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Determination of Diffusivity
and
Solubility in Two Phase Systems

by

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Determination of Diffusivity and Solubility in Two Phase Systems*

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Recently in this laboratory, the problem arose of measuring the solubility and diffusivity of superheated steam in molten lithium nitrate. Since the restrictions imposed by this type of system preclude the use of the common methods of diffusivity determination, it was found necessary to develope and extend a simple technique, which, though not new (2), has not been widely used. As shown below this technique is applicable to a wide variety of two-phase systems.

In its barest essentials the method involves following the concentration of the diffusing component, hereafter called the sorbate, in response to a step change in that concentration in a system in which total volume and temperature are constant. Both solubility and diffusivity of the sorbate in the solvent, hereafter called the sorbent, are determined simultaneously in a single experiment.

The method is applicable to solid or liquid sorbent phases. While a liquid phase will, of course, always assume a planar configuration, a solid may approximate a plane, cylinder, or sphere. The sorbent phase must be stagnant, and both sorbate and sorbent phases must be of finite extent. The sorbate must be well stirred, and it may be gaseous or liquid. A particularly convenient well-stirred sorbate is a pure gas, the concentration of which may be followed by observing the total pressure. The following description will be confined to this particular case. However, the equations presented may easily be extended to other systems.

Consider a container of known and fixed volume, maintained at a constant temperature, and containing a fixed volume of the sorbent. Initially (Condition 1) let equilibrium obtain at p_1, sorbate phase partial pressure, and c_1 sorbate concentration in the sorbent phase. This condition may be arranged, for instance, by evacuating the chamber until both concentration values are sensibly zero. At the initial time admit gas to the chamber to a known pressure (Condition 2). This known pressure determines the amount of sorbate admitted. The gas will diffuse slowly into the sorbent until eventually the pressure remains constant with time, and the system is again at equilibrium (Condition 3). The pressure p_3 determines the amount of gas remaining in the gas space, and the amount of gas absorbed may be taken by difference. From these quantities, the solubility of the gas at the pressure p_3 is determined. The cycle may now be repeated, with p_3 from the last determination becoming p_1 for the next. Obviously, determinations may be made either by adding more gas at Condition 2, or by removing some of the gas then

present. Furthermore, from the time record of pressure decay (between Conditions 2 and 3) it is possible to calculate the diffusivity of the sorbate in the sorbent. The time record of pressure will be of one of the two forms shown in Figure 1.

The Solubility Problem

Material balances may be written for the terminal conditions, 1, 2, and 3, and for the transient period. At Condition 1, the number of moles of gas in the system is

$$n_1 = n_{1_\ell} + n_{1_g} \tag{1}$$

Assuming the perfect gas law applies,

$$pV = nR\theta \tag{2}$$

and assuming further that Henry's law governs the solubility relationship,

$$p = Kc \tag{3}$$

Neither of these assumptions is necessary for establishing the pertinent material balances. However, the simplifications are convenient and will be retained. Substituting Eqs. (2) and (3) into Eq. (1) gives

$$n_1 = P_1 [(V_\ell/K) + (V_g/R\theta)] \tag{4}$$

Condition 2 is established by a step pressure increase (or decrease) at zero time.

$$n_2 = n_{1_\ell} + n_{2_g} = P_1 V_\ell/K + P_2 V_g/R\theta \tag{5}$$

Condition 3 occurs at infinite time, when equilibrium is re-established.

$$n_3 = n_2 = P_3 [(V_\ell/K) + (V_g/R\theta)] \tag{6}$$

During the transient period equilibrium does not obtain. A material balance can be written by considering the average sorbate concentration in the sorbent,

$$\bar{c} = n_\ell / V_\ell \qquad (7)$$

At any time during the transient period (between Conditions 2 and 3)

$$n_2 = V_\ell \bar{c} + p(t) V_g / R\theta \qquad (8)$$

The progress of sorption may be followed by defining the mean increment of sorbate in the sorbent.

$$W(t) = \bar{c}(t) - c_1 \qquad (9)$$

The fractional completion of sorption is given by W/W_3, and from Eqs. (3, 5, 6, and 8),

$$1 - \frac{W(t)}{W_3} = \frac{c_3 - c(t)}{c_3 - c_1} , = \frac{p(t) - p_3}{p_2 - p_3} \qquad (10)$$

It is convenient to collect several terms and define

$$L = V_g K / V_\ell R\theta \qquad (11)$$

This constant may be identified in terms of experimental variables by rearrangement of Eqs. (5) and (6).

$$L = (p_3 - p_1) / (p_2 - p_3) \qquad (12)$$

The ratio L may be called the effective volume ratio. It measures the relative capacity of the sorbent and gas volumes for the sorbate. It is practical and in many cases desirable to make several successive runs with p_3 from the last run becoming p_1 for the next. At the completion of the ith successive run, the concentration of sorbate in the sorbent, $c_{3,i}$, is

$$c_{3,i} = c_{3,0} + \frac{\dot{V}_g}{V_\ell R\theta} \sum_i (p_2 - p_3)_i \qquad (13)$$

The Diffusion Problem

Since the sorbate phase is well stirred, molecular diffusion occurs only in the sorbent phase. For a planar sorbent, the diffusion equation is

$$\partial c/\partial t - D\partial^2 c/\partial x^2 = 0 \qquad \text{for } 0 < x < X$$
$$0 < t < \infty \qquad (14)$$

where x is the sorbent depth, zero at the bottom of the sorbent vessel (or at the sorbent midplane if both faces are exposed to sorbate), and X at the interface. The boundary condition which makes this particular problem an interesting one is that which describes the transport of sorbate as the flux j across the interface of area A.

$$-dn_\ell = dn_g = Aj\,dt = -AD(\partial c/\partial x)]_X\,dt = (V_g/R\theta)\,dp$$

$$dp/dt = -AR\theta D/V_g\,(\partial c/\partial x)]_X \qquad (15)$$

It is reasonable to assume equilibrium at the interface, so that from Eqs. (3) and (11)

$$\partial c/\partial t]_X = -(D/LX)(\partial c/\partial x)]_X \qquad 0 < t < \infty,\; x = X \qquad (16)$$

Other boundary conditions may be treated in a straightforward manner. At Condition 1 the concentration is uniform and equal to c_1.

$$c(x) = c_1 \qquad \text{at } t = 0, \qquad 0 < x < X \qquad (17)$$

At Condition 3 the concentration is again uniform and equal to c_3

$$c(x) = c_3 \qquad \text{at } t = \infty, \qquad 0 < x < X \qquad (18)$$

Between Conditions 2 and 3, since there is no leakage of sorbate from the bottom of the sorbent vessel,

$$\partial c/\partial x = 0 \qquad 0 < t < \infty, \ x = 0 \qquad (19)$$

The diffusion equation and boundary conditions for the cases of cylindrical and spherical sorbent shape are completely analogous. The diffusion equation, with this particular set of boundary conditions, is mentioned only in passing in the standard references ($\underline{3}, \underline{4}$). Carman and Haul ($\underline{2}$) have collected the solutions previously available in the literature, and have presented closed-form approximations applicable to various stages of the sorption process. For constant D the general solutions are

$$(1 - W/W_3) = \sum_{n=1}^{\infty} Z_n \exp -q_n^2 T \qquad (20)$$

with

$$Z_n = \frac{2L(1 + L)}{1 + L + L^2 q_n^2} \qquad \text{(plane)} \qquad (21a)$$

$$Z_n = \frac{4L(1 + L)}{4(1 + L) + L^2 q_n^2} \qquad \text{(cylinder)} \qquad (21b)$$

$$Z_n = \frac{6L(1 + L)}{9(1 + L) + L^2 q_n^2} \qquad \text{(sphere)} \qquad (21c)$$

and T, a dimensionless time measure, defined by

$$T = Dt/X^2 \qquad (22)$$

The quantities q_n are successive positive roots of

$$\tan q + Lq = 0 \qquad \text{(plane)} \qquad (23a)$$

$$2J_1(q) + LqJ_o(q) = 0 \qquad \text{(cylinder)} \qquad (23b)$$

$$\tan q = 3q/(3 + Lq^2) \qquad \text{(sphere)} \qquad (23c)$$

A function, here denoted G, is denoted e erfc by Carslaw and Jaeger (3), who give tables of its value.

$$G(\xi) = e \ \text{erfc} \ (\xi) = \exp(\xi^2) \ \text{erfc} \ (\xi) \qquad (24)$$

