A\, c\, dx \tag{57}$$

(If initial concentration was everywhere zero).

If this is applied to our case we have

$$\bar{Q} = \rho s A \int_0^x c_0 \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \right] dx \qquad (115)$$

$$= \rho s A c_0 x - \frac{2\rho s}{\sqrt{\pi}} A c_0 \int_0^x \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \, dx \qquad (116)$$

Tne second integral can be evaluated by a series expansion of $P\left(\frac{x}{2\sqrt{kt}}\right)$. If this is used we have,

$$\bar{Q} = \rho s A c_0 x - \frac{2\rho s}{\sqrt{\pi}} A c_0 \left[\frac{x^2}{2(2\sqrt{kt})} - \frac{x^4}{4.3.1!(2\sqrt{kt})^3} + \frac{x^6}{6.5.2!(2\sqrt{kt})^5} - \frac{x^8}{8.7.3!(2\sqrt{kt})^7} + \cdots \right] \qquad (117)$$

$$\text{or} \quad \bar{Q} = \frac{2 \rho s A c_0}{\sqrt{\pi}} \left[\frac{\sqrt{\pi}}{2} x - \frac{x^2}{2(2\sqrt{kt})} + \frac{x^4}{4.3.1!(2\sqrt{kt})^3} - \frac{x^6}{6.5.2!(2\sqrt{kt})^5} + \frac{x^8}{8.7.3!(2\sqrt{kt})^7} - + \cdots \right] \qquad (118)$$

This series converges so slowly, however, for large values of x, that it is not very useful. Also, while (118) tells us that $\bar{Q}$ is directly proportional to A and to c_o , it gives no hint as to how it varies with t.

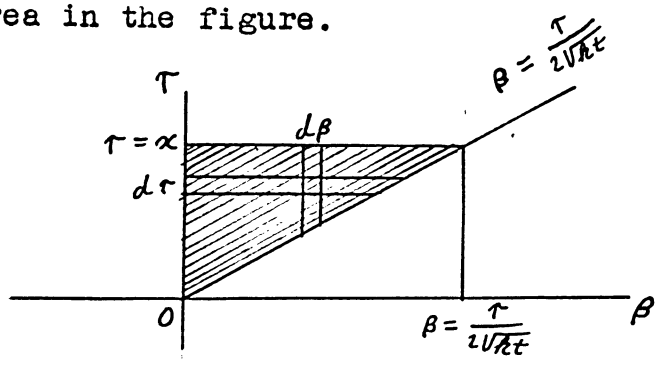
A far more profitable expression can be derived from (116) by carefully interchanging the order of integration. We will work at first only with the portion

$$\int_0^x \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \, dx \qquad (119)$$

which to avoid confusion can be written

$$I = \int_0^x \int_0^{\frac{\tau}{2\sqrt{kt}}} e^{-\beta^2} d\beta \, d\tau \qquad (120)$$

The value of the double integral I is the shaded area in the figure.



It makes no difference whether the elemental strips to be integrated are taken horizontally or vertically

$$\therefore \quad I = \int_0^{\frac{x}{2\sqrt{kt}}} \int_{\beta \cdot 2\sqrt{kt}}^{x} e^{-\beta^2} d\tau d\beta \qquad (121)$$

$$= \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} (x - \beta \cdot 2\sqrt{kt}) d\beta \qquad (122)$$

$$= x \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta + \left[\sqrt{kt}\, e^{-\beta^2} \right]_0^{\frac{x}{2\sqrt{kt}}} \qquad (123)$$

$$= x \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta + \sqrt{kt} \left(e^{-\frac{x^2}{4kt}} - 1 \right) \qquad (124)$$

$\therefore$ (116) becomes:

$$\bar{Q} = \rho s A c_0 x - \frac{2}{\sqrt{\pi}} \rho s A c_0 \left[x \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta + \sqrt{kt} \left(e^{-\frac{x^2}{4kt}} - 1 \right) \right] \qquad (125)$$

or

$$\bar{Q} = \rho s A c_0 \left[x - x \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \right] - \frac{2}{\sqrt{\pi}} \rho s A c_0 \sqrt{kt} \left(e^{-\frac{x^2}{4kt}} - 1 \right)$$

To obtain the total quantity of solute absorbed into the entire column, let $x \rightarrow \infty$

then $$\frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \rightarrow 1 \qquad (126)$$

and $$e^{-\frac{x^2}{4kt}} \rightarrow 0 \qquad (127)$$

It can readily be seen from (126) that

$$\left(x - x \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta\right) \rightarrow 0$$

$\therefore$ Equation (125) becomes

$$\bar{Q} = 2 \rho s A c_0 \sqrt{\frac{kt}{\pi}} \qquad (128)$$

Equation (128) can also be derived by a slightly different mode of reasoning. We have seen that the quantity of solute flowing past a given boundary is given by

$$Q = G(x,t) = -K \int_{A}^{\text{over}} \int_{t_1}^{t_2} \frac{\partial c}{\partial x} dt\, dA \qquad (63)$$

Since the case we are considering, all the solute inclosed in the column must have passed through the plane face $x = 0$, it follows that

$$\bar{Q} = \sum_{t=0}^{t} Q \qquad (129)$$

(Cf. (59))

$$\therefore \quad \bar{Q} = -KA \int_0^t \frac{\partial c}{\partial x} \, dt \tag{130}$$

Since

$$c = c_0 - \frac{2}{\sqrt{\pi}} c_0 \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \tag{111}$$

$$\frac{\partial c}{\partial x} = -\frac{2}{\sqrt{\pi}} c_0 \frac{\partial}{\partial x} \int_0^{\frac{x}{2\sqrt{kt}}} e^{-\beta^2} d\beta \tag{131}$$

$$= -\frac{2}{\sqrt{\pi}} c_0 \frac{\partial}{\partial \beta} \int_0^{\beta} e^{-\beta^2} d\beta \times \frac{\partial \beta}{\partial x} \tag{132}$$

where $$\beta = \frac{x}{2\sqrt{kt}} \tag{133}$$

$$\therefore \quad \frac{\partial c}{\partial x} = -\frac{2}{\sqrt{\pi}} c_0 \, e^{-\beta^2} \frac{d\beta}{dx} \tag{134}$$

$$= -\frac{2}{\sqrt{\pi}} c_0 \, e^{-\beta^2} \cdot \frac{1}{2\sqrt{kt}} \tag{135}$$

or $$\frac{\partial c}{\partial x} = -\frac{c_0}{\sqrt{\pi k t}} \, e^{-\frac{x^2}{4kt}} \tag{136}$$

$$\therefore \quad \bar{Q} = KA \int_0^t \frac{c_0}{\sqrt{\pi k t}} e^{-\frac{x^2}{4kt}} dt$$

or

$$\bar{Q} = \frac{KA c_0}{\sqrt{\pi k}} \int_0^t \frac{1}{\sqrt{t}} e^{-\frac{x^2}{4kt}} dt \qquad (137)$$

This is the general expression for quantity of solute flowing past any cross-sectional plane at a depth x. In particular, when $x = 0$,

$$e^{-\frac{x^2}{4kt}} = 1 \qquad (138)$$

and the quantity function becomes

$$\bar{Q} = \frac{KA c_0}{\sqrt{\pi k}} \int_0^t \frac{dt}{\sqrt{t}} \qquad (139)$$

$$= \frac{2KA c_0}{\sqrt{\pi k}} \times \sqrt{t} \qquad (140)$$

or $$\bar{Q} = 2 K A c_0 \sqrt{\frac{t}{\pi k}} \tag{141}$$

if we recall that

$$k = \frac{K}{s \rho} \tag{42}$$

then our equation (141) becomes

$$\bar{Q} = 2 k s \rho A c_0 \sqrt{\frac{t}{\pi k}} \tag{142}$$

or

$$\bar{Q} = 2 \rho s A c_0 \sqrt{\frac{k t}{\pi}} \tag{128}$$

as before.

This does <u>not</u> agree, as far as constants are concerned, with the equation derived by Hill[33] and used by Ricketts and Culbertson[35], which is

$$\bar{Q} = 2 A c_0 \sqrt{\frac{k' t}{\pi}} \tag{143}$$

Hence $$k' = \rho^2 s^2 k \tag{144}$$

If we assume that

$$\rho s = 1, \tag{145}$$

as it would be in the ideal case,* and as it often very nearly

* Addition of solute without changing total volume of solution.

is in practice, then our equation (128) becomes identical with Hill's (143). As Hill's[33] derivation is not given in his paper, it is impossible to determine whether he made this approximation knowingly, or whether he confused K and k, thinking them the same constant, as has been done so often in the literature.

This confusion of constants in the literature undoubtedly has had much to do with discrepancies in the reported data of different observers, as well as with apparent variations from theory. For example, the reported variation of coefficient of diffusion (k') with concentration might be attributed to the variation of s and ρ with c, rather than of the true coefficient k. Of course, there is nothing to prevent k itself from being a function of c. We don't know.

