the eq. 4 and 14 is zero. This assumption requires the use of the arithmetic mean for both a_{12} and b_{12} rather than the geometric mean. The values of the energy of mixing for both constant volume and constant pressure in Table IV range from 70 to 90% of the corresponding values in the other tables. Thus, it seems that the compression or expansion of the pure components largely accounts for the energy of mixing. This is not true of the entropies of mixing, and the value of the first term of eq. 14 is roughly the same as the sum of the other terms.

TABLE IV

VALUES OF THE CHANGE OF ENERGY AND ENTROPY AT HALF MOLE FRACTION USING THE ARITHMETIC MEAN

	C_6H_6–CCl_4	C_6H_6–C_6H_{12}	C_6H_{12}–CCl_4
$\Delta\bar{E}_V{}^M$	8.0	71	23
$\Delta\bar{E}_p{}^M$	8.7	122	34
$\Delta\bar{S}_V{}^E$	−0.04	−0.11	−0.04
$\Delta\bar{S}_p{}^E$	− .03	+ .07	.00

Partial Molal Quantities.—Expressions for the partial molal energies of mixing and the partial molal excess entropies of mixing are readily obtained from eq. 4 and 14. These equations are

$$\Delta\bar{E}_1{}^M = \frac{x_2{}^2\bar{V}_1\bar{V}_2{}^2}{\bar{V}^2}\left(\frac{2a_{12}}{\bar{V}_1\bar{V}_2} - \frac{a_{11}}{\bar{V}_1{}^2} - \frac{a_{22}}{\bar{V}_2{}^2}\right) + \left(\frac{a_{11}}{\bar{V}_1} - \frac{a_{11}'}{\bar{V}_1{}^0}\right) + \frac{x_2(\bar{V}_1 - \bar{V}_2)}{V}\left[x_1{}^2\left(\frac{\partial a_{11}}{\partial \bar{V}}\right)_{T,P,n_2} + 2x_1x_2\left(\frac{\partial a_{12}}{\partial \bar{V}}\right)_{T,P,n_2} + x_2{}^2\left(\frac{\partial a_{22}}{\partial \bar{V}}\right)_{T,P,n_2}\right] \quad (17)$$

and

$$\Delta\bar{S}_1{}^{\mathrm{E}} = \frac{x_2{}^2\bar{V}_1\bar{V}_2{}^2}{\bar{V}^2}\left(\frac{2b_{12}}{\bar{V}_1\bar{V}_2} - \frac{b_{11}}{\bar{V}_1{}^2} - \frac{b_{22}}{\bar{V}_2{}^2}\right) + \left(\frac{b_{11}}{\bar{V}_1} - \frac{b_{11}'}{\bar{V}_1{}^0}\right) + \frac{x_2(\bar{V}_1 - \bar{V}_2)}{\bar{V}}\left[x_1{}^2\left(\frac{\partial b_{11}}{\partial \bar{V}}\right)_{T,P,n_2} + 2x_1x_2\left(\frac{\partial b_{12}}{\partial \bar{V}}\right)_{T,P,n_2} + x_2{}^2\left(\frac{\partial b_{22}}{\partial \bar{V}}\right)_{T,P,n_2}\right] - R\ln\frac{\bar{V}_1{}^0}{\bar{V}} + \frac{x_2R}{\bar{V}}(\bar{V}_1 - \bar{V}_2) \quad (18)$$

The equations for the second component are obtained by interchange of subscripts. Equation 17 reduces to that given by Simons and Dunlap with the assumption that the a's are independent of the volume.