The function erfc is the error function complement

$$\text{erfc} \ (\xi) = 1 - \text{erf} \ (\xi) \qquad (25)$$

$$\text{erf} \ (\xi) = (2/\sqrt{\pi}) \int_0^\xi \exp(-\zeta^2) \, d\zeta \qquad (26)$$

and in terms of this function the approximate solutions are

$$1 - W/W_3 = (1+L)G(\sqrt{T}/L) - L \qquad \text{(plane)} \qquad (27a)$$

$$1 - \frac{W}{W_3} = (1+L)\left[\frac{b_3}{b_3+b_4} G\left(\frac{2b_3\sqrt{T}}{L}\right) + \frac{b_4}{b_3+b_4} G\left(-\frac{2b_4\sqrt{T}}{L}\right)\right] - L \quad \text{(cylinder)} \qquad (27b)$$

$$1 - \frac{W}{W_3} = (1+L)\left[\frac{b_1}{b_1+b_2} G\left(\frac{3b_1\sqrt{T}}{L}\right) + \frac{b_2}{b_1+b_2} G\left(-\frac{3b_2\sqrt{T}}{L}\right)\right] - L \quad \text{(sphere)} \qquad (27c)$$

with

$$b_1 = (1/2) \ \sqrt{(3+4L)/3} \ + 1 \qquad (28)$$

$$b_2 = b_1 - 1 \qquad (29)$$

$$b_3 = (1/2) \ \sqrt{(1 + L)} \ + 1 \qquad (30)$$

$$b_4 = b_3 - 1 \qquad (31)$$

The general solution may be presented in another form. From Eqs. (10) and (20)

$$p-p_3 = p_2-p_3 \sum_{n=1}^{\infty} z_n \exp{-q_n^2} T \tag{32}$$

$$\int_o^{\infty} (p-p_3) \, dt = (p_2-p_3) \int_o^{\infty} \sum_{n=1}^{\infty} z_n \exp{-q_n^2} T \, dt \tag{33}$$

Under the proper conditions of convergence, here satisfied,

$$\int_o^{\infty} (p-p_3) \, dt = (p_2-p_3) \sum_{n=1}^{\infty} z_n \int_o^{\infty} \exp{-q_n^2} \frac{Dt}{x^2} \, dt \tag{34}$$

$$\frac{D}{x^2} \int_o^{\infty} (p-p_3) \, dt = (p_2-p_3) \sum_{n=1}^{\infty} \frac{z_n}{q_n^2} \tag{35}$$

Analysis of Experimental Results.

Starting from Eqs. (11), (12); (3), (13); and (20), (27); or (35) experimental data may be reduced and analyzed in several ways. The use of Eqs. (11), (12); (20), (27) has been discussed in detail for the case of a planar sorbent [1]. Carman and Haul [2] discuss the use of the same equations for planar, cylindrical, and spherical sorbents.

Solubility

The solubility of sorbate in sorbent, as measured by the Henry's law constant K may be obtained from the results of several successive runs, or from a single run. When the cumulative sorbent concentrations $c_{3,i}$ given by Eq. (13)

are plotted as ordinate vs. the equilibrium pressures $p_{3,i}$ as abscissa a straight line should be obtained, if the system does in fact obey Henry's law. From Eq. (3) the inverse of the slope of this line is the Henry's law constant. Since with this procedure data from several runs are utilized, the value obtained for K may be denoted K_o, the overall value.

If it is known or may reasonably be assumed that

$$c_{3,0} \equiv c_{1,1} = 0 \qquad (36)$$

$$p_{3,0} \equiv p_{1,1} = 0 \qquad (37)$$

the plot described above will extrapolate to the origin. Successive values of the cumulative sorbent concentration give directly a value for K.

$$K_c = \frac{p_{3,i}}{c_i} = \frac{V_\ell R\theta}{V_g} \frac{p_{3,i}}{\sum_i (p_2 - p_3)_i} \qquad (38)$$

Values of K obtained by this method are equivalent to the inverse of chord slopes in the plot described above, so that K is denoted K_c.

Incremental values of K may be calculated, regardless of whether successive runs are made, by

$$K_i = \frac{\Delta p_{3,i}}{\Delta c_i} = \frac{V_\ell R\theta}{V_g} \frac{(p_{3,i} - p_{3,i-1})}{(p_2 - p_3)_i} \qquad (39)$$

Since

$$p_{3,i-1} \equiv p_{1,i} \qquad (40)$$

This method is identical to the use of Eqs. (11) and (12).

$$K_i = \frac{V_\ell R\theta L}{V_g} \qquad (41)$$

The relationships among the various calculation methods are shown graphically in Figure 2. The nature of the physical system is such that values of K_i are negatively correlated. That is, if a low value of K_i is obtained, K_{i+1} will be high. Thus experimental values of K_c and K_o will exhibit a smaller variance than values of K_i. On the other hand a value of K_i may be obtained from one run, whereas a series of runs as needed to determine K_c and K_o.

Diffusivity

When K (and hence L) is determined, the diffusivity may be calculated using Eqs. (20) and (27). Three steps are required.

1. Construct a plot of $(1 - W/W_3)$ vs. T, using the appropriate form of Eq. (20). At high values of $(1 - W/W_3)$ i.e. at low values of T the series require several terms for convergence. It is in this region that the approximations given by Eq. (27) are useful. One such plot must be constructed for each value of L. Figure 3 shows, for the plane, several plots of this type.

2. From the experimental data, calculate using Eq. (10) the values observed for $(1 - W/W_3)$ at various times, t. From the plot (Figure 3) obtain corresponding values of T.

3. As shown by Eq. (22) a plot of T vs. t should be linear and extrapolate to zero. The slope of this plot gives the diffusivity.

In the case of the plane sorbent shape, two simplifications of this general calculation method may be used.

The series Eq. (20) for the plane shows more rapid convergence than do the series for the cylinder and sphere. Thus over a considerable portion

of the experimental range, the series may be represented by one term. Using Eq. (10)

$$p - p_3 \cong Z_1(p_2-p_3) \exp -q_1^2 T \tag{42}$$

$$\log (p-p_3) \cong \log (Z_1 [p_2-p_3]) - q_1^2 T/2.303 \tag{43}$$

A semilogarithmic plot of $(p-p_3)$ vs. t should be linear, with intercept $[\log Z_1(p_2-p_3)]$ and slope $[-q_1^2 D/2.303 X^2]$. The slope of this plot gives the diffusivity.

Furthermore, rearrangement of Eq. (27a), using Eqs. (10) and (12) gives

$$F(p) \equiv (p - p_1)/(p_2 - p_1) = G(\sqrt{T}/L) \tag{44}$$

For experimentally observed values of $F(p)$, each at a given time t, obtain corresponding values of T/L^2 from a graph of $G(\xi)$ vs. (ξ). A plot of these values of T/L^2 vs. the corresponding values of t should be linear with zero intercept. The slope of this plot gives the diffusivity.

One convenient method of obtaining the time record of pressure required for diffusivity determinations is by use of a suitable pressure transducer and high-speed recorder. Instruments are available which will, with reasonable accuracy, give not only the pressure record, but also its integral. If the integral

$$I \equiv \int_0^\infty (p-p_3) \, dt \tag{45}$$

can be measured, the diffusivity can be obtained from Eq. (35) as

$$D = \frac{X^2 (p_2-p_3)}{I} \sum_{n=1}^\infty \frac{z_n}{q_n^2} \tag{46}$$

The particular convenience of this method is that the series converges quite rapidly, three terms being sufficient even at low values of L. Values of this series for the plane are shown in Figure 4.

Accuracy of the Experimental Method

If an experimental result z is calculated from independently measured quantities x, y, and if the errors in measurement of x, y are independent then the variances of x, y are additive so that the accuracy of z will be given by

$$\delta z = \sqrt{\left(\frac{\partial z}{\partial x}\right)^2 \delta x^2 + \left(\frac{\partial z}{\partial y}\right)^2 \delta y^2} \tag{47}$$

The accuracy of the measured quantities δx, δy is usually not well defined by the manufacturers of measuring instruments. If, for instance, δx, δy represent the standard deviations of x, y, then δz will be the standard deviation of the result z. Regardless, however, of the precise definition of δx, δy, it is usually possible for the experimenter to assign a useful value. If, then, the functional relationship between x, y, and z is known, δz may be predicted. The value predicted for δz, using Eq. (47) will be termed the standard error of z. The application of Eq. (47) to the standard error of the slope of a line is discussed in Appendix I. The results of this discussion are used below.

