

in the effusion cell,  $F$  is the force, and  $r$  is the radius of the hole. We shall derive the relationship between the pressure in the cell and the resultant force when a hole of finite length is used.

Clausing<sup>6</sup> has derived correction factors which are applicable to pressure determinations by the Knudsen method.<sup>7</sup> However, these factors cannot be used to calculate the pressure in a cell from the force exerted by vapor effusing from the cell because the force depends on the angular distribution of effusing molecules as well as on their number. The form of this angular distribution has also been derived by Clausing.<sup>8</sup> Changing his term for the solid angle  $d\omega/\pi$  to polar coordinates with the axis of the hole as the reference axis gives

$$K_{(\theta)}d\theta = 2\nu_1\pi r^2 T \cos\theta \sin\theta d\theta. \quad (1)$$

Where  $\theta$  is the angle measured from the reference axis,  $K_{(\theta)}d\theta$  is the number of molecules effusing per second between  $\theta$  and  $\theta+d\theta$ ,  $\nu_1$  is the number of molecules incident on the walls of the container per  $\text{cm}^2$  per second, and  $T$  is a complicated function of  $\theta$  and the length  $L$  and radius  $r$  of the hole.

The resultant force  $F$  acting on the vapor container along the axis of the hole is

$$F = \int_0^{\pi/2} p \cos\theta K_{(\theta)}d\theta = 2\nu_1\pi r^2 p \int_0^{\pi/2} T \sin\theta \cos^2\theta d\theta, \quad (2)$$

where  $p$  is the mean momentum of the molecules. Equation (2) cannot, in general, be integrated analytically; it may, however, be evaluated to any desired degree of accuracy by Simpson's method.<sup>9</sup> In the limiting case  $L/r=0$ ,  $T$  reduces to unity and Eq. (2) may be integrated to yield

$$F_0 = 2\nu_1\pi r^2 p/3 \quad (3)$$

which is the result obtainable from elementary kinetic theory,  $F_0$  designating the limiting case.

Division of Eq. (2) by Eq. (3) gives the ratio  $f$  of the force resulting from vapor effusing through a hole for which  $L/r>0$ , to the force expected under the same conditions except that  $L/r=0$ ; thus,

$$f = \frac{F}{F_0} = 3 \int_0^{\pi/2} T \sin\theta \cos^2\theta d\theta. \quad (4)$$

From Eq. (4) it follows that the relation between the pressure in a cell and the force resulting from the effusion of vapor from the cell through a hole for which  $L/r>0$  is

$$P = 2F/\pi r^2 f. \quad (5)$$

The correction factors  $f$  for values of  $L/r$  between 0.0 and 2.0 are given in column 4 of Table I. For the integration of Eq. (4) by

TABLE I. Correction factors for the effect of channel holes on the number and force of effusing molecules.

$L/r$	$K$	$K'$	$f$
0	1	1	1
0.2	0.9092	0.913	0.938
0.4	0.8341	0.831	0.877
0.6	0.7711	0.769	0.825
0.8	0.7177	0.719	0.778
1.0	0.6720	0.674	0.734
1.2	0.6320	0.633	0.694
1.4	0.5970	0.599	0.660
1.6	0.5659	0.567	0.627
1.8	0.5384	0.538	0.597
2.0	0.5136	0.512	0.570

Simpson's method,  $T \sin\theta \cos^2\theta$  was calculated at  $\theta=0, 15, 30, 45, 60, 75,$  and  $90^\circ$  for each value of  $L/r$ . The equation

$$1/f = 0.0147(L/r)^2 + 0.3490(L/r) + 0.9982 \quad (6)$$

reproduces the tabulated values of  $f$  within  $\pm 0.2$  percent over the range  $0 \leq L/r \leq 2.0$ .

For comparison, columns 2 and 3 of Table I list calculated probabilities that molecules entering one end of holes with  $L$ -to- $r$  ratios between 0 and 2.0 will escape through the other end. The values  $K$  in column 2 were calculated by Clausing.<sup>6</sup> Values  $K'$  in

column 3 were calculated by us from Clausing's equation for the angular distribution of effusing molecules [Eq. (1) in this note].

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<sup>4</sup> K. Niwa, and Z. Shibata, *J. Fac. Sci. Hokkaido Imp. Univ.* **3**, 53 (1940).

<sup>5</sup> G. Wessel, *Z. Physik* **130**, 539 (1951).

<sup>6</sup> P. Clausing, *Ann. Physik* **12**, 961 (1932).

<sup>7</sup> S. Dushman, *Scientific Foundations of Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949), pp. 18-24, 90-101.

<sup>8</sup> P. Clausing, *Z. Physik* **66**, 471 (1930).

<sup>9</sup> See any standard calculus textbook.