Calculation of solute capacity.

The following relation for calculating s has been derived by the author.

If we represent solute capacity per unit volume by ψ, we have

$$\psi = \rho s \qquad (146)$$

ψ may be calculated as follows:

To one cc of a solution of concentration c_1 (moles of solute 1, per cc of solution), add quantity of solute Δn_1 moles. Volume increases ΔV.

$$\Delta c_1 = \frac{c_1 + \Delta n_1}{1 + \Delta V} - c_1 \qquad (147)$$

$$\therefore \frac{\Delta n_1}{\Delta c_1} = \frac{\Delta n_1}{\frac{c_1 + \Delta n_1}{1 + \Delta V} - c_1} \qquad (148)$$

$$= \frac{1 + \Delta V}{1 - c_1 \frac{\Delta V}{\Delta n_1}} \qquad (149)$$

Let $\Delta n_1 \to 0$; then $\Delta V \to 0$ } (150)

and $$\frac{\partial n_1}{\partial c_1} = \frac{1}{1 - c_1 \frac{\partial V}{\partial n_1}} \qquad (151)$$

But $$\frac{\partial V}{\partial n_1} = \overline{v_1} \quad , \qquad (152)$$

the partial molal volume of solute component 1

Also by definition

$$\psi_1 = \frac{\partial n_1}{\partial c_1} \tag{153}$$

$$\therefore \quad \psi_1 = \frac{1}{1 - c_1 \bar{v}_1} \tag{154}$$

and

$$S_1 = \frac{1}{\rho(1 - c_1 \bar{v}_1)} \tag{155}$$

The calculation of S therefore is dependent upon data for density and partial molal volume at the concentration desired, and of course at the given temperature.

The velocity relation.

One other interesting relation for the case of diffusion into a semi-infinite column, should be considered. That is the velocity relation. We have seen that for our case

$$\frac{dQ}{dt} = -KA\frac{\partial c}{\partial x} \qquad (63)$$

The quantity of solute diffusing past any cross sectional plane of a slab in the steady state (See p.27) is given by

$$\frac{dQ}{dt} = A(c_0 - c_1)v \qquad (156)$$

$$\text{or} \qquad \frac{dQ}{dt} = A(c_0 - c_1)\frac{dx}{dt} \qquad (157)$$

where v is the constant velocity of flow of solute (the root mean square velocity of the solute particles(?)) and c_0 and c_1 are the concentrations of the faces of the slab.

Let us consider now the velocity with which the moving boundary of solution is advancing into the pure medium in our case. Let $\bar{x}$ = depth of this boundary at any given time, i.e., $\bar{x}$ is a function of t. If we assume that the diffusion is so slow that it can be broken up into an infinite number of steady states, then $\frac{\partial c}{\partial x}$ in (63) is constant between x = 0, c = c_0, and x = $\bar{x}$, c = 0.

$$\therefore \quad c = -\frac{c_0}{\bar{x}}x + c_0 \qquad (158)$$

$$\text{and} \qquad \frac{\partial c}{\partial x} = -\frac{c_0}{\bar{x}} \qquad (159)$$

$\therefore$ Equation (63) becomes

$$\frac{dQ}{dt} = \frac{AK c_0}{\bar{x}} \tag{160}$$

By equating (63) and (157), we have for the plane at depth zero:

$$A(c_0 - 0) v_0 = -AK \frac{\partial c}{\partial x}$$

$$v_0 = -\frac{K}{c_0} \frac{\partial c}{\partial x} \tag{161}$$

or, substituting (159):

$$v_0 = \frac{K}{\bar{x}} \tag{162}$$

Since in the steady state velocity is independent of depth, for constant cross section,

$$v_0 = \bar{v}, \tag{163}$$

the velocity of the moving boundary,

and $$\bar{v} = \frac{K}{\bar{x}} \tag{164}$$

$$\therefore \quad \frac{d\bar{x}}{dt} = \frac{K}{\bar{x}} \tag{165}$$

and $$\bar{x}^2 = 2Kt \tag{166}$$

$$\therefore \quad K = \frac{\bar{x}^2}{2t} \tag{5}$$

which is Procopiu's expression, where $\bar{x}$ is the distance the boundary has moved in time t. The author has been unable to derive Stefan's law (4) by a similar mode of reasoning. It is important to note that the constant which would be obtained from (5) is not k, but K.

Equation (164) is of interest because it is the link that connects the Stokes-Einstein equation (12) with the Einstein Brownian movement equation (8). It should be noted that here again the constant is K, and not k.

By substituting (166) in (160) we have:

$$dQ = \frac{A K c_0}{\sqrt{2Kt}}\, dt \tag{167}$$

$$\therefore \quad Q = \frac{A K c_0}{\sqrt{2K}} \int_0^t \frac{dt}{\sqrt{t}} \tag{168}$$

$$\therefore \quad Q = A c_0 \sqrt{2Kt} \tag{169}$$

for the quantity of solute flowing through open end in time t,

$$\therefore \quad \bar{Q} = A c_0 \sqrt{2\kappa t} \ , \qquad (170)$$

which does not agree, as regards constant factor, with either of the expressions previously discussed. This discrepancy is attributed to the invalidity of the assumption made in deriving (158).

Deviations from theory.

Before going into the experimental study of nickel sulfate a few words should be said regarding deviations to be expected from the general theory discussed. These deviations are conveniently discussed under four heads:

(1) Deviations due to faulty analogy with heat. Solute diffusion may be accompanied by an irreversible absorption into the medium, so that a corrective term A would have to be added to the general diffusion law. (See P. 25, equation (45)).

(2) Variation with the solute. There is only one kind of heat to flow, but there are as many cases of solute diffusion as there are combinations of solutes and solvents. The solute particles may not obey Stokes

law exactly, in which case the Stokes-Einstein law becomes inexact.

In the case of diffusion of electrolytes, the rate of diffusion is slowed down (See the Nernst theory p. 8). The simple Fick's law equation is still valid for electrolytes if we clearly understand what is meant by "concentration" of an electrolyte. It would be better to use "activity" at least for concentrated solutions where interionic attraction becomes a prominent factor. Hydration and association effects, and complex ions would be expected to introduce further complications.

The variation of diffusion coefficient with concentration, which by analogy with heat we might have expected, has been discussed already (pp. 8, 43).

(3) Variation with the solvent. Variation with medium would also be expected from the analogy between heat and solute flow. The Stokes-Einstein law gives a quantative treatment of this variation, in terms of viscosity of the medium. Unfortunately other factors such as association of solvent molecules, and the fact that the solvent also diffuses, enter in.

(4) The variation with temperature. This factor has been mentioned under Historical (P. 8). Corrective expressions of the form

$$k = k_0 (1 + \alpha \theta) \qquad (171)$$

have been derived; where k_0 is diffusion constant at $0^\circ C.$, α is temperature coefficient of k, and θ is the temperature.

4. EXPERIMENTAL

Cases studied.

The case studied experimentally has already been referred to (P. 36). It is that of diffusion into a finite rectangular parallelopiped of agar gel, with one end only open, and all other faces impermeable. The face exposed was maintained at a constant concentration and the gel was initially devoid of solute. The solid was not allowed to reach the opposite end, so that for all practical purposes the solid considered was of infinite depth. The total quantity of solute absorbed and the concentration at various depths were determined for different boundary concentrations and different times, with temperature and cross sectional area constant. Equations (111) and (127) or (143) for the semi-infinite diffusion column would therefore be expected to hold. Cylinders with one end exposed were also tried, but with little success.

Diffusion procedure.

The solute used in all experiments to date has been Merck's nickel sulfate, and the diffusion medium, 1% agar gel. The melted agar was poured into the mold and allowed to solidify for one hour. The entire mold was then placed into a closed jar containing a large volume (6 liters) of $NiSO_4$ solution, which was in turn immersed in a water

bath kept at 25.00° ± 0.02°C , during the entire time of diffusion, by means of a gas thermostat. Five cc. samples of the solution were removed from the vicinity of the exposed face at the beginning and end of the period of diffusion. As the concentration so determined never varied more than 0.5%, stirring was deemed unnecessary and the average of the two readings was taken as the constant concentration at the boundary.

Construction of molds.

Special attention was given to the molds. The rectangular parallelopiped was constructed from a U-shaped wooden frame saturated with paraffin, and slotted to receive two glass plates 19.36 cm X 8.25 cm. Before each run the plates were carefully cleaned by alternate washing with Na OH and concentrated $H N O_3$, followed by washing with distilled water until the p_H of the washings after long soaking was approximately that of the distilled water used, 6. This was done to make the agar adhere better and thereby to minimize seepage of solution between the gel and the walls of the mold. All joints in the mold were made solution tight by sealing with paraffin. The dimensions of the exposed face were 6.67 cm X 2.49 cm = 16.59 $cm.^2$ The cylinders were made simply by stoppering one end of sections

of glass tubing of large bore. In spite of careful cleaning of the cylinders, however, seepage was excessively great and the results obtained for this case must be regarded as only rough.