Wood[28] has attempted to correlate the excess entropy of mixing at infinite dilution of one component in the other with the difference between the entropy of vaporization of the component to an ideal gas at an arbitrary concentration and that of argon to the same concentration in the gas phase. Such correlation could only exist if the solvent was considered to be merely an inert diluent, but the effect of the solvent was shown to be very marked. Equation 18 reduces to

$$\Delta\bar{S}_1{}^E = \frac{2b_{12}}{\bar{V}_2{}^0} - \frac{b_{22}\bar{V}_1{}^\infty}{(\bar{V}_2{}^0)^2} - \frac{b_{11}'}{\bar{V}_1{}^0} + \frac{\bar{V}_1{}^\infty - \bar{V}_2{}^0}{\bar{V}_2{}^0}\left(\frac{\partial b_{22}}{\partial \bar{V}}\right)_{T,P,n_2} - R\ln\frac{\bar{V}_1{}^0}{\bar{V}_2{}^0} + R\left(\frac{\bar{V}_1{}^\infty - \bar{V}_2{}^0}{\bar{V}_2{}^0}\right) \quad (19)$$

for the partial molar excess entropy of the first component at infinite dilution in the second component. Here $\bar{V}_1{}^\infty$ is the partial volume of the first component at infinite dilution. The effect of the solvent and the interaction between the unlike molecules is quite apparent. Even under the stringent conditions that the molar volumes are identical and that the volume of the solution is additive in the volume of the components, the three terms $b_{12}/\bar{V}^0$, $b_{22}/\bar{V}^0$ and $b_{11}/\bar{V}^0$ still appear. Only under the additional condition that b_{22} be zero would the partial molar excess entropy of the solute be dependent upon its properties alone.

[28] S. E. Wood, *J. Chem. Phys.*, **15**, 358 (1947).

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[CONTRIBUTION FROM THE VIRAL AND RICKETTSIAL SECTION, RESEARCH DIVISION, AMERICAN CYANAMID COMPANY]

The Calculation of Reduced Moments of Refractive Index Gradient Curves Obtained in Diffusion Experiments by Means of Rayleigh Fringes

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RECEIVED OCTOBER 10, 1956

A method has been devised for calculating reduced second and fourth moments of gradient curves obtained in diffusion experiments by means of Rayleigh fringes. Theoretical calculations and experimental data indicate that the reduced second moment can be measured with an accuracy of about 0.1%.

Although the free diffusion of homogeneous substances in liquids has been studied extensively with the Rayleigh method,[1] there is little published work on heterogeneous systems. Baldwin,[2] Dunlop[3] and Akeley[4] have shown that moments of the refractive index gradient curves are useful for measuring average diffusion constants of a heterogeneous system. Baldwin has named D_{2m} and $D^2{}_{4m}$ the reduced second and fourth moments, respectively.

$$D_{2m} \equiv \frac{m_2}{2t} \quad (1)$$

$$D^2{}_{4m} \equiv \frac{m_4}{12t^2} \quad (2)$$

In a non-interacting ($D_{\mathrm{ij}} = 0$; i ≠ j) heterogeneous system in which all the solutes have the same refractive index increment we have

$$D^{s}{}_{2m} = \overline{D^{s}} = \Sigma\, x_{\mathrm{i}}D^{s}{}_{1} \quad (3)$$

where x_{i} is the weight fraction of component i.

[1] (a) L. G. Longsworth, THIS JOURNAL, **75**, 5705 (1953); (b) J. M. Creeth, *ibid.*, **77**, 6428 (1955).

[2] R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5235 (1955).

[3] P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5238 (1955).

[4] D. F. Akeley and L. J. Gosting, *ibid.*, **75**, 5685 (1953).

Theory

The moments of the refractive index gradient curve may be expressed in a form suitable for calculation from the data obtained by means of the Rayleigh fringes.