Solubility

The overall Henry's law constant K_o is the inverse of a slope b which may be obtained by the method of least squares. In order to obtain an approximate expression for the standard error of K_o, several simplifying definitions

and assumptions may be made.

Define

$$y_i \equiv c_{3,i} = \frac{V_g}{V_\ell R\theta} \sum_i (p_2 - p_3)_i \tag{48}$$

$$x_i \equiv p_{3,i} \tag{49}$$

Assume

$$\delta V_g \cong \delta V_\ell \cong \delta\theta \cong \delta R = 0 \tag{50}$$

$$\delta p_{2,i} \cong \delta p_{3,i} \equiv \delta p \tag{51}$$

$$\delta x_i \equiv 0 \tag{52}$$

$$y_i = b\, x_i \tag{53}$$

$$\Delta x_i \equiv \Delta x \tag{54}$$

$$(p_2 - p_3)_i \equiv \Delta p \tag{55}$$

so that

$$\frac{\delta y}{y}\Bigg]_i = \frac{\sqrt{2i\,\delta p^2}}{\displaystyle\sum_i (p_2 - p_3)_i} \cong \frac{\delta p}{\Delta p} \sqrt{\frac{2}{i}} \tag{56}$$

then from Eq. (A27)

$$\frac{\delta b}{b} \cong \frac{\sqrt{2}\,\delta p}{\Delta p} \; \frac{\sqrt{\displaystyle\sum i^3 - 2\bar{i}\sum i^2 + \bar{i}^2 \sum i}}{\displaystyle\sum i^2} \tag{57}$$

where the summations are taken from i = 0 to the final number of successive

runs.

$$\frac{\delta K_o}{K_o} = \frac{\delta b}{b} \geqslant \frac{\sqrt{2}\,(1+L)\,\delta p}{(P_2-P_1)} \cdot \frac{\sqrt{\sum i^3 - 2\bar{i}\sum i^2 + \bar{i}^2 \sum i}}{\sum i^2} \tag{58}$$

The assumptions made in obtaining this result are that

(1) Errors in all measurements except pressure (concentration) are negligible (Eq. 50).

(2) All pressure errors are of equal magnitude. Values of x_i are considered to be known without error (Eqs. 51, 52).

(3) Values of x_i, y_i are equally spaced. (Eqs. 54, 55).

(4) The data, when plotted, do not deviate from a line through the origin (Eq. 53).

These assumptions allow reduction of more general expressions to a standard error ratio which is a function only of the number of observations, i. This ratio is shown in Figure 5.

The incremental value of the Henry's law constant K_i is calculated from Eq. (41). Again making the first two assumptions above, Eq. (47) gives

$$\delta L = \sqrt{\left(\frac{-1}{P_2-P_3}\right)^2 \delta p_1^2 + \left(\frac{-L}{P_2-P_3}\right)^2 \delta p_2^2 + \left(\frac{L+1}{P_2-P_3}\right)^2 \delta p_3^2} \tag{59}$$

$$\delta L \cong \sqrt{2(L^2 + L + 1)}\quad [(\delta p/(P_2-P_3))] \tag{60}$$

$$\frac{\delta K_i}{K_i} \bigg/ \frac{\delta p}{P_2-P_1} = \frac{\delta L}{L} \bigg/ \frac{\delta p}{P_2-P_1} \equiv E_i \cong \sqrt{\frac{2(L^4 + 3L^3 + 4L^2 + 3L + 1)}{L^2}} \tag{61}$$

The value of the function E_i is shown in Figure 6.

The value of the effective volume ratio may be set by the design of the experimental apparatus. Values of 0.1 to 10 are practical; the range $0.4 < L < 2.5$ is particularly desirable because of the plateau in E_i in this range.

While the standard error of K_i is a minimum at $L = 1$, that of K_o decreases with L, as shown by Eq. (58). The standard error of the mean $\overline{K}_i$ of several determinations of K_i decreases as the square root of the number of determinations. The ratio of these standard errors is shown in Figure 7.

Diffusivity

When the diffusivity is calculated from Eq. (20, 27) as described above, it is obtained from the slope b of a line. In order to obtain a useful form of the results of Appendix I, restrictive assumptions may be made:

(1) Errors in all measurements except pressure (concentration) are negligible.

(2) The logarithmic standard error of T is constant.

$$\delta T_i \cong k\, T_i \tag{62}$$

Values of t_i are known without error.

(3) The data, when plotted, do not deviate from a line through the origin.

With these assumptions, from Eq. (A 17)

$$\frac{\delta D}{D} \cong \frac{\delta b}{b} = k\, \frac{\sqrt{\sum (t_i - \overline{t})^2 t_i^2}}{\sum t^2} \tag{63}$$

It is not reasonable to assume, as in the case of K_o, that individual values of t_i are equally spaced. However once a spacing is selected, Eq. (63) need be evaluated only once as it is a function only of the independent variable t. In a series of runs made in this laboratory, t_i were selected from 1 to 2000 or more seconds in intervals of 1 sec. up to t = 10, 10 sec. to t = 100, 50 sec. to t = 300, 100 sec. to t = 1000, and 250 sec. thereafter. This choice was made arbitrarily to provide fairly equal pressure decrements for each time interval. The standard error ratio for this choice of t_i is shown in Figure 8.

For calculation of the standard error in T, T may be regarded as a function of $S \equiv (1-W/W_3)$ and of L, given implicitly by Eq. (20). Straight-forward but algebraically complicated calculation yields expressions for the derivatives $\partial T/\partial S$ and $\partial T/\partial L$. These expressions are themselves series which are much too cumbersome for repeated application. Since all that is needed is an approximate expression, reference may be made to Figure 3. This figure shows that plots of T vs. S are similar in shape throughout a large range of L, and that the effect of L is to shift the plot on the T axis. From Figure 3 it is apparent that over a fairly large range of S,

$$\delta \ln T = \frac{\delta T}{T} \cong 12 \, \delta S \tag{64}$$

The standard error of S may be obtained from an equation analogous to Eq. (60). At the optimum value of L = 1,

$$\delta S = \sqrt{8(1 - S + S^2)} \; \delta p/(p_2 - p_1) \tag{65}$$

Over the same range of S in which Eq. (64) is valid, Eq. (65) becomes

$$\delta S \cong 2.6 \, \delta p/(p_2 - p_1) \tag{66}$$

so that from Eq. (62, 64, 66)

$$k \equiv \delta T_i / T_i \cong 12 \, \delta S \geqslant 30 \, \delta p / (p_2 - p_1) \tag{67}$$

If the diffusivity is calculated instead from Eq. (46), it may be assumed that all errors are negligible compared with that in the continuously recorded pressure, so that

$$\frac{\delta D}{D} \cong \frac{\delta I}{I} \tag{68}$$

From Eq. (45)

$$\frac{\partial}{\partial p} (I) = \frac{\partial}{\partial p} \int_0^\infty (p - p_3) \, dt = \int_0^\infty dt \tag{69}$$

As a practical matter, the integral I has zero value after a time of the order of x^2/D, so that the integral, Eq. (69) need not have a value of infinity.

$$\delta I = \left(\frac{\partial I}{\partial p} \right) \delta p \cong \frac{x^2}{D} \, \delta p \tag{70}$$

then, from rearrangement of Eq. (46), using Eq (12, 70)

$$\frac{\delta D}{D} \cong \frac{\delta p}{p_2 - p_3} \cdot \frac{1}{\sum \frac{Z n}{q n^2}} = \frac{\delta p}{p_2 - p_1} \cdot \frac{1 + L}{\sum \frac{Z n}{q n^2}} \tag{71}$$

The value of the standard error of the slope (Eq. 63, Figure 8) is roughly 0.5, so that from Eq. (67), for calculation of D by Eqs. (20) and (27)

$$\frac{\delta D}{D} \geqslant 15 \, \frac{\delta p}{p_2 - p_1} \tag{72}$$

The value of the function $(1 + L) / \sum Z n / q n^2$ (Eq. 71)

is roughly 10 to 25, so that the standard error of D calculated by the integral

method (Eq. 46) is the same as that of D calculated by the slope method.