Slicing of agar.

The agar cake after removal from the mold was sliced on a specially constructed slicing table, and the individual slices melted by boiling water and analyzed for nickel. In some instances where total solute only was to be determined, the slices were cut larger and inaccurately.

Electroanalysis.

All analyses were made electrolytically according to the method of Smith[41]. To each sample was added 1.2 grams of $(NH_4)_2SO_4$, 30 cc of 6 N NH_4OH, and water to make 100 cc. The nickel was plated on a cylinder of platinum gauze. The anode was a rotating spiral of platinum. The current was kept at two amperes and the voltage ranged from about 3.5 to 4.5. Electrolysis was stopped when drops tested on a spot plate gave no pink color with dimethyl glyoxime. A slight correction was necessary due to the fact that the anode dissolved very slowly and plated in part on the cathode. The deposit of nickel on the cathode was removed from time to time by dipping in nitric acid.

5. DATA

Form of presentation.

The data determined is presented in two forms: (1) the original data, aside from slight corrections for solution of anode; (2) derived tables of data. Reliability of individual readings is indicated by mean deviations in original weights only. The reliability of derived figures is indicated only by the retaining of the proper number of significant figures.

Tables of data.

(1) Original data.

(a) Slice runs with rectangular parallelopiped.

The depth - volume data for slices given in Table 1 below holds for all subsequent tables referring to slice runs. For convenience, therefore, each slice will henceforth be referred to only by its number.

The following symbols and units have been used in the tables:

A = area of face exposed, in $cms.^2$

x = average depth of slice, in cms.

Δx = thickness of slice, in cms.

ΔV = volume of slice, in $cms.^3$

Δw = weight of Ni in slice, in grams (corrected

for anode solution).

Corrected Δw = weight of Ni reduced to the same boundary concentration basis.

Av. Δ w: First column (no. 6) indicates mean deviations; second column (no. 7) indicates the correct number of significant figures.

The figures given in columns 2 and 3, and 4 and 5 under Δw and corrected Δw are for two independent check runs.

$\bar{Q}$ = total quantity of solute absorbed, in grams (columns 2 to 8, inc. of Table 2 and following), or in moles (column 9).

c_o = boundary concentration, in grams per 5 cc. sample of solution (columns 2 to 7, inc.), in grams per cc. (column 8), or in moles per liter (column 9).

c = concentration of Ni in agar at depth x, in grams per cc. (column 8), or in moles per liter (column 9).

t = time in hours, or in seconds.

k' = coefficient of diffusion in $cm.^2/sec.$ (Hill).

Table 1

c_o = 0.137 M., t = 24 hours

1 No.	x	Δx	ΔV*	2 Δ w	3	4 corrected Δ w	5
1	0.32	0.63	10.53	0.0618	0.0619	0.0618	0.0622
2	0.95	0.63	10.53	0.0270	0.0252	0.0270	0.0253
3	1.59	0.63	10.53	0.0092	0.0081	0.0092	0.0081
4	2.22	0.63	10.53	0.0024	0.0020	0.0024	0.0020
5	2.86	0.63	10.53	0.0004	0.0002	0.0004	0.0002
6	3.49	0.63	10.53	0.0000	0.0000	0.0000	0.0000
7	4.44	1.27	21.07	------	------	------	------
8	6.35	2.54	42.13	------	------	------	------
9	8.89	2.54	42.13	------	------	------	------
R	----	----	-----	------	------	------	------
Q	----	----	-----	0.1008	0.0974	0.1008	0.0978
c_o (1)	----	----	-----	0.0402	0.0399		
~~e (2)~~							
c_o (2)	----	----	-----	0.0399	0.0399		
av. c_o	----	----	-----	0.04005 ±0.00015	0.0399 ±0.0000	0.0400	0.0400

No.	6 Av. Δ w	7	8 c (g/cc)	9 c (mol/l)
1	0.06200 ± 0.00020	0.0620	0.00589	0.100
2	0.02615 ± 0.00085	0.0262	0.00249	0.0424
3	0.00865 ± 0.00055	0.0087	0.00083	0.014
4	0.00220 ± 0.00020	0.0022	0.00021	0.0036
5	0.00030 ± 0.00010	0.0003	0.00003	0.0005
6	0.00000 -------	0.0000	0.00000	0.0000
7	------- -------	------	-------	-------
8	------- -------	------	-------	-------
9	------- -------	------	-------	-------
Remainder	------- -------	------	-------	-------
Total ($\bar{Q}$)	0.0993 ± 0.0015	0.099	0.099	0.0017
Av. c_o	0.0400	0.0400	0.00801	0.137

* A = 16.59 cm.²

Table 2

Slice run: c_o = 0.274 M., t = 24 hours

1 No.	2 Δw (1)	3 Δw (2)	4 Corrected Δw	5
1	0.1045	0.1098	0.1045	0.1100
2	0.0599	0.0505	0.0599	0.0506
3	0.0234	0.0176	0.0234	0.0177
4	0.0078	0.0047	0.0078	0.0047
5	0.0024	0.0010	0.0024	0.0010
6	0.0004	0.0000	0.0004	0.0000
7	0.0004	------	0.0004	------
$\bar{Q}$	0.1988	0.1836	0.1988	0.1840
c_o (1) before	0.080750 ± 0.000050	0.0804		
c_o (2) after	0.07985 ± 0.00025	0.07995 ± 0.00045		
Av. c_o	0.08030 ± 0.00045	0.08017 ± 0.00023	0.0803	0.0803

No.	6 Av. Δw	7	8 c (g/cc)	9 c (mol/l)
1	0.1072 ± 0.0027	0.107	0.0102	0.173
2	0.0552 ± 0.0046	0.055	0.0052	0.089
3	0.0205 ± 0.0028	0.020	0.0019	0.032
4	0.0062 ± 0.0015	0.006	0.0006	0.01
5	0.0017 ± 0.0007	0.0017	0.00016	0.0027
6	0.0002 ± 0.0002	0.0002	0.00002	0.0003
$\bar{Q}$	0.1914 ± 0.0074	0.191	0.191	0.00326
Av. c_o	0.0803	0.0803	0.0161	0.274

Table 3

Slice runs: c_o = 0.3726 M., t = 24 hours

1 No.	2 Δw (1)	3 Δw (2)	4 Corrected Δw	5
1	0.1619	0.1591	0.1619	0.1597
2	0.0641	0.0683	0.0641	0.0685
3	0.0230	0.0241	0.0230	0.0242
4	0.0060	0.0072	0.0060	0.0072
5	0.0014	0.0014	0.0014	0.0014
6	0.0002	0.0002	0.0002	0.0002
7	0.0001	0.0000	0.0001	0.0000
8	0.0002	------	0.0002	------
9	0.0000	------	0.0000	------
$\bar{Q}$	0.2569	0.2603	0.2569	0.2612
c_o (1)	0.10940 ± 0.00020	0.1087		
c_o (2)	0.1091	0.1090		
Av. c_o	0.10925 ± 0.00015	0.10885 ± 0.00015	0.1092	0.1092

No.	6 Av. Δw	7	8 c (g/cc)	9 c (mol/l)
1	0.1608 ± 0.0011	0.161	0.0153	0.261
2	0.0663 ± 0.0022	0.066	0.0063	0.11
3	0.0236 ± 0.0006	0.0236	0.00224	0.0382
4	0.0066 ± 0.0006	0.0066	0.00063	0.011
5	0.0014 ± 0.0000	0.0014	0.00013	0.0023
6	0.0002 ± 0.0000	0.0002	0.00002	0.0003
7	0.00005 ± 0.00005	0.00005	0.000002	0.00004
8	0.0001 ± 0.0001	0.0001	0.000002	0.00004
$\bar{Q}$	0.2590 ± 0.0021	0.259	0.259	0.00441
Av. c_o	0.1092	0.1092	0.02186	0.3726

Table 4

Slice run: c_o = 0.4742 M., t = 24 hours

1 No.	2 Δw	8 c (g/cc)	9 c (mol/l)
1	0.2151	0.02042	0.3479
2	0.0834	0.00793	0.135
3	0.0266	0.00252	0.0431
4	0.0084	0.00080	0.014
5	0.0025	0.00024	0.0040
6	0.0007	0.00007	0.001
7	0.0006	0.00003	0.0005
8	0.0007	0.00002	0.0003
9	0.0000	0.00000	0.0000
$\bar{Q}$	0.3380		0.005759
c_o (1)	0.1393		
c_o (2)	0.1387		
Av. c_o	0.13900 ± 0.00030	0.02783	0.4742

