spectively). The slopes ρ for the least squares lines, with standard deviations, are: line I, $\rho = -2.20(\pm 0.26)$; line II, $\rho = -2.09(\pm 0.07)$. The similar values of ρ show that the substituents X have quantitatively similar effects of $\Delta F°$ for reactions 1 and 14. The scatter of points about line I is greater than would be expected from random errors; the standard deviation of points from line I is about ten times the average standard deviation in log $K°_X$.[30] The scatter could be accounted for by a dependence of $\Delta S°$ on X, or by potential energy terms of a type not operative for reaction 14 (for example, the O–Fe bond could have some double bond character).

Equilibrium constants for the proton exchange reaction 15 have been calculated by Judson and Kilpatrick[31] using the equation developed from electrostatic theory by Sarmousakis.[32]

$$XC_6H_4OH + C_6H_5O^- \rightleftarrows XC_6H_4O^- + C_6H_5OH \quad (15)$$

Parameters were adjusted to give agreement between calculated and observed values for *meta* derivatives. Differences between calculated and observed values for *para* derivatives were then calculated as a measure of resonance effects.

We have used the Sarmousakis equation to calculate K_H/K_X, the equilibrium constant for reaction 16.

$$XC_6H_4OFe^{2+} + C_6H_5O^- \rightleftarrows XC_6H_4O^- + C_6H_5OFe^{2+} \quad (16)$$

As far as possible the conventions were those used by Judson and Kilpatrick. An internal dielectric constant of 2.00 was used. The center of the dipole was taken as the mid-point of the line from the benzene ring to the projection of the outermost atom on the axis of the ring. Estimates of the focal radius, molecular cavity volume and interatomic distances were made from structural considerations.[33] For *m*-nitrophenol calculated and experimental values of K_H/K_X agreed for an effective charge on the iron atom of 0.86, with the C–O–Fe bond angle taken as 120°.[34,35] The same effective charge and C–O–Fe bond angle were used to calculate K_H/K_X for the *para* derivatives. Calculated and observed values of log K_H/K_X are: X = *p*-NO_2, calcd. = 0.73, obsd. = 2.46; X = *p*-Br, calcd. = 0.29, obsd. = 0.10; X = *p*-CH_3, calcd. = −0.06, obsd. = −1.05. The differences between calculated and observed values of log K for reactions 15 and 16 may be compared. Values of $\log(K_{obsd.}/K_{calcd.})$ are: reaction 15,[31] X = *p*-NO_2, 1.81; X = *p*-Br, −0.08; X = *p*-CH_3, −0.20; reaction 16, X = *p*-NO_2, 1.73; X = *p*-Br, −0.19; X = *p*-CH_3, −0.99. The differences are a measure of the inadequacy of the simple model with localized charge. The calculations take no account of the redistribution of charge through conjugation and polarization.

Acknowledgment.—I am very much indebted to Professor W. C. Vosburgh for many helpful discussions and for his continued interest in this work.

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[30] The point for phenol itself, which lies furthest from the line, was checked carefully at two concentrations of phenol (0.255 and 0.0518 *M*) using both an analytical "Mallinckrodt" product that was not further purified, and a carefully fractionated sample. All four results agreed within the limits of experimental error. Similar results for two phenol concentrations may be regarded as evidence against polynuclear iron(III)–phenol species being important under the chosen conditions.

[31] C. M. Judson and M. Kilpatrick, THIS JOURNAL, **71**, 3115 (1949).

[32] J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

[33] The O–Fe bond distance was taken as 1.26 Å., the sum of the single bond covalent radius of the oxygen atom and the ionic radius of the iron(III) ion.

[34] The iron atom was assumed to be in the plane of the aromatic ring, *trans* to the nitro group. This configuration gives a slightly smaller repulsive charge–dipole interaction. However, the assumption of free rotation does not lead to significantly different results. For a C–O–Fe bond angle of 100°, calculated and experimental values agree for an effective charge of 0.75; for a bond angle of 180° an effective charge of 0.94 gives agreement.