$$\frac{(2s)!t^s}{S!}\overline{D^s} = \int_{-\infty}^{\infty} x^{2s}\left(\frac{\partial n}{\partial x}\right)\mathrm{d}x \qquad (4)$$

$$\frac{(2s)!t^s}{S!}\overline{D^s} = \int_{-\infty}^{x_2} x^{2s}\frac{\partial n}{\partial x}\,\mathrm{d}x + \int_{x_2}^{x_3} x^{2s}\frac{\partial n}{\partial x}\,\mathrm{d}x + \cdots\cdots \int_{x_{n-3}}^{x_{n-1}} x^{2s}\frac{\partial n}{\partial x}\,\mathrm{d}x + \int_{x_{n-2}}^{\infty} x^{2s}\frac{\partial n}{\partial x}\,\mathrm{d}x \qquad (5)$$

$$\frac{(2s)!t^s}{S!}\overline{D^s} \cong \int_{-\infty}^{x_2} x^{2s}\frac{\partial n}{\partial x}\,\mathrm{d}x + \left(\frac{x_2 + x_3}{2}\right)^{2s}\frac{1}{J} + \cdots\cdots \left(\frac{x_{n-3} + x_{n-2}}{2}\right)^{2s}\frac{1}{J} + \int_{x_{n-2}}^{\infty} x^{2s}\frac{\partial n}{\partial x}\,\mathrm{d}x \qquad (6)$$

In eq. 6, $(\partial n/\partial x)$ is the refractive index gradient normalized to unit area; x_i is the distance from the first moment to the minimum of fringe i; J is the total number of fringes, and N is the largest integer which is smaller than J.

Before eq. 6 can be used, expressions for the first and last integrals must be developed. The approximation used in eq. 6 is not a good one for widely spaced fringes. For this reason it is desirable to start the summation at the second fringe and terminate it at the next to the last fringe. Creeth[1b] has pointed out that information obtainable from the outer fractional fringes is very important in the analysis of heterogeneous systems. Therefore, a reasonable procedure is to approximate that part of the experimental refractive index curve beyond the second fringe by an error function passing through the second and the one-half fringe. In deriving an expression for the "tails" one first evaluates the integral $1/\sqrt{\pi}\int_{-\infty}^{Z_2} \alpha^n e^{-\alpha^2}\,\mathrm{d}\alpha$ using integration by parts. The transformation $x = \sqrt{2\sigma^2}\,\alpha$ where $\sigma^2 = {}^1/_2\,(x_2 - x_{0.5})^2/(Z_2 - Z_{0.5})^2$ is then made. One can then arrive at eq. 7 and 8 by another simple step if he remembers that the error function passing through the second and the one-half fringes does not in general have its origin at the first moment.

$$\int_{-\infty}^{x_2} x^2\frac{\partial n}{\partial x}\,\mathrm{d}x \cong \left[\left(\frac{x_2 - x_{0.5}}{Z_2 - Z_{0.5}}\right)\left(\frac{\lambda_2}{1 - H(Z_2)}\right)^{1/2} + |x_2| - \left|Z_2\left(\frac{x_2 - x_{0.5}}{Z_2 - Z_{0.5}}\right)\right|\right]^2\left(\frac{1 - H(Z_2)}{2}\right) \qquad (7a)$$

$$\lambda_2 = {}^1/_2\,[Z_2H'(Z_2) + (1 - H(Z_2))] \qquad (7b)$$

$$H(Z_j) = \frac{j - {}^1/_2J}{{}^1/_2J} \qquad (7c)$$

$$\int_{-\infty}^{x_2} x^4\frac{\partial n}{\partial x}\,dx \cong \left[\left(\frac{x_2 - x_{0.5}}{Z_2 - Z_{0.5}}\right)\left(\frac{\Gamma_2}{2\{1 - H(Z_2)\}}\right)^{1/4} + |x_2| - \left|Z_2\left(\frac{x_2 - x_{0.5}}{Z_2 - Z_{0.5}}\right)\right|\right]^4\left(\frac{1 - H(Z_2)}{2}\right) \qquad (8a)$$

$$\Gamma_2 = Z_2{}^3H'(Z_2) + 3/2Z_2H'(Z_2) + 3/2[1 - H(Z_2)] \qquad (8b)$$

In eq. 7 and 8, $H(Z_i)$ is the normalized error function tabulated in the "Tables of Probability Functions"[5] and $H'(Z_i)$ is its derivative. It is to be noted that most of the variables in eq. 7 and 8 do not depend on time and need only be evaluated once in an experiment.