Table 5

Slice runs: c_Δ = 0.6977 M., t = 24 hours

1 No.	2 Δw (1)	3 Δw (2)	4 Corrected Δ w	5
1	0.3084	0.2941	0.3084	0.2948
2	0.1097	0.1185	0.1097	0.1188
3	0.0419	0.0454	0.0419	0.0455
4	0.0135	0.0147	0.0135	0.0147
5	0.0039	0.0042	0.0039	0.0042
6	0.0010	0.0007	0.0010	0.0007
7	0.0005	0.0008	0.0005	0.0008
8	0.0005	0.0003	0.0005	0.0003
9	0.0000	0.0000	0.0000	0.0000
$\bar{Q}$	0.4794	0.4787	0.4794	0.4798
c_o (1)	0.2046	0.2041		
c_o (2)	0.2045	0.2040		
Av. c_o	0.204550 ± 0.000050	0.204050 ±0.000050	0.2045	0.2045

No.	6 Av. Δ w	7	8 c (g/cc)	9 c (mol/l)
1	0.2966 ± 0.0018	0.297	0.0282	0.481
2	0.1142 ± 0.0045	0.114	0.0108	0.185
3	0.0437 ± 0.0018	0.044	0.0042	0.071
4	0.0141 ± 0.0006	0.0141	0.00134	0.0228
5	0.00405 ± 0.00015	0.0040	0.00038	0.0065
6	0.00085 ± 0.00015	0.0008	0.00008	0.001
7	0.00065 ± 0.00015	0.0006	0.00003	0.0005
8	0.0004 ± 0.0001	0.0004	0.00001	0.0002
$\bar{Q}$	0.47960 ± 0.00020	0.4796		0.008172
Av. c_o	0.2045	0.2045	0.04095	0.6977

Table 6

Slice runs: c_o = 0.9346 M., t = 24 hours

1 No.	2 Δ w (1)	3 Δ w (2)	4 Corrected Δ w	5
1	0.3758	0.3738	0.3713	0.3738
2	0.1746	0.1783	0.1725	0.1783
3	0.0715	0.0707	0.0707	0.0707
4	0.0312	0.0243	0.0308	0.0243
5	0.0144	0.0087	0.0142	0.0087
6	0.0062	0.0027	0.0062	0.0027
7	0.0040	0.0025	0.0040	0.0025
8	0.0015	0.0029	0.0015	0.0029
9	------	0.0022	------	0.0022
R	0.0001	0.0055	0.0001	0.0055
$\bar{Q}$	0.6793	0.6716	0.6713	0.6716
c_o (1)	0.2785	0.2749		
c_o (2)	0.2760 ± 0.0011	0.2729 ± 0.0012		
Av. c_o	0.2772 ± 0.0012	0.2739 ± 0.0010	0.2739	0.2739

No.	6 Av. Δw	7	8 c (g/cc)	9 c (mol/l)
1	0.3725 ± 0.0012	0.372	0.0353	0.601
2	0.1754 ± 0.0029	0.175	0.0166	0.283
3	0.0707 ± 0.0000	0.0707	0.00671	0.114
4	0.0275 ± 0.0032	0.027	0.0026	0.044
5	0.0114 ± 0.0027	0.011	0.0010	0.018
6	0.0044 ± 0.0017	0.004	0.0004	0.006
7	0.00325 ± 0.00075	0.0032	0.00015	0.0026
8	0.0022 ± 0.0007	0.0022	0.000052	0.00089
9	0.0011 ± 0.0011	0.001	0.00002	0.0004
$\bar{Q}$	0.67145 ± 0.00015	0.6714		0.01144
Av. c_o	0.2739	0.2739	0.05484	0.9346

Table 7

Slice runs: c_o = 0.9346 M., t = 6 hours

1 No.	2 Δw (1)	3 Δw (2)	4 Corrected Δw	5 Corrected Δw
1	0.2532	0.2462	0.2572	0.2502
2	0.0412	0.0395	0.0419	0.0401
3	0.0069	0.0095	0.0070	0.0097
4	0.0013	0.0039	0.0013	0.0040
5	0.0007	0.0014	0.0007	0.0014
6	0.0001	0.0006	0.0001	0.0006
7	0.0007	0.0004	0.0007	0.0004
8	0.0000	0.0000	0.0000	0.0000
$\bar{Q}$	0.3041	0.3015	0.3089	0.3064
c_o (1)	0.2698	0.2695		
c_o (2)	0.2695	0.2695		
Av. c_o	0.26965 ± 0.00015	0.26950 ± 0.00000	0.2739	0.2739

No.	6 Av. Δw	7	8 c (g/cc)	9 c (mol/l)
1	0.2537 ± 0.0035	0.254	0.0241	0.411
2	0.0410 ± 0.0009	0.0410	0.00389	0.0664
3	0.0083 ± 0.0013	0.008	0.0008	0.01
4	0.0026 ± 0.0013	0.003	0.0003	0.005
5	0.00105 ± 0.00035	0.0010	0.000095	0.0016
6	0.00035 ± 0.00025	0.0003	0.00003	0.0005
7	0.00055 ± 0.00015	0.0005	0.00002	0.0004
8	0.00000	0.0000	0.00000	0.0000
$\bar{Q}$	0.3076 ± 0.0012	0.308		0.00525
Av. c_o	0.2739	0.2739	0.05484	0.9346

Table 8

Slice run: c_o = 0.9346 M., t = 12,1/6 hours

1 No.	2 Δw	4 Cor. Δw	8 c (g/cc)	9 c (mol/l)
1	0.3192	0.3221	0.0306	0.521
2	0.1183	0.1193	0.0113	0.192
3	0.0360	0.0363	0.0034	0.058
4	0.0133	0.0134	0.0012	0.021
5	0.0052	0.0053	0.00050	0.0086
6	0.0024	0.0024	0.00023	0.0039
7	0.0027	0.0027	0.00013	0.0022
8	0.0020	0.0020	0.000047	0.00081
9	0.0007	0.0007	0.00002	0.0003
$\bar{Q}$	0.4998	0.5042		0.00859
c_o (1)	0.2720			
c_o (2)	0.27100 ± 0.00050			
Av. c_o	0.27150 ± 0.00050	0.2739	0.05484	0.9346

Table 9

Slice runs: c_o = 0.9346 M., t = 18 hours

1 No.	2 Δw (1)	3 Δw (2)	4 Corrected Δw	5 Corrected Δw
1	0.3636	0.3462	0.3656	0.3488
2	0.1633	0.1554	0.1643	0.1565
3	0.0614	0.0515	0.0618	0.0519
4	0.0195	0.0151	0.0196	0.0153
5	0.0058	0.0043	0.0058	0.0043
6	0.0018	0.0017	0.0018	0.0017
7	0.0016	0.0015	0.0016	0.0015
8	0.0020	0.0011	0.0020	0.0011
9	0.0005	0.0011	0.0005	0.0011
$\bar{Q}$	0.6195	0.5779	0.6230	0.5822
c_o (1)	0.2733	0.2719		
c_o (2)	0.27155 ± 0.00035	0.2720		
Av. c_o	0.27240 ± 0.00090	0.271950 ±0.000050	0.2739	0.2739

No.	6 Av. Δw	7	8 c (g/cc)	9 c (mol/l)
1	0.3572 ± 0.0084	0.357	0.0339	0.578
2	0.1604 ± 0.0039	0.160	0.0152	0.259
3	0.0568 ± 0.0049	0.057	0.0054	0.092
4	0.0174 ± 0.0021	0.017	0.0016	0.027
5	0.00505 ± 0.00075	0.0050	0.00047	0.0081
6	0.00175 ± 0.00005	0.00175	0.000166	0.00283
7	0.00155 ± 0.00005	0.00155	0.0000736	0.00125
8	0.00155 ± 0.00045	0.0015	0.000035	0.00061
9	0.0008 ± 0.0003	0.0008	0.00002	0.0003
$\bar{Q}$	0.603 ± 0.020	0.60		0.010
Av. c_o	0.2739	0.2739	0.05484	0.9346

Table 10

Slice run: c_o = 0.9346 M., t = 36 hours

1 No.	2 Δ w	4 Cor. Δ w	8 c (g/cc)	9 c (mol/l)
1	0.3772	0.3822	0.0363	0.618
2	0.2408	0.2440	0.0232	0.395
3	0.1105	0.1120	0.0106	0.181
4	0.0480	0.0487	0.00462	0.0787
5	0.0203	0.0206	0.00195	0.0333
6	0.0067	0.0068	0.00065	0.011
7	0.0040	0.0041	0.00019	0.0033
8	0.0018	0.0018	0.000043	0.00073
9	0.0008	0.0008	0.00002	0.0003
$\bar{Q}$	0.8101	0.8210		0.014
c_o (1)	0.2705			
c_o (2)	0.2701			
Av. c_o	0.27030 $\pm$ 0.00020	0.2739	0.05484	0.9346

(b) Total solute runs with rectangular parallelopiped.