[35] A small effective charge on the iron is in qualitative agreement with Pauling, *J. Chem. Soc.*, 1461 (1948), who considers that ionic charges are shared by solvating molecules.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE U. S. NAVAL RADIOLOGICAL DEFENSE LABORATORY]

Ion Exchange as a Separations Method. IX. Gradient Elution Theory[1]

BY EDWARD C. FREILING

RECEIVED SEPTEMBER 13, 1954

Ion-exchange column theory is applied to elutions made with both discontinuously and continuously graded eluants. Equations are derived for the resulting peak locations and peak widths. These equations are applied to a hypothetical example. The limitations of the theory are discussed.

Introduction

In the application of ion-exchange chromatography to the separation of a relatively large number of similar substances, such as the rare earths and amino acids, use of a constant strength of eluant does not permit the most efficient utilization of the time required for separation. For example, in separating the fission product rare earths, it is found that an eluant of relatively low concentration or *p*H is necessary to achieve good separation of Gd and Eu. Using the same eluant strength for the remainder of the run, however, one finds that the separation of the remaining rare earths is much greater than necessary. To reduce the time involved, recourse is frequently had to stepwise increases in eluant strength, as illustrated by the work of Ketelle and Boyd[1a] and Freiling and Bunney.[2] Stein and Moore[3] have successfully applied this technique to the separation of amino acids.

Gradient elution, *i.e.*, elution with a continuously

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[1] Paper presented before the Chemistry Division at the 121st Meeting of the American Association for the Advancement of Science, Berkeley, Calif., December, 1954.

[1a] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947).

[2] E. C. Freiling and L. R. Bunney, *ibid.*, **76**, 1021 (1954).

[3] W. H. Stein and S. Moore, *J. Biol. Chem.*, **192**, 663 (1951).

changing eluant strength, was developed by Alm and Williams[4] in an effort to overcome the tendency of elution bands to "tail." It has been applied to the separation of amino acids by Williams[5] and to rare earths by Nervik.[6]

Although ion-exchange column theory has been discussed by a number of authors[7-9] as yet no theoretical guide has been available for the development of procedures involving changes in eluant strength. It is in an effort to supply this need that this paper treats such processes in the light of the theory developed by Mayer and Tompkins.[7] The equations derived here will consequently be subject to the same limitations as those of the basic theory and should therefore be expected to become less applicable as the quantity of material to be separated is increased.

The degree of separation achieved between two substances in chromatographic elution is primarily represented by two properties of the elution history curve, *viz.*, the distance between the peak positions of these substances and the relative sharpness of the peaks in comparison with this distance. Mayer and Tompkins,[7] by using the normal curve of error to approximate the shape of the elution curve, have shown that these properties are closely related to C_1 and C_2 (the equilibrium ratios of the fraction of each substance in the resin phase to the fraction in solution in a given column plate) and P (the number of plates involved in the separation) by equations of the type

$$t = \frac{P^{1/2}(F - C)}{[C(1 + C)]^{1/2}} \qquad (1)$$

where t is the number of σ units between F and C, C is equal to the peak location in free column volume units, and F is the number of free column volumes that have passed through the column.

What will be considered here, then, is: (1) the method of determining C, P and cross contamination from an elution history curve; (2) the prediction of peak locations obtained with a graded eluant; and (3) the prediction of peak widths obtained with a graded eluant.

Theory

Determination of C, P and Cross Contamination.—To obtain reasonably accurate values of C, P and cross contamination, the shape of an elution history curve must be known in considerable detail. When a peak is contained in a relatively small number of fractions, or when the sizes of the fractions are not uniform, this detail of shape is not readily apparent. Because the shape of an elution peak can be approximated by an error curve,[7,8] however, the detail can be easily reconstructed by plotting the peak on linear-probability graph paper.[10] If the abscissa is plotted in free column volume units and the ordinate in σ units this becomes essentially a graph of t *vs.* F. One aspect of such a graph which is immediately obvious is the ease with which the cross contamination at any point may be determined. The C value of any adsorbate is the value of F at which $t = 0$. Let the value of F at the point $t = \sqrt{2}$ be denoted by F_e. Then, by substituting in eq. 1 and solving for P

$$P = 2C(C + 1)/(F_e - C)^2$$

which is simply Matheson's equation.[11]

An example of a graph of this type is illustrated in Fig. 1 with data taken from Freiling and Bunney.[2] Here, C_{Gd} is found to be 21.4 and C_{Eu} is 25.4. At the point $F = 23$, 0.20% of the Eu has come off the column, while 0.27% of the Gd has yet to be eluted. From the Gd curve one calculates $P = 1170$, while according to the Eu curve, $P = 1169$. The excellent agreement is obviously fortuitous.