Conclusions

The experimental method described here offers the following advantages:

1. applicability to several types of experimental systems,

2. simultaneous measurement of two parameters,

3. simplicity of construction and execution,

4. rapid determinations.

The method suffers from the common fault of many transient response

techniques in that it is of only modest precision. Nevertheless determinations

of both diffusivity and solubility may be made to an accuracy better than that

which is required for many engineering design calculations.

Nomenclature

Symbol	Meaning, Consistent Units
b	slope of least square line
b_1, b_2, b_3, b_4	defined constants, Eq. (27-30), dimensionless
c	concentration of sorbate in sorbent, mole/liter
D	diffusivity, $cm^2/sec.$
E	defined standard error ratio, Eq. (49), dimensionless
F	defined pressure function, Eq. (34), dimensionless
G	defined function, Eq. (23)
I	defined pressure integral, (Eq. (45) mm Hg sec
j	flux of matter, $mole/cm^2$ second
J_i	Bessel function of i order
k	logarithmic standard error of T, dimensionless
K	Henry's law constant, mm Hg. liter/mole
L	effective volume ratio, dimensionless
n	number of moles
p	pressure, mm Hg.
q	roots of Eq. (22)
R	gas law constant, 62.361 mm Hg. liter/g. mole $^\circ K$
S	defined fraction of completion of sorption, Eq. (10), dimensionless
t	time, seconds
T	dimensionless time measure

V	volume, cm^3
W	concentration increment, mole/liter
x	linear dimension, cm.
X	Depth of planar sorbent, radius of spherical or cylindrical sorbent, cm.
Z	defined constant, Eq. (20), dimensionless
θ	temperature, $^{\circ}K$
$=$	equality
$\cong$	approximate equality
$\equiv$	identity or definition
$\sum$	summation
$>$	greater than
$<$	less than
∂	partial differential operator
d	total differential operator
δ	standard error
exp	exponential function
log	logarithm, base 10
ln	logarithm, base e
s	estimated standard deviation
s^2	estimated variance
tan	tangent

Subscripts

    1, 2, 3   conditions 1, 2, 3 as described in text

g gas or sorbate

i i^{th} successive run

ℓ liquid or sorbent

Superscripts

- average value

$\wedge$ least square estimate of parameter

Literature Cited

1. Camp, F.W., Ph. D. Dissertation, Princeton University, 1962

2. Carman, P.C., and Haul, R.A.W., Pro. Roy. Soc. (London) <u>222A</u> 109 (1954)

3. Carslaw, H.S., and Jaeger, J.C., "Conduction of Heat in Solids, "Oxford, London, 1947

4. Crank, J., "The Mathematics of Diffusion, "Oxford, London, 1956

Acknowledgment

Table 1

Values of q_n for use in Equation 20

L	plane				cylinder				sphere			
	q_1	q_2	q_3	q_4	q_1	q_2	q_3	q_4	q_1	q_2	q_3	q_4
∞	1.571	4.712	7.854	10.995	2.405	5.520	8.654	11.810	3.142	6.283	9.425	12.556
10	1.632	4.736	7.866	11.004	2.485	5.555	8.677	11.814	3.232	6.330	9.456	12.590
6	1.671	4.748	7.875	11.011	2.533	5.579	8.691	11.820	3.286	6.361	9.477	12.606
4	1.716	4.765	7.885	11.018	2.589	5.608	8.710	11.833	3.349	6.388	9.503	12.626
3	1.759	4.782	7.896		2.641	5.635	8.730	11.848	3.406	6.434	9.528	12.645
2	1.837	4.816	7.917	11.041	2.734	5.689	8.767	11.875	3.519	6.502	9.578	12.683
1.5	1.907	4.849	7.938		2.816	5.743	8.803	11.903	3.591	6.566	9.626	12.720
1	2.029	4.913	7.979	11.086	2.950	5.841	8.874	11.956	3.726	6.681	9.716	12.793
0.8	2.107	4.959	8.009	11.108	3.031	5.908	8.923	11.995	3.807	6.758	9.778	12.845
.6	2.216	5.032	8.058	11.144	3.139	6.012	9.002	12.058	3.908	6.865	9.874	12.926
.4	2.381	5.163	8.151	11.215	3.290	6.168	9.142	12.175	4.056	7.030	10.033	13.069
.2	2.645	5.454	8.392	11.409	3.511	6.463	9.440	12.453	4.235	7.295	10.330	13.369
.1	2.863	5.761	8.708	11.701	3.655	6.700	9.730	12.766	4.345	7.487	10.575	13.651
0.0	3.142	6.283	9.425	12.566	3.832	7.016	10.173	13.320	4.712	7.854	10.995	14.137

Appendix

Standard Error of the Slope of a Line

It is often the case that experimental data are graphed as a line and that the slope of the line is the desired result. One useful method of obtaining the slope is that of least squares. This method is by no means the only one available but it has the advantages that

a) it is well known and commonly accepted, and

b) computational formulae are well-known and well suited for desk computation.

From a group of data, (x_i, y_i) the slope is computed from

$$b = \sum{}' xy / \sum{}' x^2 \tag{A1}$$

with

$$\sum{}' xy \equiv \sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) \tag{A2}$$

$$\sum{}' x^2 \equiv \sum_{i=1}^{n} (x_i - \bar{x})^2 \tag{A3}$$

The variance of the least - square slope may be calculated from

$$s^2(b) = s^2(\hat{y}) / \sum{}' x^2 \tag{A5}$$

$$s^2(\hat{y}) = \frac{1}{n-2} \left(\sum{}' y^2 - b \sum{}' xy \right) \tag{A6}$$

This variance is a measure of the scatter of the data from the least - square line. It is not an uncommon experimental situation, however, to have successive values (x_i, y_i) highly correlated. Such a situation may arise, for instance, if these values are taken from a continuous recorder trace. In this case, Eq. (A5) may give a variance for the slope which approaches zero. But if the accuracy of measurement is not as good as the precision (which is improved by correlation) then this variance is not a useful measure of the accuracy of the slope.

An expression for the standard error of the slope of a line may be obtained by applying Eq. (47) to Eq. (A1). Assume that the values of x_i are known without error.

$$\delta b = \sqrt{\sum \left(\frac{\partial b}{\partial y_i} \right)^2 \delta y_i^2} \tag{A7}$$

$$\frac{\partial b}{\partial y_i} = \frac{(x_i - \bar{x})}{\sum' x^2} \tag{A8}$$

Several special cases are of interest.

Case 1: $\qquad \delta y_i \equiv \delta y$ $\hfill$ (A9)

$$\delta b = \sqrt{\frac{\sum (x_i - \bar{x})^2 \delta_y^2}{\sum' x^2}} = \frac{\delta y}{\sum' x^2} \sqrt{\sum' x^2} \tag{A10}$$

$$\frac{\delta b}{b} = \frac{\delta y}{\sum' xy} \sqrt{\sum' x^2} \tag{A11}$$

Case 2: $\qquad \delta y_i = kx_i$ $\qquad\qquad\qquad$ (A 12)

$$\delta b = \frac{k}{\sum' x^2} \sqrt{\sum (x_i - \bar{x})^2 x_i^2} \qquad\qquad \text{(A 13)}$$

$$= \frac{k}{\sum' x^2} \sqrt{\sum x_i^4 - 2\bar{x} \sum x_i^3 + \bar{x}^2 \sum x_i^2} \qquad \text{(A 14)}$$

Case 3: $\qquad \delta y_i = ky_i$ $\qquad\qquad\qquad$ (A 15)

$\qquad$ and $\quad y_i = bx_i$ $\qquad\qquad\qquad$ (A 16)

$\qquad\qquad\qquad\qquad\qquad\qquad$ (A 17)

$$\frac{\delta b}{b} = \frac{k}{\sum' x^2} \sqrt{\sum x_i^4 - 2\bar{x} \sum x_i^3 + \bar{x}^2 \sum x_i^2}$$

Case 4: $\qquad \delta y = ky_i/\sqrt{i}$ $\qquad\qquad\qquad$ (A 18)

$\qquad$ and $\quad y = bx_i$ $\qquad\qquad\qquad$ (A 19)

$$\frac{\delta b}{b} = \frac{k}{\sum' x^2} \sqrt{\sum (x_i - \bar{x})^2 \frac{x_i^2}{i}} \qquad\qquad \text{(A 20)}$$

$$= \frac{k}{\sum' x^2} \sqrt{\sum \frac{x_i^4}{i} - 2\bar{x} \sum \frac{x_i^3}{i} \sum \frac{x_i^2}{i}} \qquad \text{(A 21)}$$