Table 11

1. c_o = 0.274 M., t = 24 hours

Run no.	1	2	3*	4*
$\bar{Q}$	0.1902	0.1921	0.1988	0.1836
c_o (1)	0.08090	0.07970		
	± 0.00060	± 0.00020		
c_o (2)	0.07955	0.07975		
	± 0.00015	± 0.00025		
Av. c_o	0.08022	0.079725	0.08030	0.08017
	± 0.00068	± 0.000025	± 0.00045	± 0.00023
Cor. $\bar{Q}$	0.1904	0.1934	0.1988	0.1840
Cor. c_o	0.0803	0.0803	0.0803	0.0803

Av. $\bar{Q}$ 0.1916 ± 0.0044 grams; 0.00327 moles
Cor. c_o 0.0803 grams/5cc. ; 0.274 moles/liter

2. c_o = 0.9346 M., t = 24 hours

Run no.	1	2	3*	4*
$\bar{Q}$	0.6911	0.6777	0.6793	0.6716
c_o (1)	0.2804	0.2794		
c_o (2)	0.2810	0.2803		
Av. c_o	0.28070	0.27985	0.2772	0.2739
	± 0.00030	± 0.00045	± 0.0012	± 0.0010
Cor. $\bar{Q}$	0.6744	0.6634	0.6713	0.6716
Cor. c_o	0.2739	0.2739	0.2739	0.2739

Av. $\bar{Q}$ 0.6702 ± 0.0034 grams; 0.0114 moles
Cor. c_o 0.2739 grams/5 cc. 0.9346 moles/liter

3. c_o = 0.9346 M., t = 36 hours

Run no.	1	2*
$\bar{Q}$	0.8045	0.8101
c_o (1)	0.2804	0.2705
c_o (2)	0.2810	0.2701
Av. c_o	0.28070 ± 0.00030	0.27030 ± 0.00020

Run no.	1	2*
Cor. $\bar{Q}$	0.7850	0.8210
Cor. c_o	0.2739	0.2739

Av. $\bar{Q}$ 0.803 ± 0.018 g.
0.014 moles

Cor. c_o 0.2739 g./5 cc.
0.9346 moles/l.

Data marked * in Table 11 has been copied from preceding tables. All other total solute data, not included in Table 11, is also to be found in Tables 1 to 10 on Slice runs.

(c) Total solute runs with cylinders

Table 12

1. Cylinder #1. c_o=0.9346 M., t = 24 hours; A = 17.52 $cm.^2$

Run no.	1	2	3
$\bar{Q}$	1.2057	0.7993	1.0342
c_o (1)	0.2785	0.2761	0.2749
c_o (2)	0.2760	0.2741	0.2729
	± 0.0011	± 0.0012	± 0.0012
Av. c_o	0.2772	0.2751	0.2739
	± 0.0012	±0.0010	± 0.0010
Cor. $\bar{Q}$	1.191	0.7960	1.0342
Cor. c_o	0.2739	0.2739	0.2739
Av. $\bar{Q}$	1.01 ± 0.14 grams ; 0.020 moles		
Cor. c_o	0.9346 moles/liter		

2. Cylinder #2. c_o = 0.9346 M., t = 24 hours ; A 7.92 $cm.^2$

Run no.	1	2	3	4	5	6
$\bar{Q}$	0.4006	0.3554	0.2830	0.3933	0.2671	0.3591
c_o (1)	0.2794	0.2794	0.2785	0.2761	0.2749	0.2733
c_o (2)	0.2803	0.2803	0.2760	0.2741	0.2729	0.27155
			±0.0011	±0.0012	±0.0012	±0.00035
Av. c_o	0.27985	0.27985	0.2772	0.2751	0.2739	0.27240
	±0.00045	±0.00045	±0.0012	±0.0010	±0.0010	±0.00090
Cor. $\bar{Q}$	0.3921	0.3478	0.2797	0.3915	0.2671	0.3611
Cor. c_o	0.2739	0.2739	0.2739	0.2739	0.2739	0.2739
Av. $\bar{Q}$	0.340 ± 0.044 grams ; 0.0058 moles					
Cor. c_o	0.2739 grams/5 cc. ; 0.9346 moles/l.					

3. Cylinder #3. c_o = 0.9346 M., t = 24 hours; A = 2.85 $cm.^2$

Run no.	1	2
$\bar{Q}$	0.2091	0.1889
c_o (1)	0.2733	0.2733
c_o (2)	0.27155 ± 0.00035	0.27155 ± 0.00035
Av. c_o	0.27240 ± 0.00090	0.27240 ± 0.00090
Cor. $\bar{Q}$	0.2102	0.1900
Cor. c_o	0.2739	0.2739
Av. $\bar{Q}$	0.200 ± 0.010 grams ; 0.0034 moles	
Cor. c_o	0.2739 grams/5 cc. ; 0.9346 moles/liter	

(2) Derived Tables of Data

Table 13

Total solute absorbed, for rectangular parallelopiped

c_o (moles/l)	$\bar{Q}$ (moles)	$\sqrt{k'}$	k' (cm²/sec.)
0.137	0.0017	2.256×10^{-3}	5.09×10^{-6}
0.274	0.00327	2.169	4.70
0.3726	0.00441	2.152	4.63
0.4742	0.00576	2.208	4.87
0.6977	0.008172	2.129	4.53
0.9346	0.0114	2.218	4.92

t = 86,400 sec. (24 hours)
A = 16.59 cm²

Table 14

Total solute absorbed, for rectangular parallelopiped

t (sec.)	$\bar{Q}$ (moles)	$\sqrt{t}$	$\sqrt{k'}$	k'
21,600	0.00525	147.0	2.042×10^{-3}	4.17×10^{-6}
43,800	0.00859	209.2	2.348	5.51
64,800	0.010	254.6	2.246	5.04
86,400	0.0114	293.9	2.218	4.92
129,600	0.014	359.9	2.224	4.95

c_o = 0.9346 moles/liter
A = 16.59 cm²

Av. k' for the 10 independent readings of Tables 13 and 14
$= (4.84 \pm 0.27) \times 10^{-6}$ cm²/sec. (4.8)

Av. $\sqrt{k'} = (2.199 \pm 0.061) \times 10^{-3}$ (2.20)

Table 15

Total solute absorbed, for cylinders

Diam. in cm.	Area in $cm.^2$	$\bar{Q}$ in moles	$\sqrt{k'}$	k'
1.90	2.85	0.0034	3.850×10^{-3}	14.8×10^{-6}
3.17	7.92	0.0058	2.363	5.59
4.72	17.52	0.020	3.684	13.6
Rect.	16.59	0.0114	2.218	4.92

$t = 86,400$ sec.
$c_o = 0.9346$ moles/liter

Table 16

Slice runs, rectangular parallelopiped, constant t (86,400 (sec.))

x (cm.)	c for c_0 = 0.137M	0.274	0.3726	0.4742	0.6977	0.9346
			Experimental			
0.32	0.100 M	0.173	0.261	0.3479	0.481	0.601
0.95	0.0424	0.089	0.11	0.135	0.185	0.283
1.59	0.014	0.032	0.0382	0.0431	0.071	0.114
2.22	0.0036	0.01	0.011	0.014	0.0228	0.044
2.86	0.0005	0.0027	0.0023	0.0040	0.0065	0.018
3.49	0.0000	0.0003	0.0003	0.001	0.001	0.006
4.44			0.00004	0.0005	0.0005	0.0026
6.35			0.00004	0.0003	0.0002	0.00089
8.89			0.00000	0.0000	0.0000	0.0004
			Theoretical*			
0.32	0.09949	0.1990	0.2706	0.3444	0.5066	0.6787
0.95	0.04094	0.08189	0.1114	0.1417	0.2084	0.2793
1.59	0.01127	0.02253	0.03063	0.03898	0.05735	0.07683
2.22	0.00208	0.00417	0.00566	0.00721	0.01060	0.01420
2.86	0.00025	0.00049	0.00067	0.00085	0.00126	0.00168
3.49	0.00001	0.00003	0.00004	0.00005	0.00007	0.00009
4.44	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
6.35	* Calculated from equation (111), using Probability					
8.89	Tables, and the value of k from Tables 13 and 14.					
	% Deviation of Experimental from Theoretical					
0.32	- 0.51	+13.	+ 3.7	- 1.0	+ 5.1	+ 1.2
0.95	- 3.7	- 8.0	0.0	+ 4.9	+11.	- 1.4
1.59	-27.	- 39.	- 25.	- 11.	- 25.	- 48.
2.22	- 71.	-150.	- 83.	-100.	- 120.	- 210.
2.86	-100.	- 440.	- 230.	-340.	- 400.	- 940.
3.49	+100.	-1000.	- 650.	-2000.	-1400.	-6700.
	Negative sign indicates Experimental > Theoretical					
	% Deviation of experimental c from mean, on check runs ‡					
0.32	± 0.33	± 2.52	± 0.69		± 0.61	± 0.32
0.95	3.27	8.36	3.33		3.95	1.66
1.59	6.32	1.33	2.50		4.12	0.0
2.22	9.10	24.2	9.10		4.29	1.16
2.86	33.3	41.2	0.0		3.71	23.7
3.49		100.	0.0		17.7	38.6
4.44			100.		23.1	23.1

‡ From Column 6, Tables 1 to 10.