Prediction of Peak Locations.—A graphical representation of adsorbate peak locations and eluant boundaries at any time during the course of a run performed with discontinuous eluant gradations is shown in Fig. 2. Here, the distance l which a peak or boundary has traveled down a column of total length L is plotted against time t. U is the linear flow velocity of the eluant, V_n the volume of the nth eluant, A the cross-sectional area of the column, and f the fractional void space. The courses of two adsorbates with C values C_n' and C_n'', respectively, in the nth eluant are shown. The first adsorbate is typical of the specific case in which the peak appears in the eluate during elution with the second eluant after a total volume V' of eluant and dead volume has come off the column. The second adsorbate typifies the generalization to n eluants.

Consider, now, the case of the first adsorbate. The peak begins to move down the column at $t = 0$ with a linear velocity $U/(1 + C_1')$. Later, at a time V_1/AUf, the boundary between the first and second eluants begins to move down the column with linear velocity U. For the peak and boundary to meet after a time t_1 each must travel a distance l_1 which is given by either

$$l_1 = \left(\frac{U}{1 + C_1'}\right) t_1$$

or

$$l_1 = U\left(t_1 - \frac{V_1}{AUf}\right)$$

Equating and solving for t_1 gives

$$t_1 = \frac{V_1(1 + C_1')}{AUfC_1'}$$

whence

$$l_1 = V_1/AfC_1'$$

The time, t_2, required for the peak to travel the remaining distance down the column while being eluted with the second eluant is

$$t_2 = (L - l_1)\frac{(1 + C_2')}{U}$$

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[4] R. Alm, R. J. P. Williams and A. Tiselius, *Acta Chim. Scand.*, **6**, 826 (1952).

[5] R. J. P. Williams, *The Analyst*, **77**, 905 (1952).

[6] W. Nervik, to appear in *J. Phys. Chem.*

[7] S. W. Mayer and E. R. Tompkins, THIS JOURNAL, **69**, 2866 (1947).

[8] T. Vermeulen and N. K. Hiester, *Ind. Eng. Chem.*, **44**, 636 (1952).

[9] Further references may be found in O. Samuelson, "Ion Exchangers in Analytical Chemistry," Chapter V, John Wiley and Sons, Inc., New York, N. Y., 1953.

[10] The possible assistance of probability graphs in making chromatographic elution calculations was suggested by Dr. S. W. Mayer.

[11] L. A. Matheson, private communication to E. R. Tompkins cited in *J. Chem. Education*, **26**, 98 (1949).

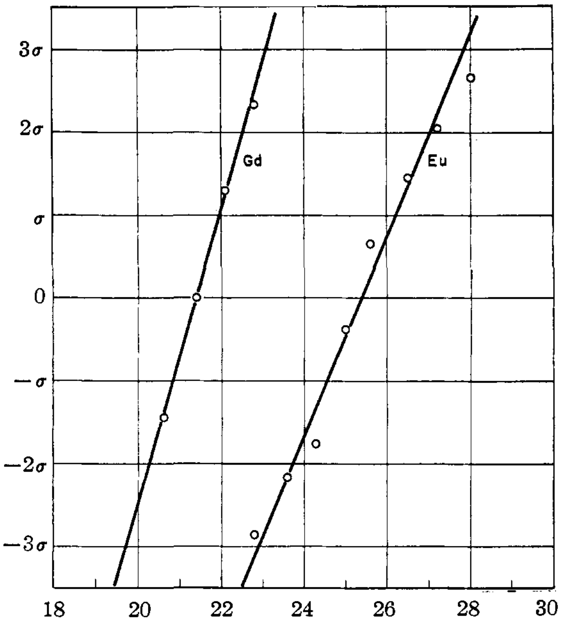

Fig. 1.—Integral elution history curve (replotted from data of Freiling and Bunney).