Case 5:   If the x_i are equally spaced so that

$$x_i = i\Delta x \qquad \text{(A 22)}$$

then

$$\sum{}' x^2 = \Delta x^2 \sum{}' i^2 \qquad \text{(A 23)}$$

and

$$\sqrt{\sum x_i^4 - 2\bar{x} \sum i^3 + \bar{x}^2 \sum x_i^2} = \Delta x^2 \sqrt{\sum i^4 - 2\bar{i} \sum i^3 + \bar{i}^2 \sum i^2} \qquad \text{(A 24)}$$

Then Case 2 becomes

$$\delta b = \frac{k}{\sum{}' i^2} \sqrt{\sum i^4 - 2\bar{i} \sum i^3 + \bar{i}^2 \sum i^2} \qquad \text{(A 25)}$$

and Case 3 becomes

$$\frac{\delta b}{b} = \frac{k}{\sum{}' i^2} \sqrt{\sum i^4 - 2\bar{i} \sum i^3 + \bar{i}^2 \sum i^2} \qquad \text{(A 26)}$$

and Case 4 becomes

$$\frac{\delta b}{b} = \frac{k}{\sum{}' i^2} \sqrt{\sum i^3 - 2\bar{i} \sum i^2 + \bar{i}^2 \sum i} \qquad \text{(A 27)}$$
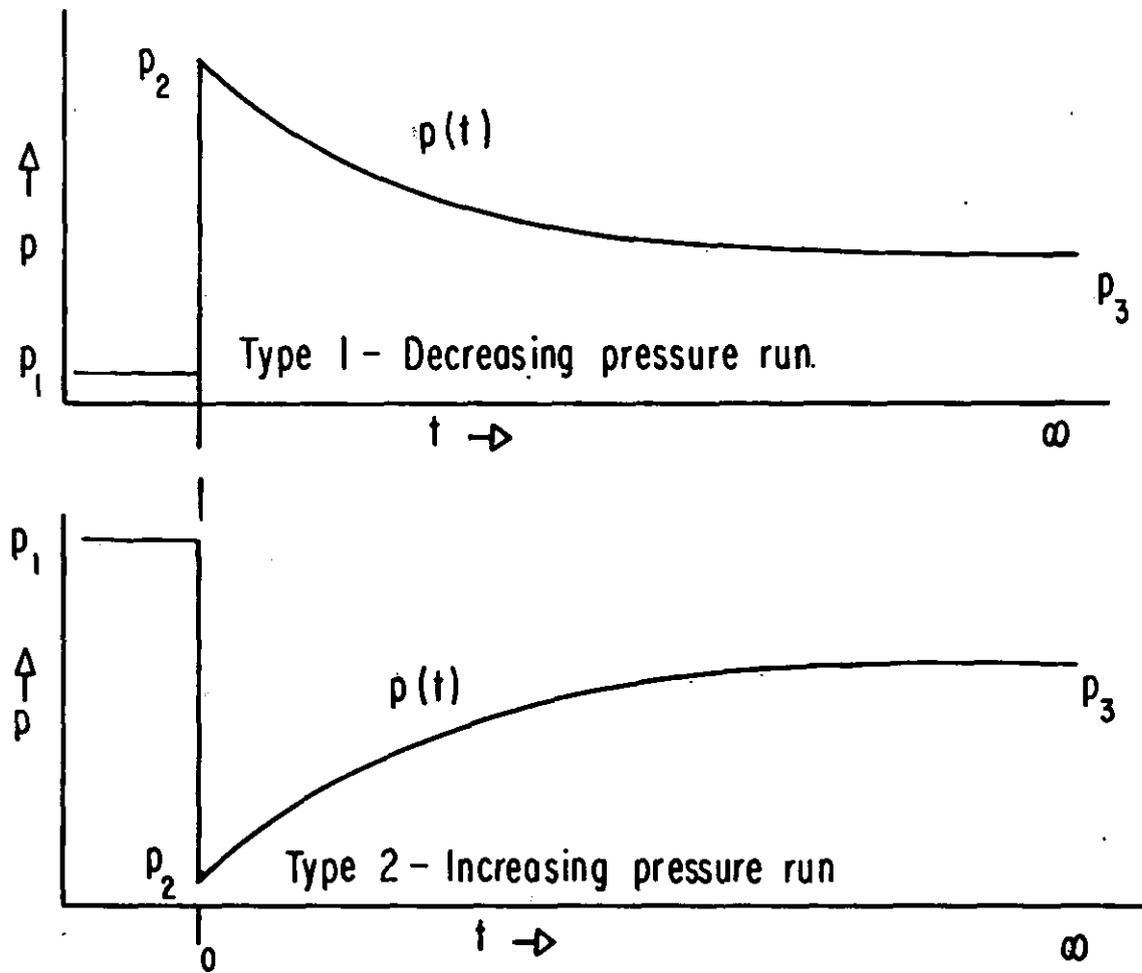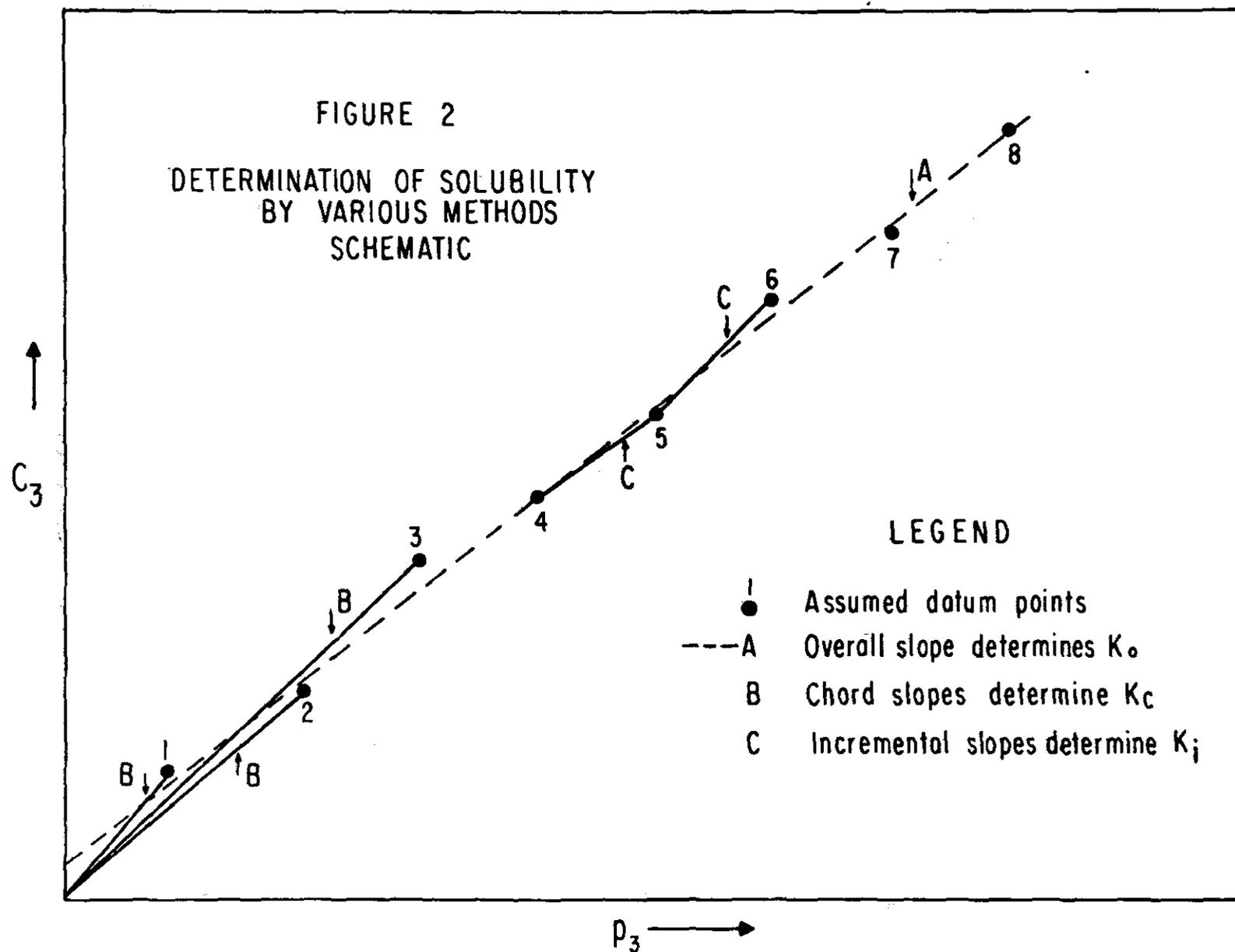
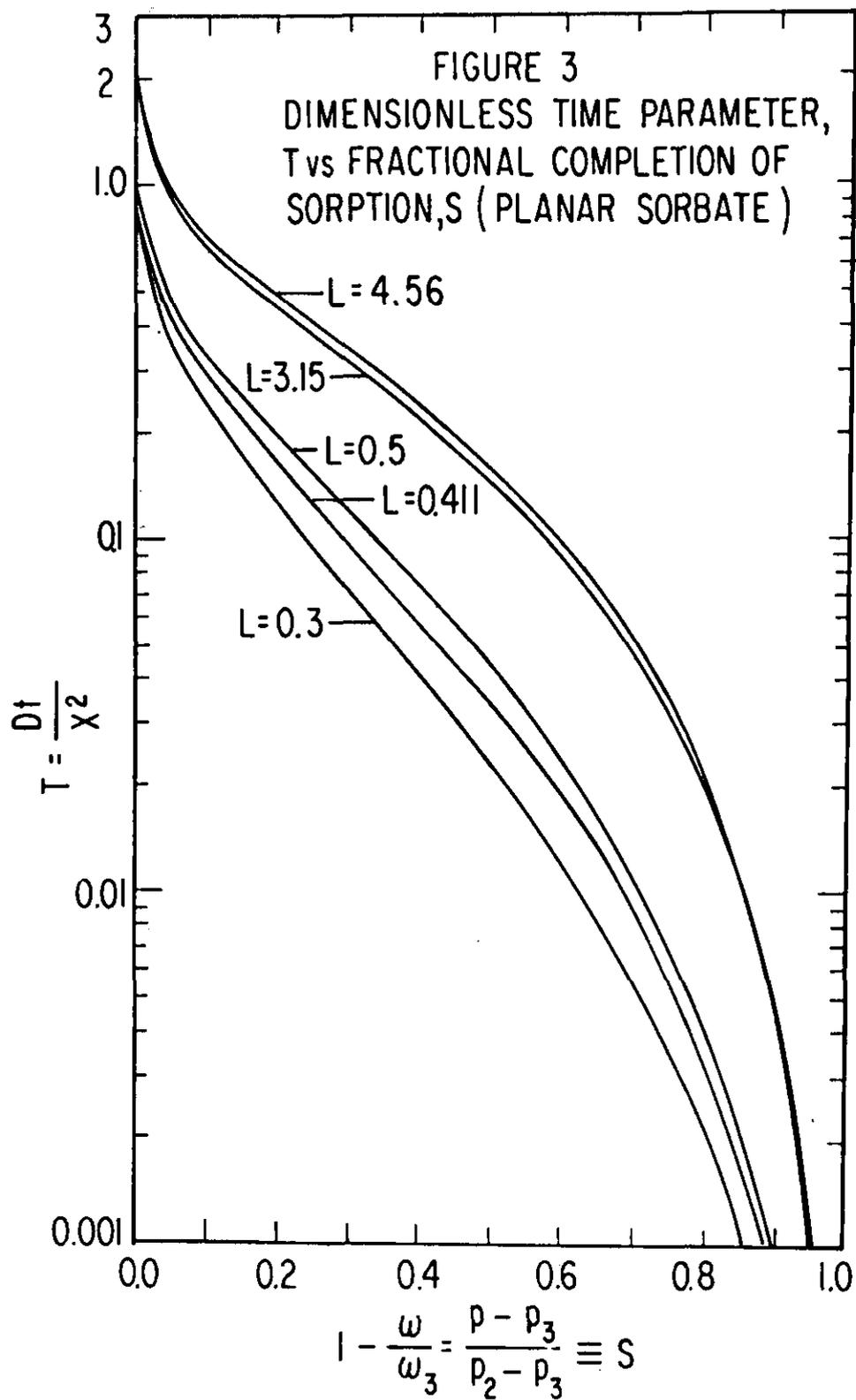FIGURE 1. SCHEMATIC FORM OF EXPERMENTAL PRESSURE RECORD