Table 17

Slice runs, rectangular parallelopiped, constant c_o (0.9346 (M.))

x (cm.)	c for t = 21,600 sec.	43,800	64,800	86,400	129,600
			Experimental		
0.32	0.411 M.	0.521	0.578	0.601	0.618
0.95	0.0664	0.192	0.259	0.283	0.395
1.59	0.01	0.058	0.092	0.114	0.181
2.22	0.005	0.021	0.027	0.044	0.0787
2.86	0.0016	0.0086	0.0081	0.018	0.0333
3.49	0.0005	0.0039	0.00283	0.006	0.011
4.44	0.0004	0.0022	0.00125	0.0026	0.0033
6.35	0.0000	0.00081	0.00061	0.00089	0.00073
8.89		0.0003	0.0003	0.0004	0.0003
			Theoretical		
0.32	0.4524	0.5821	0.6412	0.6787	0.7244
0.95	0.03533	0.1350	0.2152	0.2793	0.3702
1.59	0.00047	0.01355	0.04168	0.07683	0.1455
2.22	0.00000	0.00056	0.00467	0.01420	0.04411
2.86		0.00000	0.00028	0.00168	0.01000
3.49			0.00000	0.00009	0.00168
4.44				0.00000	0.00009
		% Deviation of Experimental from Theoretical			
0.32	+ 9.1	+ 11.	+9.8	+1.2	+15.
0.95	- 88.	- 42.	- 21.	- 1.4	- 6.8
1.59	- 2000	- 310.	- 120.	- 48.	- 24.
2.22		-3400.	- 480.	- 210.	- 79.
2.86			- 2800.	- 940.	- 200.
3.49				-6700.	- 530.
4.44					- 3600.
		% Deviation of experimental c from mean, on check runs			
0.32	± 1.38		± 2.36	± 0.32	
0.95	2.19		2.44	1.66	
1.59	15.7		8.50	0.0	
2.22	50.0		12.1	1.16	
2.86	33.3		14.9	23.7	
3.49	71.5		2.86	38.6	
4.44	27.3		3.23	23.1	
6.35			29.0	31.8	
8.89			37.5	100.	

Calculations.

The weights given under Δw and $\bar{\varphi}$ in columns 2 and 3 of the first ten tables, represent the original weights measured, minus a slight correction for anode solution. It was found that the anode lost approximately 0.002 grams per hour. Under the conditions of the electro-analysis used, all of this apparently plated on the cathode in the absence of agar, and about one half plated out, if appreciable agar was present in the solution. The corrections used therefore were:

- 0.0011 grams per hour, with agar
- 0.0021 grams per hour, without agar.

Since the average analysis lasted about 30 minutes, these corrections in most cases were in the neighborhood of - 0.0005 and -0.0010 grams, respectively.

Since the boundary concentration was never quite the same for any two check runs, it was necessary to reduce the weights obtained, to the weights which would have been obtained had the concentration not changed. This was easily done, on the assumption that the concentration function (113) is valid for at least slight changes in concentration.

$$c = c_0 \left[1 - P \left(\frac{x}{2\sqrt{Dt}} \right) \right] \qquad (113)$$

Therefore, for constant x and t,

$$\frac{c}{c'} = \frac{c_o}{c_o'} \qquad (172)$$

But average $$c = \frac{\Delta w}{\Delta V} \qquad (173)$$

∴ For the same volume,

$$\frac{\Delta w}{\Delta w'} = \frac{c_o}{c_o'} \qquad (174)$$

or $$\Delta w' = \frac{c_o'}{c_o} \Delta w \qquad (175)$$

$\Delta w'$ so calculated is the "corrected Δw" of Tables 1 to 10 (columns 4 and 5).

The check corrected values of Δw were then averaged to give column 6, which includes mean deviations. Column 7 gives the same averages correct to one doubtful decimal place. Significant figures only were used to indicate reliability in subsequent calculations.

$\bar{Q}$ in each case was obtained by adding together all these Δw's (columns 2 to 5). $\bar{Q}$ in moles was obtained by dividing the average $\bar{Q}$ (in grams) by the molecular weight of nickel, 58.68 (column 9).

The original data for c_o was in terms of grams per 5 cc pipette sample. The volume of the pipette at 25° C. was found by calibration to be 4.994 ± 0.004 cc. By dividing by this figure, c_o in grams per cc was obtained (column 8). By further dividing by the milli-molar weight

of nickel (0.05868), c_o in moles per liter of solution (molarity) was obtained (column 9).

In each case, c was calculated by dividing Δ w by ΔV, to get grams per cc (column 8), and then by 0.05868, to get moles per liter (column 9). This is an average concentration for the entire slice. ΔV was obtained by

$$\Delta V = A \, \Delta x \tag{176}$$

$$A = 6.67 \times 2.49 \text{ cm.} = 16.59 \text{ cm.}^2$$

for rectangular parallelopiped.

The coefficient of diffusion (k') in tables 13, 14, and 15 was calculated from Hill's[33] quantity equation

$$\bar{Q} = 2 A c_o \sqrt{\frac{k' t}{\pi}} \tag{143}$$

$$\therefore \quad k' = 7.856 \times 10^5 \, \frac{\bar{Q}^2}{A^2 c_o^2 t} \, , \tag{177}$$

where c_o is in moles per liter and $\bar{Q}$ is in moles.

The theoretical c's in Tables 16 and 17 were calculated from equation (113) for the given c_o , x, and t, using Probability Tables.[42] The average value of k' from Tables 13 and 14, instead of the true k was used in these calculations, i.e.: ρs was assumed equal to unity.

Curves.

The $\bar{Q}$ - c_o data from Table 13 is plotted in Graph 1.

The $\bar{Q} - \sqrt{t}$ data from Table 14 is plotted in Graph 2.

The experimental c $-x$ data for constant time, from Table 16 is plotted in the family of black curves of Graph 3. The four red curves plotted on the same graph, indicate the variation of concentration of slice with boundary concentration, for the first four slices.

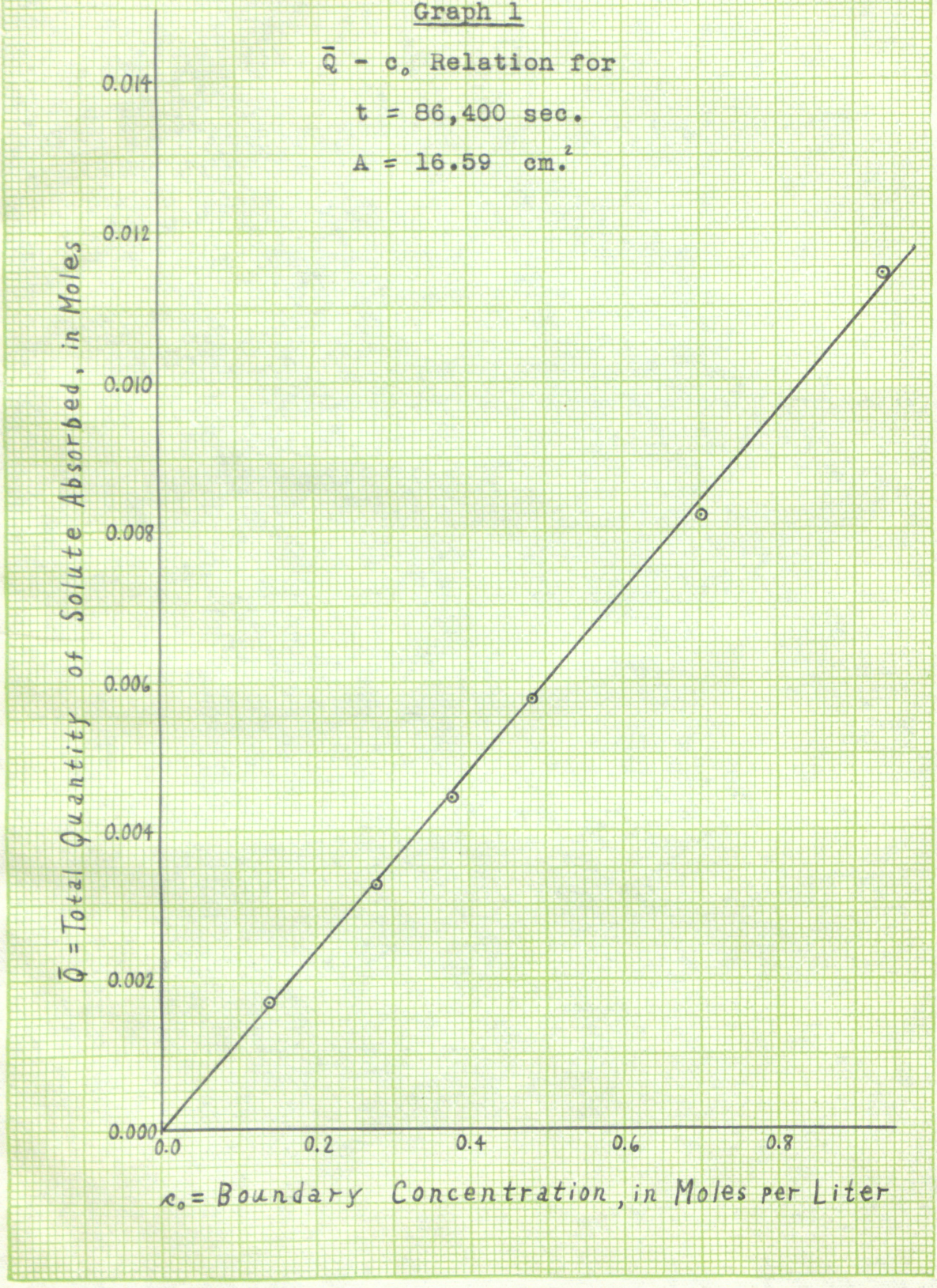
It did not seem profitable to plot the data of Tables 15 and 17.