Now the total time must satisfy the equation

$$t_1 + t_2 = \frac{V}{AUf}$$

When the preceding values are substituted for t_1 and t_2 and the resulting equation solved for V there results

$$V = ALf + V_1 + C_2'\left((ALf - \frac{V_1}{C_1'}\right)$$

Here ALf is the dead volume and will henceforth be designated by V^*.

Generalizing, the second adsorbate begins traveling through the nth region at a time t_{n-1} with a linear velocity $U/(1 + C_n'')$. The boundary begins at a time $L\Sigma V_n/UV^*$ with a linear velocity U. Peak and boundary meet at the time t_n and distance l_n given by

$$l_n = U\left(t_n - \frac{L\Sigma V_n}{UV^*}\right)$$

Now

$$t_n = \frac{l_n(1 + C_n'')}{U}$$

$$l_n = \frac{L\Sigma V_n}{C_n''V^*} \qquad (2)$$

Proceeding as in the specific case and dropping the double-prime designation, the general equation is obtained

$$V_t = V^* + \Sigma V_n + C_{n+1}\left(V^* - \sum \frac{V_n}{C_n}\right) \qquad (3)$$

Here, the first two terms equal the total volume coming off the column before the appearance of the $(n + 1)$th eluant in the eluate. The last term is the volume of the $(n + 1)$th eluant that comes off the column before the appearance of the peak.

In the case of continuously graded eluant, the equation for the peak position is obtained by integrating eq. 2, thus

$$\int_{V^*}^{V_f} \frac{\mathrm{d}V}{C} = V^* \qquad (4)$$

where V_f is the volume at the peak.

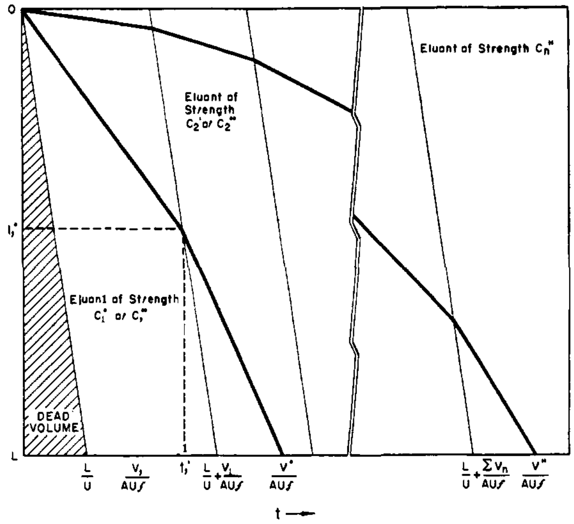

Fig. 2.—Progress of peak concentrations during the course of a run made with discontinuously graded eluant.

Prediction of Peak Widths.—Suppose an adsorbate to be contained in an infinitesimally thin layer at the top of a column of resin. Suppose, also, that a volume V_1 of eluate, in which the C value of the adsorbate is C_1, is passed through the column. If this is followed by a neutral fluid which quantitatively removes all eluant from each plate, but leaves the adsorbate in the resin phase intact, the fraction of the adsorbate on the pth plate after the passage of the nth plate free volume is given by Mayer and Tompkins as

$$S_{n_1,p} = \frac{(n_1 + p - 1)!}{(n_1 - 1)!p!}\,\frac{C_1^{n_1}}{(1 + C_1)^{n_1+p}}$$

where $n_1 = V_1P_1/V^*$. Vermeulen and Hiester have pointed out that this is C_1 times the pth term in the binomial expansion of

$$\left[\frac{C_1}{1 + C_1} + \frac{1}{1 + C_1}\right]^{n_1 + p - 1}$$

and consequently $S_{n_1,p}$ is a maximum when $p = n_1/C_1$. For large values of n_1 and p this maximum is approximated by