FIGURE 2

DETERMINATION OF SOLUBILITY
BY VARIOUS METHODS
SCHEMATIC

LEGEND

| | Assumed datum points
- - -A   Overall slope determines K_o
B   Chord slopes determine K_c
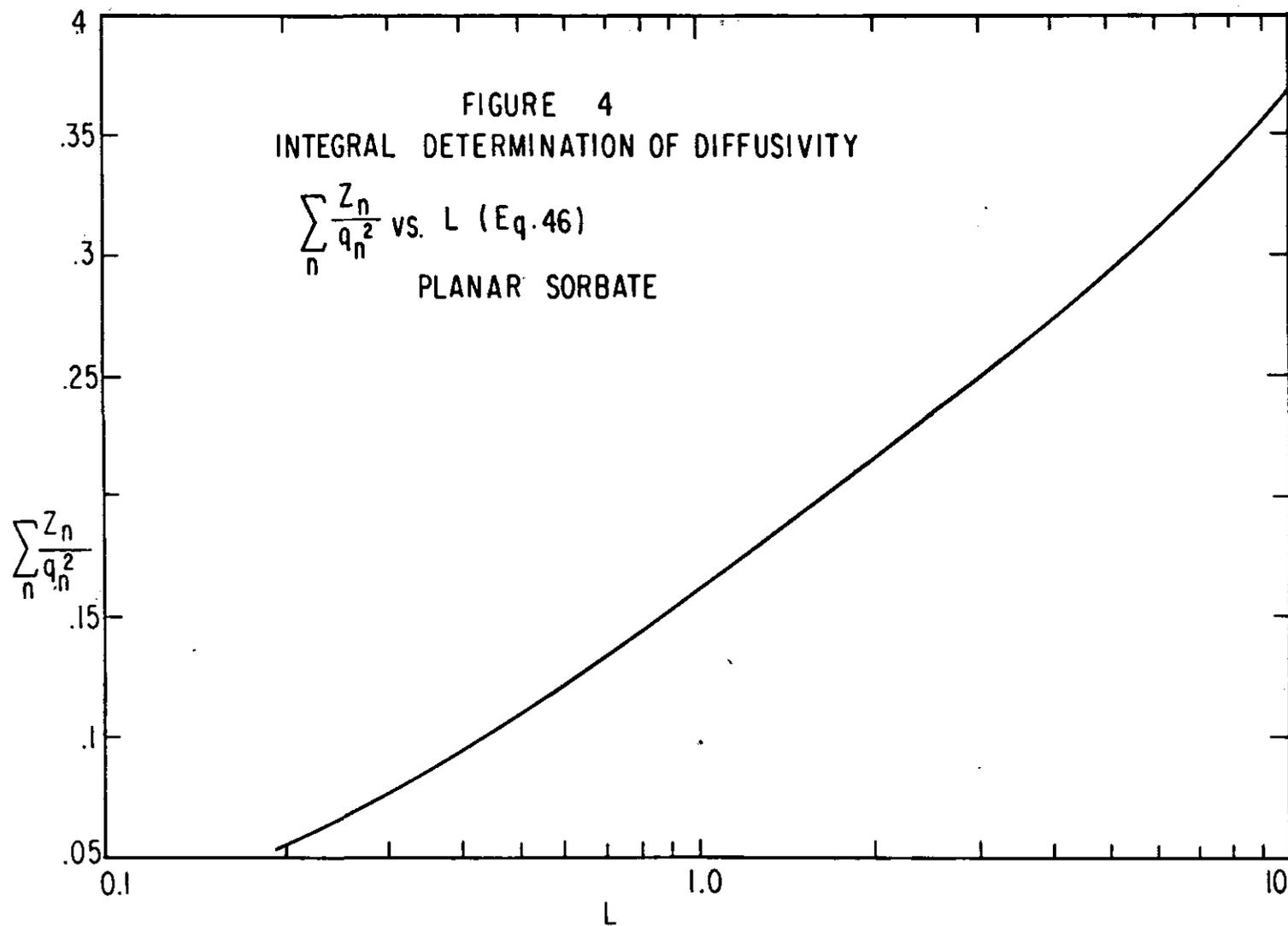C   Incremental slopes determine K_i