## Concentration Dependence of Differential Capacity in Electrolytes at the Electrocapillarity Maximum

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FROM an electrolyte such as aqueous NaF which exhibits no ionic adsorption on cathodic polarization at an ideal polarized electrode,<sup>1</sup> information concerning the structure of the double layer at this electrode can be obtained from the dependence of differential capacitance on concentration at the electrocapillarity maximum potential (abbreviated as "ecm" potential): the potential at which there is no charge on the electrode.<sup>1</sup>

When a negative potential numerically greater than the ecm potential is applied, the resulting double layer probably consists of a negative charge density on the metal electrode, a charge-free layer of thickness  $x_0$  beginning at the electrode, and a diffuse space-charge layer of excess positive ions and fewer-than-normal negative ions extending from  $x=x_0$  into the material. The total differential capacitance per unit area is  $C_T^d = d\sigma_m/dV_a = d\sigma_m/dV_0$ . Here  $\sigma_m$  is the charge density on the electrode,  $V_a$  is the applied potential, and  $V_0$  is a (negative) potential referred to the ecm potential as zero. The distance  $x_0$  may be interpreted as the sum of the ionic radius of the nearest positive ions and the diameter of any hydrated water molecules possibly present between the ions and the electrode.

Work of the author in progress is concerned with a theoretical treatment of the dependence of  $C_T^d$  on  $V_0$ . The resulting expression for  $C_T^d$  at  $V_0=0$  is particularly simple and is  $C_T^d = C_1^0/[1+\gamma]$ . Here,  $C_1^0 = \kappa_1^0/4\pi x_0^0$  and  $\gamma = \kappa_1^0 L_D^0/\kappa_2^0 x_0^0$ .  $\kappa_1^0$  and  $\kappa_2^0$  are the differential dielectric constants<sup>2</sup> of the charge-free layer and the diffuse layer, respectively, for  $V_0=0$ , and  $L_D^0$  is the Debye length for ions in the diffuse part of the double layer for  $V_0=0$ .<sup>3</sup>  $C_1^0$  is the differential capacitance of the charge-free region for  $V_0=0$ ;  $C_T^d$  is therefore the series combination of this capacitance and that of the diffuse double layer.

If  $C_T^d$ ,  $L_D^0$ , and  $\kappa_2^0$  are known from experiment,  $\kappa_1^0/x_0^0$  can be unambiguously obtained. Table I shows the results of such a

TABLE I.

Normality	Experimental $C_T^d$ at $V_0=0$ ( $\mu\text{f}/\text{cm}^2$ )	$L_D^0/\kappa_2^0$ (cm)	$x_0/\kappa_1^0$ (cm)	Theoretical $C_T^d$ at $V_0=0$ ( $\mu\text{f}/\text{cm}^2$ )
$10^{-3}$	5.98	$1.216 \times 10^{-8}$	$2.64 \times 10^{-9}$	5.81
$10^{-2}$	13.04	$3.842 \times 10^{-9}$	$2.95 \times 10^{-9}$	12.80
$10^{-1}$	20.67	$1.216 \times 10^{-9}$	$3.060 \times 10^{-9}$	20.70
0.660	24.83	$4.740 \times 10^{-10}$	$3.086 \times 10^{-9}$	25.00
0.916	25.71	$4.028 \times 10^{-10}$	$3.037 \times 10^{-9}$	25.50

calculation for five concentrations of NaF at  $25^\circ\text{C}$ . The data are recent accurate results of Grahame.<sup>4</sup> The value of  $C_T^d$  at  $V_0=0$  was obtained by graphical interpolation of Grahame's curves of  $C_T^d$  versus  $V_a$  and from Grahame's results for the ecm potential.<sup>4</sup> In column three,  $L_D^0$  was calculated from the known concentration and a static dielectric constant of 78.5;<sup>5</sup> the same value was used for  $\kappa_2^0$ . Small changes in these latter two quantities with electrolyte

concentration were neglected. The first two quantities in column four represent small differences between large numbers and are thus rather inaccurate. It is apparent, however, that the ratio  $x_0^0/\kappa_1^0$  is substantially independent of electrolyte concentration in the range here considered. The average of the last three quantities in this column is  $x_0^0/\kappa_1^0 = 3.061 \times 10^{-9}$  cm. The resulting value of  $C_1^0$  is  $28.9 \mu\text{f}/\text{cm}^2$ . This average value of  $x_0^0/\kappa_1^0$ , a single number derived from the experimental data, was then used to compute the values of  $C_T^d$  shown in the final column of the table. Agreement between theoretical and experimental values of  $C_T^d$  is excellent for all concentrations.