$$S_{\max} = S_{n_1,n_1/C_1} = C_1[2\pi n_1 (1 + C_1)]^{-1/2}$$

The distribution can be approximated by a normal error curve with a value of σ equal to $[n_1(1 + C_1)]^{1/2}/C_1$. The number of σ units between any plate and the plate of maximum solute concentration is then given by

$$t = \frac{C_1(p - p_{\max})}{[n_1(1 + C_1)]^{1/2}}$$

The effect of a new eluant on the solute distribution can now be treated by the following approach. Consider the same process to have occurred with a quantity $V_{1,2}$ of eluant in which the value of C is C_2. The same distribution results if $V_{1,2}$ is so chosen that $(p - p_{\max})/t$ remains the same. Therefore, if the process is carried out on a column of P_2 plates, the condition for equivalent distribution becomes

$$\frac{V_{1,2}}{V_1} = \frac{n_{1,2}}{n_1} = \frac{C_2^2(1 + C_1)}{C_1^2(1 + C_2)}$$

The plate of maximum adsorbate concentration is given by

$$(P_{\max})_{1,2} = n_{1,2}/C_2$$

After substitution this becomes

$$(p_{\max})_{1,2} = (p_{\max})_1 \frac{C_2(1 + C_1)}{C_1(1 + C_2)}$$

If a volume V_2 of the second eluant were now put through the column, the peak would move to plate

$$(p_{\max})_2 = \frac{P}{V^*}\left(\frac{V_1}{C_1} + \frac{V_2}{C_2}\right)$$

The distribution would be equivalent to that obtained by elution with a volume $V_2^{\text{eq}} = V_{1,2} + V_2$ of the second eluant, in which case the peak would have moved to plate.

$$(p_{\max})_2^{\text{eq}} = \frac{P}{V^*}\left(\frac{V_1C_2(1 + C_1)}{C_1^2(1 + C_2)} + \frac{V_2}{C_2}\right)$$

Generalizing, after passage of the *n*th eluant volume

$$(p_{\max})_n = \frac{P}{V^*}\sum \frac{V_i}{C_i} \tag{5}$$

$$\frac{(1 + C_n)}{C_{n2}} V_n^{\text{eq}} = \sum \frac{1 + C_iV_i}{C_i^2} \tag{6}$$

and

$$\frac{(1 + C_n)}{C_n}(p_{\max})_n^{\text{eq}} = \frac{PV_n^{\text{eq}}}{V^*C_n} \tag{7}$$

Obviously eq. 5 is just another form of eq. 2. Equation 1 may now be rewritten in the more suitable form

$$t^2 = \frac{PC}{C + 1}\left(\frac{V - V_f}{V_f - V^*}\right)^2 \tag{8}$$

In the case of a stepwise elution, where the peak is entirely eluted with eluant of strength C_f, the shape of the curve is obtained by substitution of the appropriate equivalent quantities in eq. 8. Thus, since $V^{\text{eq}} - V_f^{\text{eq}} = V - V_f$

$$t^2 = \frac{P(V - V_f)^2}{V^*C_f^2\sum \frac{(1 + C_i)}{C_i^2} V_i}$$

If each eluant is stronger than the preceding one, the effect is a sharpening of the elution peak beyond that which would be expected from the number of plates in the column.

In the case of gradient elution, *i.e.*, a continuously varying eluant strength, eq. 6 and 7 become

$$\frac{(1 + C)}{C^2}[V^{\text{eq}} - (V^*)^{\text{eq}}] = \int_{V^*}^{V}\frac{\mathrm{d}V}{C^2} + \int_{V^*}^{V}\frac{\mathrm{d}V}{C} \tag{9}$$

and

$$P_f^{\text{eq}} = \frac{P[V_f^{\text{eq}} - (V^*)^{\text{eq}}]}{C_fV^*} \tag{10}$$

If, in the region of C_f, C is a slowly varying function of the volume, V_f^{eq} and P_f^{eq} may be applied just as in the discontinuous case. The result is given by

$$t^2 = \frac{P(V - V_f)^2}{C_f^2\left(1 + \frac{1}{V^*}\int_{V^*}^{V_f}\frac{\mathrm{d}V}{C^2}\right)} \tag{11}$$

This situation is sometimes met in practice. For example, if the strength of the eluant is being steadily increased by replacing each portion that passes into the column with an equal portion of a stronger eluant, the increase in strength will tend to be linear at first but will gradually level off to that of the stronger eluant. If, in the region of C_f, C varies appreciably with the volume, the result obtained by this procedure is an approximation of the peak shape.