Graph 1

$\bar{Q}$ - c_o Relation for

t = 86,400 sec.

A = 16.59 cm.^{2}

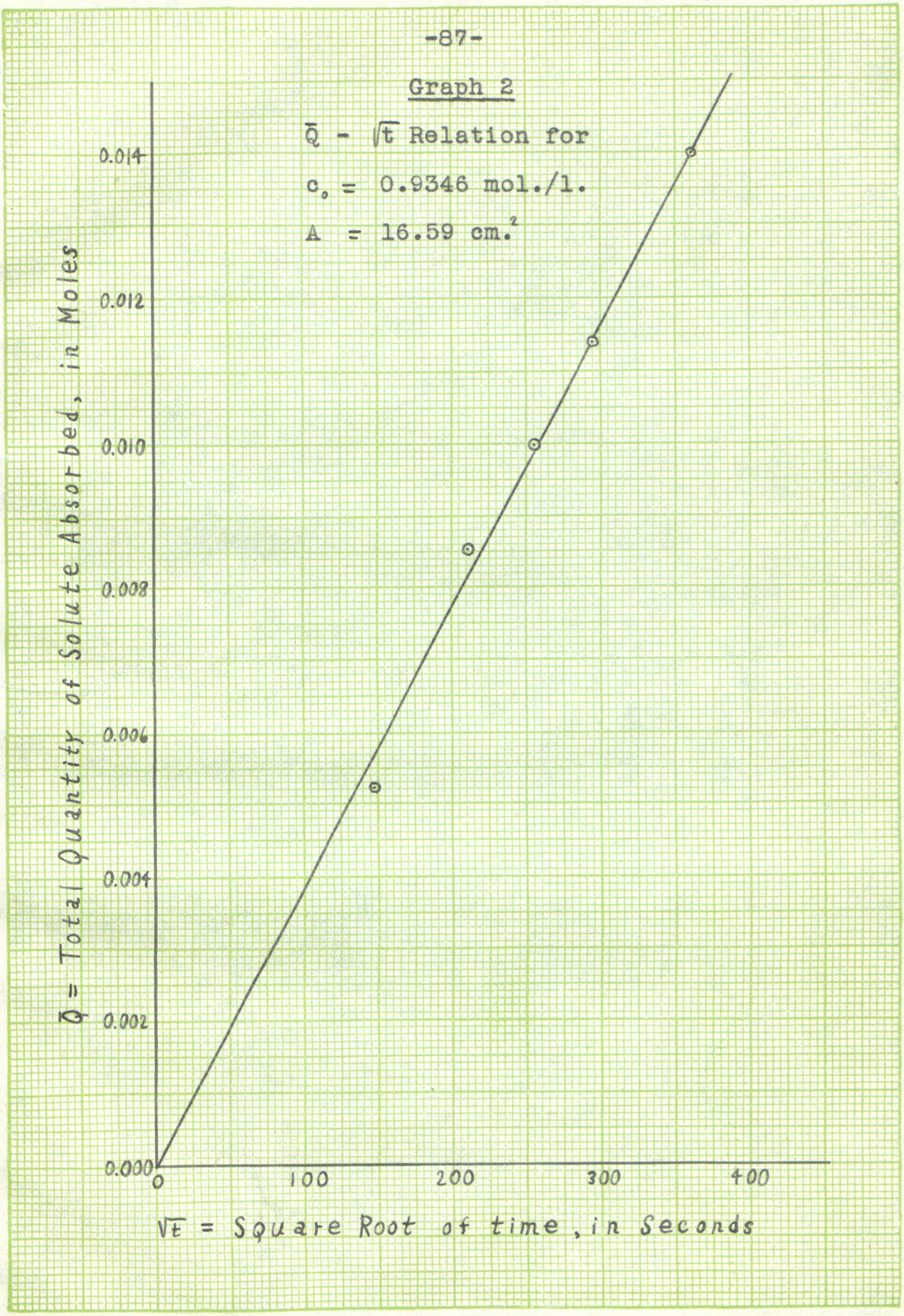


Graph 2

$\bar{Q}$ - $\sqrt{t}$ Relation for

c_o = 0.9346 mol./l.

A = 16.59 cm.^{2}



Graph 3

Concentration - depth curves

for constant time

t = 86,400 sec.

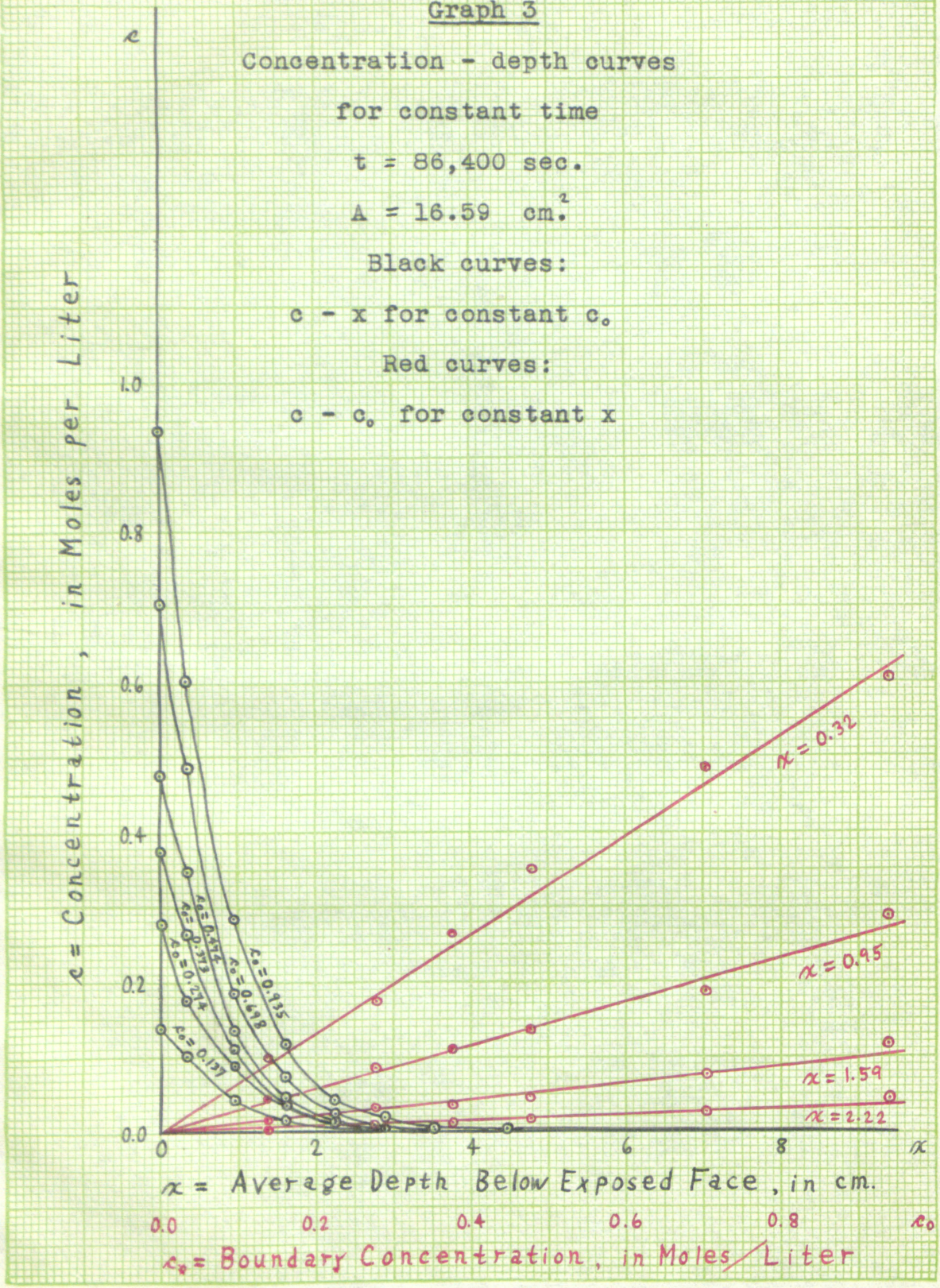
A = 16.59 cm.^{2}

Black curves:

c - x for constant c_o

Red curves:

c - c_o for constant x



x = Average Depth Below Exposed Face, in cm.