The first-order term for the concentration dependence of the diffusion coefficient is an odd function[1b] and will not contribute to even moments calculated from the total gradient curve. If there is no interaction of flows, one can obtain the weight average diffusion coefficient of a concentration dependent polydisperse system from the reduced second moments. The standard deviation of the diffusion coefficients of a polydisperse system with non-interacting flows may be estimated from the reduced second and fourth moments.[2,6]

$$\sigma_D^2 = \overline{D^2} - \overline{D}^2 = D^2{}_{4m} - D^2{}_{2m} \qquad (9)$$

Experimental

The diffusion coefficient of sucrose in water for $\Delta C = 0.70$ and $\overline{C} = 0.35$ g./100 ml. ($J = 94.08$) has been measured at 1° in the Spinco model H electrophoresis–diffusion apparatus. The Rayleigh fringes were analyzed on a comparator made by the David W. Mann Precision Instruments Company, Lincoln, Massachusetts. It was equipped with a projection system which gives a magnification factor of 36.

Results

The diffusion coefficients for sucrose calculated by the usual method[1a] and by means of reduced moments are tabulated for different times in Table I. All distances were measured from the position of the mean refractive index. For most systems this will be a good approximation to the first moment. For concentration dependent systems with skewed boundaries it will, of course, be necessary to correct for the first moment.

TABLE I

DIFFUSION COEFFICIENT FOR SUCROSE AT 1° (CM.^{2} SEC.$^{-1}$)

Time (sec.)	$10^6 \times D$ (Longsworth)	$10^6 \times D_{2m}$	$10^6 \times D_{4m}$
5,854	2.418	2.415	
7,894	2.411	2.411	2.410
9,874	2.416	2.406	
11,374	2.415	2.417	
14,014	2.405	2.415	2.411
15,394	2.412	2.417	2.419
18,514	2.419	2.409	
Av.	2.414	2.413	

Curves for three hypothetical diffusion experiments, each involving the diffusion of two solutes, have been constructed from the "Tables of Probability Functions" by double interpolation. The assumed conditions are presented in Table II. The times quoted were those actually used in constructing the individual curves. The reduced

TABLE II

CONDITIONS FOR THREE HYPOTHETICAL DIFFUSION EXPERIMENTS WITH TWO SOLUTES

Exp. no.	$\overline{D}$	J	t(sec.)
I	$2.000 \times 10^{-7} \times 0.5 + 1.389 \times 10^{-7} \times 0.5 = 1.694 \times 10^{-7}$	98.36	5×10^5
II	$2.000 \times 10^{-7} \times 0.98 + 4.500 \times 10^{-7} \times 0.02 = 2.050 \times 10^{-7}$	98.36	2.222×10^5
III	$2.000 \times 10^{-7} \times 0.90 + 1.800 \times 10^{-6} \times 0.1 = 3.600 \times 10^{-7}$	98.36	4×10^5

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(5) "Tables of Probability Functions," Vol. I, National Bureau of Standards.

(6) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1945, pp. 420–421.

TABLE III

COMPARISON OF CALCULATED WITH ACTUAL VALUES

Integral	Exp. 1 Actual	Exp. 1 Computed	Exp. 2 Actual	Exp. 2 Computed	Exp. 3 Actual	Exp. 3 Computed
$\frac{1}{2t}\left[\int_{-\infty}^{x_2} x^2 \frac{\partial n}{\partial x}\,dx + \int_{x_{96}}^{\infty} x^2 \frac{\partial n}{\partial x}\,dx\right]$	0.448	0.446	0.536	0.534	1.655	1.615
$\frac{1}{2t}\left[\int_{x_2}^{x_9} x^2 \frac{\partial n}{\partial x}\,dx + \int_{x_{89}}^{x_{96}} x^2 \frac{\partial n}{\partial x}\,dx\right]$	.627	.628	.757	.757		
$\frac{1}{2t}\left[\int_{x_9}^{x_{89}} x^2 \frac{\partial n}{\partial x}\,dx\right]$	.621	.621	.757	.757		
$\frac{1}{2t}\int_{-\infty}^{\infty} x^2 \frac{\partial n}{\partial x}\,dx$	1.694	1.695	2.050	2.048	3.600	3.568