A more general approach to the problem may be taken as follows. Suppose a gradient elution to be carried out up to a volume V_a, at which the C value of the adsorbate is C_a, and that the remainder of the elution is performed at the constant eluant strength C_a. If V_a is taken prior to the peak, the number of σ units between V_a and the peak may be taken as an approximation of the number of σ units that would have intervened between V_a and V_f, the volume at which the peak would have occurred had the gradient continued. If V_a is greater than V_f, the intervening σ units may be approximated by the number between V_a and the peak which would have had to be obtained in order to produce the shape of the elution curve occurring after V_a using only eluant of strength C_a. Thus, according to eq. 9 and 10

$$V_a^{\text{eq}} - V^{*\text{eq}} = \frac{C_a^2}{1 + C_a}\int_{V^*}^{V_a}\frac{(1 + C)}{C^2}\,\mathrm{d}V$$

$$V_f^{\text{eq}} - V_a^{\text{eq}} = V_f - V_a$$

and

$$P_f^{\text{eq}} = \frac{P(V_f^{\text{eq}} - V^{*\text{eq}})}{V^*C_a}$$

From eq. 4

$$V_f = V_a + C_aV^* - C_a\int_{V^*}^{V_a}\frac{\mathrm{d}V}{C}$$

Eliminating V_f

$$V_f^{\text{eq}} - V_a^{\text{eq}} = C_aV^* - C_a\int_{V^*}^{V_a}\frac{\mathrm{d}V}{C}$$

$$V_f^{\text{eq}} - V^{*\text{eq}} = \frac{C_a^2}{1 + C_a}\int_{V^*}^{V_a}\frac{(1 + C)}{C^2}\,\mathrm{d}V + C_aV^* - C_a\int_{V^*}^{V_a}\frac{\mathrm{d}V}{C}$$

Substituting into eq. 8, rearranging, and dropping the subscript a

$$t^2 = PC\left[\frac{C}{V^*}\int_{V^*}^{V}\frac{\mathrm{d}V}{C^2} - \frac{1}{V^*}\int_{V^*}^{V}\frac{\mathrm{d}V}{C} + 1 + C\right]^{-1}\left[1 - \frac{1}{V^*}\int_{V^*}^{V}\frac{\mathrm{d}V}{C}\right]^2 \tag{12}$$

Example.—Consider the elution of two adsorbates whose C ratio at any concentration of eluate is $C''/C' = 1.30$. Let $C(V)$ be given by

$$C' = 102.3 - 2.303\ V/V^*$$

and

$$C'' = 133.0 - 2.994\ V/V^*$$

Then, according to eq. 4, $V_f' = 40.1$, $C_f' = 10$, $V_f'' = 42.3$ and $C_f'' = 6.5$. At V_f'' the value of C' is 5.0.

Comparing these values with constant strength elution values, if C' had been 39.1 throughout, C'' would have been 50.9, giving $V_f' = 40.1$ and $V_f'' = 51.9$. It is therefore seen that gradient elution considerably decreases the distance between peaks (in this case by a factor of 5.4.).

Assuming $P = 1000$, the peaks eluted with constant eluant strength would be separated by 9.41 σ units of the first peak. According to the approximation given by eq. 11 they are separated by something greater than 7.13 σ units by gradient elution. Application of eq. 12 shows that gradient elution actually separates them by 9.44 σ units. The large decrease in peak separation is therefore offset by peak sharpening. The calculated integral elution history curves are shown in Fig. 3.

Discussion

The equations presented here are subject to the same limitations as are those derived by Mayer and Tompkins, *viz.*, linear isotherms and near equilibrium column conditions. These authors have further indicated that the approximation of elution curves by Gaussian distribution curves becomes more accurate as P and C take on larger values. In the derivations used here, it has been necessary to apply this approximation both when the number of plates traversed by the adsorbate is small (at the beginning of a run) and when C is small (at the end of a run).