FIGURE 3
DIMENSIONLESS TIME PARAMETER,
T vs FRACTIONAL COMPLETION OF
SORPTION, S (PLANAR SORBATE)

FIGURE 4
INTEGRAL DETERMINATION OF DIFFUSIVITY

$$\sum_n \frac{Z_n}{q_n^2} \text{ vs. } L \text{ (Eq. 46)}$$
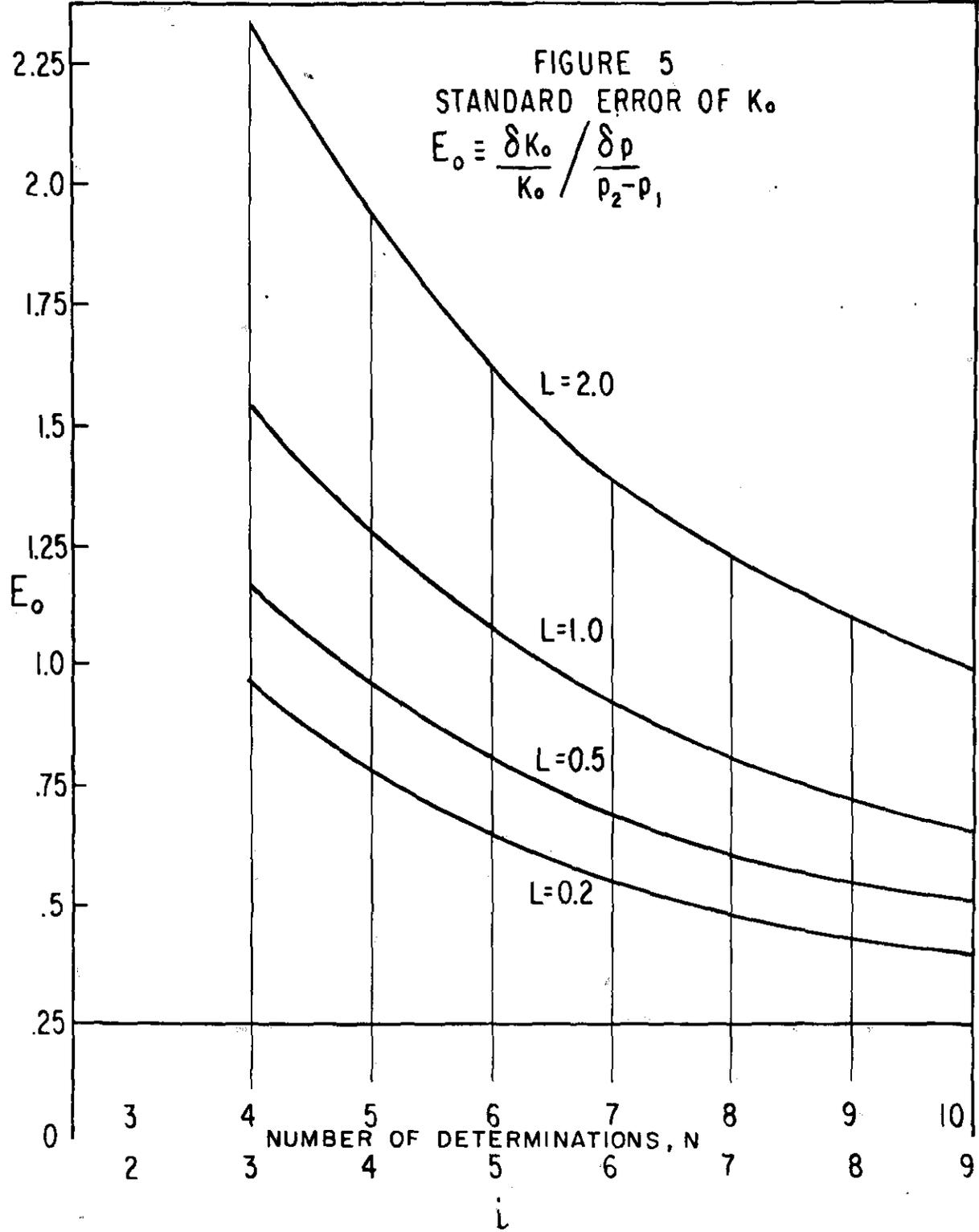
PLANAR SORBATE

FIGURE 5
STANDARD ERROR OF K_0

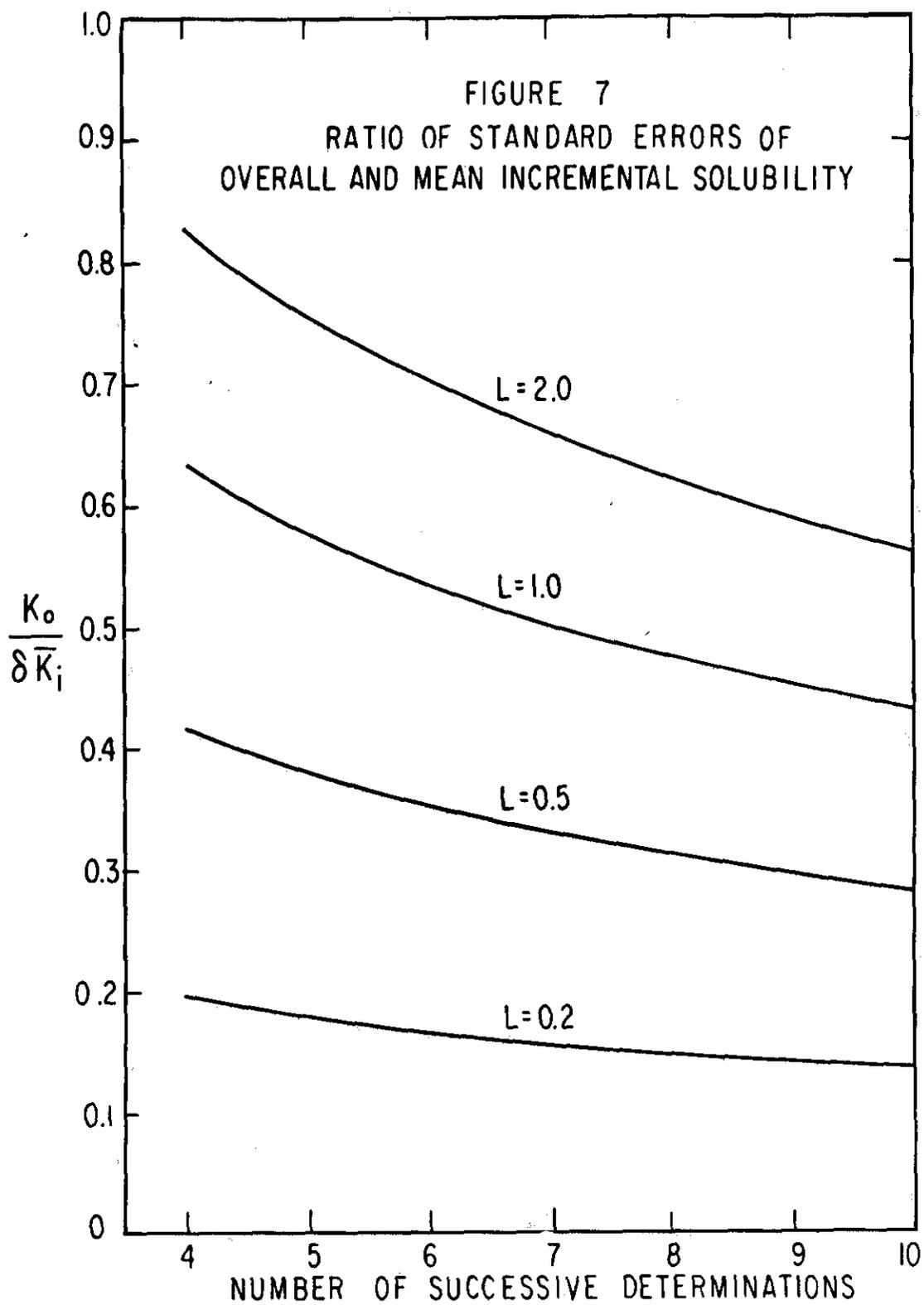$$E_o \equiv \frac{\delta K_o}{K_o} \Big/ \frac{\delta p}{p_2 - p_1}$$