0.0 0.2 0.4 0.6 0.8 c_o

c_o = Boundary Concentration, in Moles/Liter

6. DISCUSSION

Results obtained.

The coefficient of diffusion for nickel sulfate in 1% agar gel has been determined, for 25.00°C. ± 0.02° and within the concentration range of 0.137 to 0.9346 molar, as

$$(4.84 \pm 0.27) \times 10^{-6} \ cm^2/sec.$$

This constant has been calculated on the basis of Hill's quantity function for the semi-infinite diffusion column, with the initial and boundary conditions:

$$\left.\begin{aligned} c &= 0 \quad , \ when \ t = 0 \\ c &= c_o \ , \ when \ x = 0, \end{aligned}\right\} \qquad (87)$$

namely:

$$\bar{Q} = 2 A c_o \sqrt{\frac{k' t}{\pi}} \ , \qquad (143)$$

and is therefore k' , not k, or K (See P. 51).

By plotting $\bar{Q}$ as a function of c_o , and of $\sqrt{t}$, linear curves were obtained for the case of diffusion into one exposed face of a rectangular parallelopiped of agar gel. (See Graphs 1 and 2). Excessive errors due to seepage prevented the drawing of any definite conclusions as regards similar relations for the cylinders.

The concentration-depth curves (Graph 3) plotted from the data of Table 16, agree in general form

at least, with the theoretical equation:

$$c = c_o \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{k't}}} e^{-\beta^2} d\beta \right] \qquad (111)$$

Approximately linear curves for c as a function of c_o for constant x and t were also obtained.

Errors.

Since the experimental errors in $\bar{Q}$, A, and c_o are squared in calculating k' (See equation (177)), it is more satisfactory to consider $\sqrt{k'}$, which from the data of Tables 13 and 14 is

$$(2.199 \pm 0.061) \times 10^{-3}.$$

This is roughly a 2.7% deviation and is consistent with the estimated errors in $\bar{Q}$, A, and c_o. The observed variations in $\bar{Q}$ for check runs, range from about 0.05% (Table 5) to about 3% (Table 9).

The % deviations in $\bar{Q}$ for the cylinders ranged from 5% (Cylinder #3) to 14% (Cylinder #1) (See Table 12). This excessive error is attributed to the unavoidable seepage which occurs when an all glass mold is used, especially when its perimeter is small as compared to its cross sectional area, as is the case with the cylinder.

This is sufficient, it is believed, to account for the lack of constancy of k' when computed for the cylinders using equation (143).

In Tables 16 and 17, the experimental concentrations (c) for various values of α, t, and c_o, are compared with the theoretical values calculated from equation (113) using Probability Tables[42], and the average value of k' from Tables 13 and 14. Except for the first and second slices in each case, the deviation between Experimental and Theoretical, is far in excess of that between check experimental runs. It is also perhaps significant that while the experimental value is usually slightly smaller than the theoretical for the first slice, it is invariably much larger than theoretical for dilute slices.

In an attempt to explain this discrepancy, the following possible factors of error have been studied:

(1) Experimental errors in determining c. The above considerations obviously rule this out, unless there is a systematic error in ΔV or in Δw, which seems unlikely. Similarly for errors in c_o and t.

(2) Experimental errors in slicing, the first slice being consistently cut too thin and all the subsequent slices being therefore less remote from the exposed face than expected. This could account for the

sign of the deviation between Experimental and Theoretical, but hardly for its magnitude.

(3) Errors due to error in k. It was found that the experimental error in k (taken as $k' = (4.84 \pm 0.27) \times 10^{-6}$) produced an error in c comparable to the deviation between Theoretical and Experimental for the first two slices, but that this factor was entirely inadequate to account for the deviations in the more dilute slices.

(4) Error due to using Hill's k' from equation (143) in equation (111), in place of the true k which is given by

$$k = \frac{k'}{\rho^2 s^2} \qquad (144)$$

We have not yet been able to obtain sufficient data on partial molal volumes of $NiSO_4$, to evaluate s. It is hoped that this may be done in the near future. However, if ρs is approximately unity, as has been assumed, then this error in identifying k' with k is also inadequate.

(5) Error due to the fact that the experimental concentrations are averages for slices of finite thickness, instead of true mathematical point concentrations. The magnitude of this error has not been examined.

(6) Systematic error due to seepage. This would have only a slight influence on the deviations of the first two slices where c is large, but it would become the

predominating factor for the slices of low concentration. Moreover it would be in accord with the sign of the deviation mentioned above.

(7) Fundamental theoretical errors in deriving equation (111). It does not seem probable, however, that equation (111) should be less valid than equation (143), which was derived from it without additional assumptions.

All things considered, therefore, it seems to the writer that factor (6) is undoubtedly the most important in accounting for the deviations between Experimental and Theoretical concentrations:

Conclusions drawn.

The linearity of the $\bar{Q}$-x_0 and $\bar{Q}$-$\sqrt{t}$ curves (Graphs 1 and 2), as well as the constancy of k' (Tables 13 and 14), indicate the validity of equation (143) within the limits of experimental error.

Within the range of concentrations studied, the coefficient of diffusion, k' , appears to be independent of concentration. If $s\rho \doteq 1$, as has been assumed, then the value we have determined for Hill's constant (k') is likewise approximately the value of k and K . If the retarding influence of the agar is slight, as is probable (but see p.10), then the coefficient we have determined for an agar medium must be of the same order of magnitude at

least, as the coefficient for diffusion in pure water. Our constant for $NiSO_4$ in agar agrees in order of magnitude with diffusion constants for other electrolytes, both in agar and in water, as given in the literature. (See Historical).

The $c - x$ curves (Graph 3) in general form agree with the theoretical concentration function (111). In the light of the facts considered under Errors, we may also conclude that the concentration data of Tables 16 and 17, within the limits of experimental error, is in agreement with equation (111).

Therefore, within the limits of experimental error, the theoretical treatment of solute diffusion as analogous to heat conduction, together with all the assumptions made in the derivations, appear justified.

Outside the limits of our experimental error, however, there are undoubtedly deviations from theory. Many of these have already been discussed at the end of the Mathematical section (p.58). The most important factors in our case, outside of the purely experimental one of seepage, are the following:

(1) Deviation of electrolytes from theory. It would be interesting to compare our k' with the K from the Nernst equation.[13] The two constants should agree (neglecting the ρs factor), if only we could ascertain

the correct values for c_o (activities, instead of apparent concentrations); or, working backwards, we might equate the constants and have a new method for calculating activities.

(2) Irreversible adsorption of $NiSO_4$ into the agar medium.

(3) Hydrolysis of $NiSO_4$ to produce the very slowly diffusing $Ni(OH)_2$.

In the light of our empirical method of derivation, and until the influence of these unknown factors has been elucidated, it would perhaps be safer to look upon our k' as an empirical constant, valid for the range of conditions considered, regardless of what may be the true nature of the diffusant or the true mechanism for diffusion.

7. SUMMARY.

(1) A complete mathematical treatment of the theory of solute diffusion has been presented, the fundamental assumption being that solute diffusion is formally analogous to heat conduction.

(2) Concentration and quantity functions, which agree with Hill's have been derived for the case of diffusion into a semi-infinite column, with the initial and boundary conditions:

$$\left.\begin{aligned} c &= 0 \quad , \; t = 0 \\ c &= c_0 \; , \; x = 0 \end{aligned}\right\} \tag{87}$$

(3) These equations have been tested experimentally for the case of diffusion of nickel sulfate into 1% agar gel at 25° C., within the concentration range: 0.137 to 0.9346 molar, and the time range: 6 hours to 36 hours.

(4) The diffusion coefficient for nickel sulfate in 1% agar gel at 25.00° C. ± 0.02° , and within the concentration range: 0.137 to 0.9346 molar, has been found to be:

$$(4.84 \pm 0.27) \times 10^{-6} \text{ cm}^2/\text{sec.}$$

8. ACKNOWLEDGMENT

The work described in this thesis is perhaps rather unique in that it has been carried out under two successive research directors.

To Dr. Robert C. Cantelo at whose suggestion this work was begun, the author wishes to express his gratitude. Without the intellectual encouragement which Dr. Cantelo always gave, and the confidence he inspired, it is doubtful whether so abstruse a study would ever have been hazarded.

When Dr. Cantelo left the University a year ago, Dr. Earl F. Farnau was kind enough to assume the responsibilities of research director. Without the keen interest which Dr. Farnau has taken and the sound advice he has given - both theoretical and experimental - this problem could never have reached its present form.

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