The peak shape equations involve still more approximations, and must therefore be used with more caution than the peak location equations. Of these, equation 12 appears to be the more exact. Because of the nature of the approximations involved, it would be expected to hold better in the region nearer the peak.

A more quantitative evaluation must await the present accumulation of experimental data.

With regard to the practical question of ease of computations based on eq. 12, consider the general case of a linearly decreasing C value

$$C = A - BV/V^*$$

for which eq. 12 becomes

$$t^2 = \frac{PC}{B}\,\frac{[\ln C/(A - B) + B]}{BC + 1 - C/(A - B) + B + \ln C/(A - B)}$$

In the example chosen it was found that the denominator could be represented by B^2C over the entire range of calculation at the sacrifice of only 3% accuracy. The equation then reduced to the very simple form

$$t = \frac{P^{1/2}}{B}\,[B + \ln C/(A - B)]$$

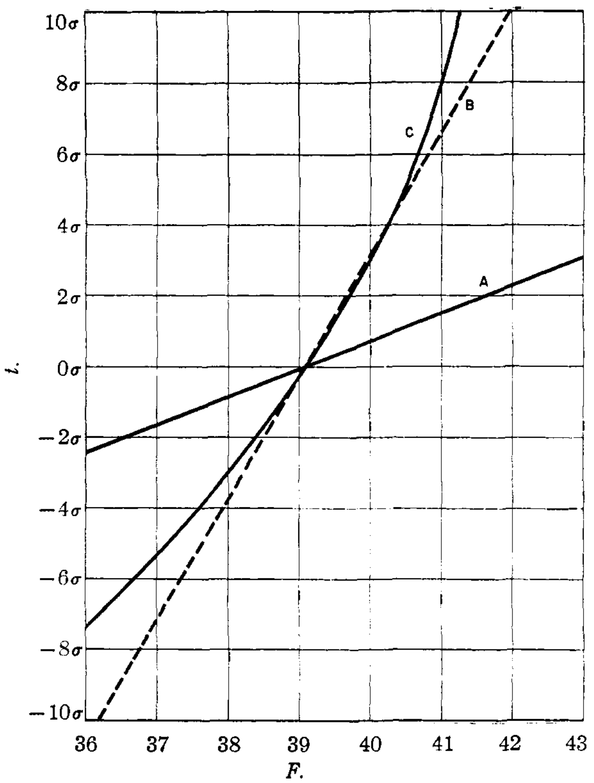

Fig. 3.—Integral elution history curves (calcd. from example in text): A, constant strength elution; B, gradient elution, approximate equation; C, gradient elution, exact equation.

It is quite likely that similar simplifications will be found in many of the cases to which eq. 12 is applied.

Acknowledgments.—The author is grateful to Dr. E. R. Tompkins for encouraging discussions, helpful suggestions and reviewing the manuscript, to Mr. Jarvis Todd for advice on the clarity of presentation.

SAN FRANCISCO, CALIF.

[CONTRIBUTION NO. 1269 FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficients of Lithium and Potassium Perchlorates in Dilute Aqueous Solutions at 25°

BY HERBERT S. HARNED, HERMAN W. PARKER AND MILTON BLANDER

RECEIVED DECEMBER 15, 1954

The differential diffusion coefficients of lithium and potassium perchlorates have been determined at 25° by the conductometric method at concentrations between 0.001 and 0.01 molar. Theoretical considerations indicate that at low concentrations the activity coefficients of these electrolytes are nearly identical. This result differs from previous conclusions derived from freezing point data.

By employing the conductometric method devised in this Laboratory,[1] the diffusion coefficients of lithium and potassium perchlorates recorded in Table I have been determined at the concentrations designated.

Theoretical Considerations.—For 1–1 electrolytes, the theory of Onsager and Fuoss[2] is represented by the equation

$$\mathfrak{D} = 16.629 \times 10^{10} T(\overline{\mathfrak{M}}/c)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right) \quad (1)$$

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(1) H. S. Harned and D. M. French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945); H. S. Harned and R. L. Nuttall, THIS JOURNAL, **69**, 736 (1947).

(2) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).