$L = 2.0$

$L = 1.0$

$L = 0.5$

$L = 0.2$

E_o

NUMBER OF DETERMINATIONS, N

i

FIGURE 6
STANDARD ERROR OF K_i

$$E_i \equiv \frac{\delta K_i}{K_i} \bigg/ \frac{\delta p}{p_2 - p_1}$$
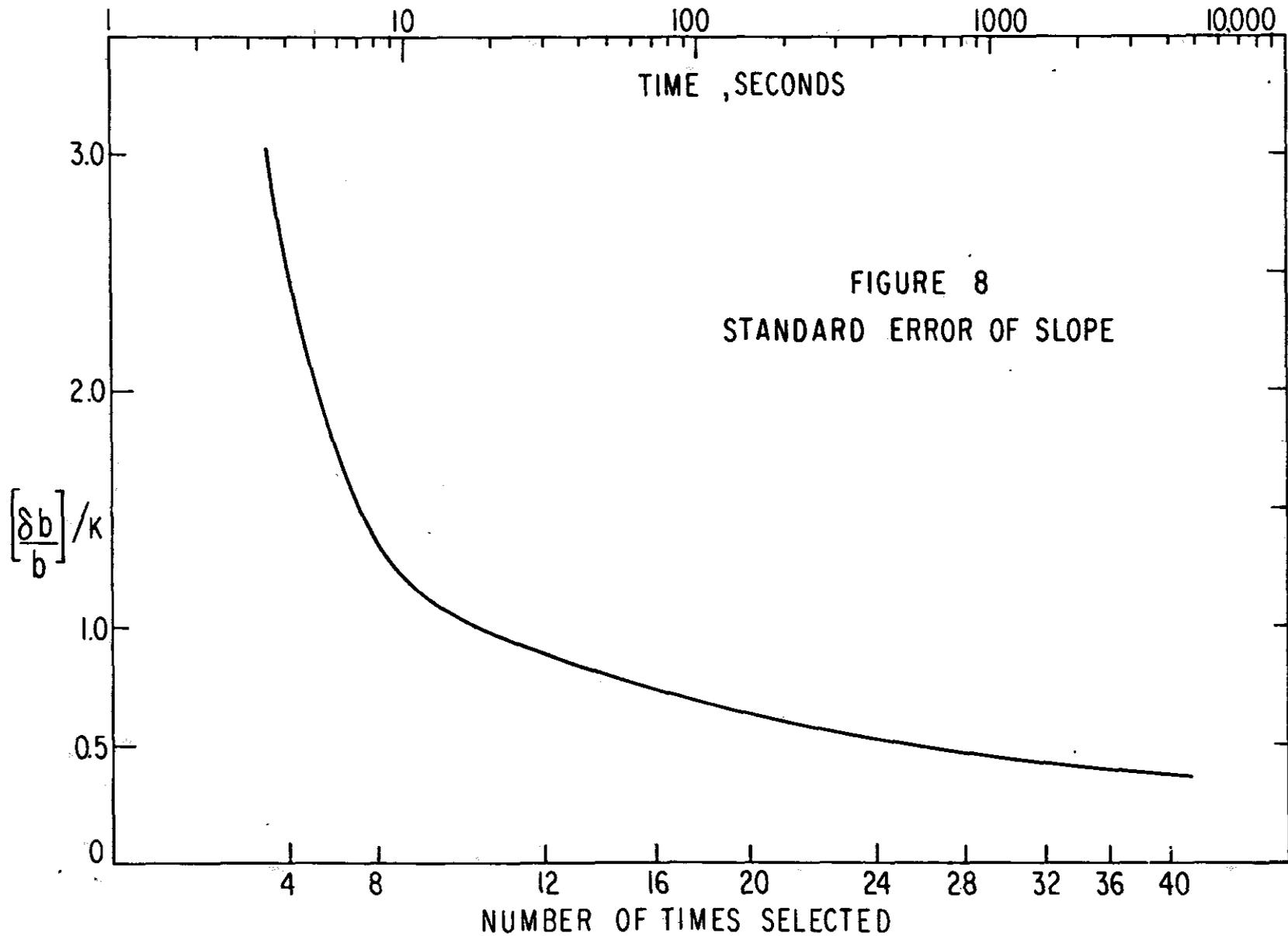
FIGURE 7
RATIO OF STANDARD ERRORS OF
OVERALL AND MEAN INCREMENTAL SOLUBILITY
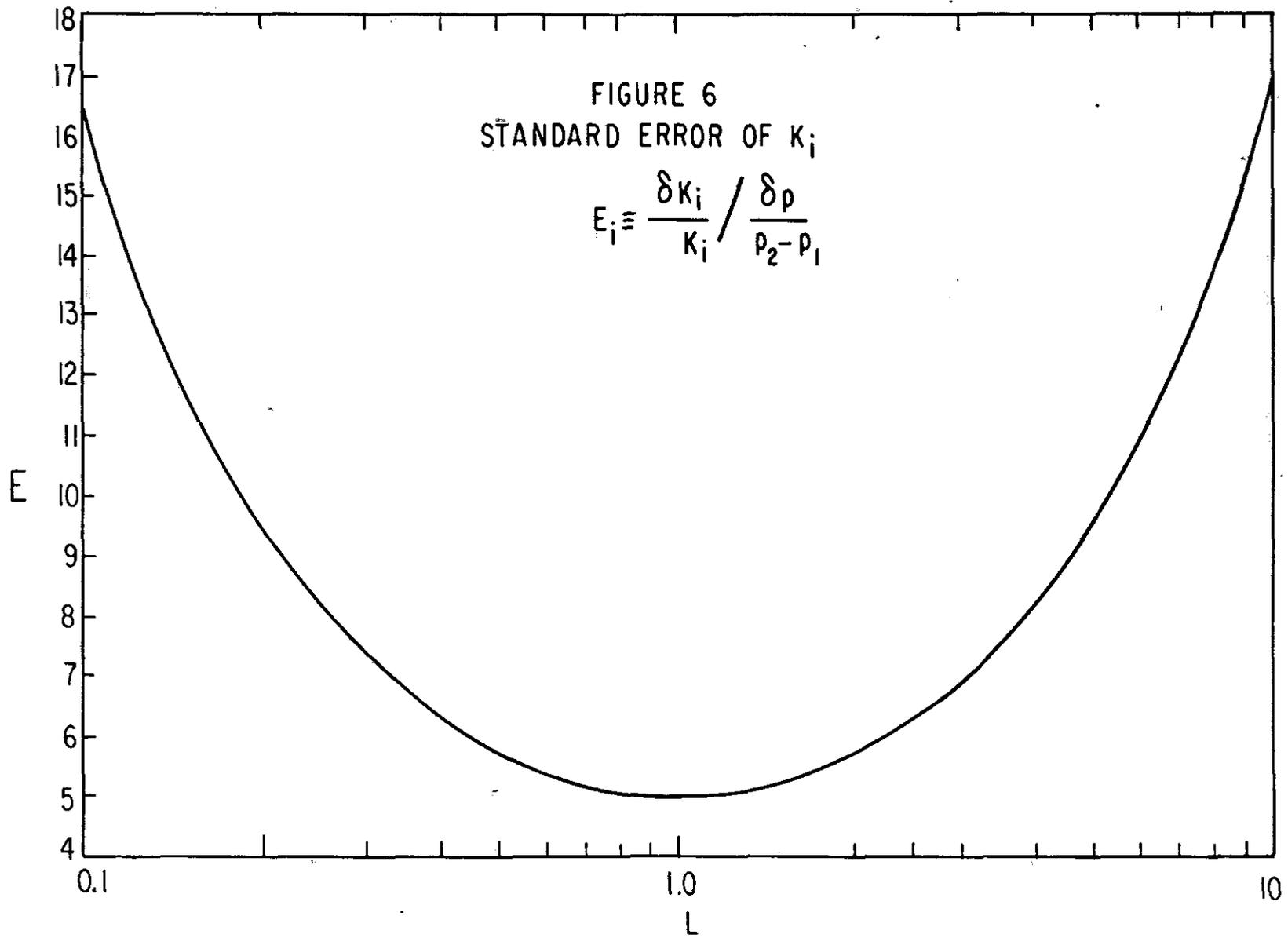
FIGURE 8
STANDARD ERROR OF SLOPE