TABLE IV

COMPARISON OF REDUCED FOURTH MOMENTS

	Exp. 1 Actual	Exp. 1 Computed	Exp. 2 Actual	Exp. 2 Computed
D^2_{4m}	2.964×10^{-14}	2.951×10^{-14}	4.325×10^{-14}	4.252×10^{-14}
σ_D	0.30×10^{-7}	0.27×10^{-7}	0.35×10^{-7}	0.23×10^{-7}

moments calculated for different portions of the curves are presented in Table III. The computed values were obtained by the use of eq. 6 and 7. The last integral in eq. 6 was evaluated from the positions of fringes 96 and 98.[7] The actual values were calculated using eq. 10.

$$\int_{x_j}^{x_i} x^2 \frac{\partial n}{\partial x}\,dx = \Sigma 2t\, X_k D_k\,[\lambda^k{}_i - \lambda^k{}_j] \qquad (10a)$$

$$\frac{D_l}{D_m} = \left(\frac{Z^m}{Z^l}\right)^2 \qquad (10b)$$

$$\sum_k x_k H(Z^k{}_j\ ) = \frac{j = {}^1/_2 J}{{}^1/_2 J} \qquad (10c)$$

X_k is the weight fraction of component k. Equations 10b and c were solved numerically by double interpolation in the "Tables of Probability Functions." Difficulties with signs for λ and Γ are perhaps best avoided by considering all variables involved as being positive and separating any integrals crossing the zero axis into two integrals.

Table IV compares the reduced fourth moments and the σ_D calculated from the eq. 8 and 9 with the actual values.

Discussion

Most of the error in the computation arises from the first and last integrals in eq. 6.

The above results suggest that one can compute reduced second moments which are within 0.1% of the correct values for systems in which there is not too large a range of diffusion constants. It is also possible to obtain useful information about the amount of dispersion in the system by comparing the reduced second and fourth moments. Experiment 3 (see Table II) corresponds to a highly improbable situation: *e.g.*, a protein contaminated with 10% of a low molecular weight polypeptide. In this case the error is considerably larger than 0.1%.

Preliminary experiments with polydisperse systems[8] indicated that data obtained at different times during the run are reproducible to 0.1–0.2%. A final evaluation of the accuracy obtainable with actual polydisperse systems will have to be made on the basis of model experiments.

Although the calculations involved are laborious, there will be systems for which the extra effort will be justified. It may be possible to make use of high speed calculators.

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(7) No definite rule can be given for choosing the optimum fringes for calculating the last integral of eq. 6. In general one should use for the second fringe the highest numbered fringe or fractional fringe for which accurate measurements can be made.

(8) S. L. Burson, Jr., M. J. Fahrenbach, L. H. Frommhagen, B. A. Riccardi, R. A. Brown, J. A. Brockman, H. V. Lewry and E. L. R. Stokstad, THIS JOURNAL, **78**, 5874 (1956).

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The Apparent Molar Refraction of Lanthanum Perchlorate in Aqueous Solution

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RECEIVED NOVEMBER 29, 1956

The apparent molar refraction, dispersion, volume and the partial molal volume of lanthanum perchlorate in aqueous solution have been determined. The results have been interpreted in terms of the Fajans theory as well as by Böttcher's modified refraction equation.

Introduction

The chemistry of the lanthanon elements has assumed new importance by the recognition of their relationship to the actinides, and accurate measurements of chemical and physical properties of the lanthanons has made possible helpful predictions and extrapolations to the actinides. A quantity which has received little attention for these elements

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(1) Taken from the M.S. thesis of Norman W. Silcox, Univ. of Mass., June, 1955.