The value of  $x_0^0/\kappa_1^0$  is the most interesting result of this analysis. If  $\kappa_1^0$  is taken as 78.5,  $x_0^0$  is 24Å. This large a value of  $x_0^0$  would require several water molecules between the nearest positive ion and the electrode. Such a distribution is unlikely. The most reasonable explanation of these results is that the ions are hydrated with single water molecules between nearest ions and the electrode. If we assume that  $\kappa_1^0$  for the water molecule is partly saturated by the local field of the positive ion and has an initial value of 10 at  $V_0=0$ , then  $x_0^0=3.1\text{Å}$ . This value is reasonable for the combined radius of a  $\text{Na}^+$  ion and the diameter of the hydrated water molecule. Further,  $\kappa_1^0 \cong 10$  allows the full curve versus  $V_0$  to be explained theoretically, as will be demonstrated in a later paper. The author is greatly indebted to Professor Grahame for permission to use his fine data prior to publication.

<sup>1</sup> D. C. Grahame, Chem. Revs. **41**, 441 (1947).

<sup>2</sup> D. C. Grahame, J. Chem. Phys. **18**, 903 (1950).

<sup>3</sup>  $x_0^0$  is the value of  $x_0$  at  $V_0=0$ .

<sup>4</sup> Private communication.

<sup>5</sup> Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publishing Corporation, New York, 1940) p. 367.

## The Application of a High-Speed Digital Computer to Molecular Vibration Problems\*

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WE have devised and used a code with which the SEAC<sup>1</sup> has been applied to the solution of the characteristic equations common to all molecular vibration problems. An iteration procedure has been used to find all the eigenvalues of a matrix of order 12. The method has also been used to handle a large number of smaller matrices of order 6. The entire computation is quite rapid, and high accuracy is preserved throughout. The code is applicable not only to similar equations derived from other types of physical problems but also to much larger matrices. The time required to solve completely a typical 12 by 12 matrix is of the order of one to two hours. For a 6 by 6 matrix the time is around 15 minutes. Results are printed out directly and can be given to as many as 11 significant figures.

For computational convenience the familiar  $GF$  formulation,<sup>2</sup>  $GFL=LA$ , was replaced by its symmetrized equivalent,<sup>3</sup>  $D'FDY=YA$ , where  $L=DY$ ,  $D$  gives the transformation from mass-adjusted Cartesian to internal coordinates, the prime indicates matrix transposition, and the other symbols have their usual significance.<sup>2</sup> The use of  $(D'FD-I\lambda_\alpha)y_\alpha=0$  has other practical advantages. It is easy to set up  $D$  directly, and the need for  $G$  is avoided. Symmetry factoring can still be applied with the aid of Cartesian symmetry coordinates; internal symmetry coordinates are not necessary. Characteristic vectors in terms of the mass-adjusted Cartesian coordinates are useful. If the  $l$ 's are needed they

can be obtained easily from  $l=Dy$ . It is not necessary to consider redundancies.

The iteration procedure used to solve  $(D'FD-I\lambda_\alpha)y_\alpha=0$  is conventional.<sup>4</sup> Let  $D'FD=A$ , let  $y_\alpha$  be the correct vector appropriate to  $A$  and  $\lambda_\alpha$ , let  $y_\alpha^{(n)}$  and  $\lambda_\alpha^{(n)}$  be the  $n$ th approximations to  $y_\alpha$  and  $\lambda_\alpha$ , respectively. Then the iteration scheme proceeds essentially as follows. An arbitrary vector  $y_\alpha^{(n)}$  is used to obtain an approximation to the largest root  $\lambda_\alpha^{(n)}$  by means of the familiar Rayleigh quotient  $\lambda_\alpha^{(n)} = y_\alpha'^{(n)} A y_\alpha^{(n)} / y_\alpha'^{(n)} y_\alpha^{(n)}$ . The vector  $y_\alpha^{(n)}$  is then improved by  $y_\alpha^{(n+1)} = A y_\alpha^{(n)} / \lambda_\alpha^{(n)}$ . This process is continued until convergence of successive approximations to  $y_\alpha$  is obtained. This automatically ensures convergence to  $\lambda_\alpha$ . After the largest root has been found the matrix  $A$  is modified by the scheme  $A_\beta = A - [\lambda_\alpha (y_\alpha y_\alpha') / (y_\alpha' y_\alpha)]$ , and the entire procedure is repeated with  $A_\beta$ ,  $y_\beta^{(n)}$ , and  $\lambda_\beta^{(n)}$ . The iteration routine and matrix modifications are carried out until all the roots and vectors, including those which are zero, have been found. Normally an iteration is continued until the first nine significant figures of each element of the vector are stationary. Each complete iteration step, from the  $n$ th to the  $(n+1)$ th approximation, takes about  $\frac{1}{3}$  to  $\frac{1}{2}$  second. The number of iterations required increases sharply if two roots happen to be close but not degenerate. No difficulty was encountered in separating the vectors which correspond to fundamentals only a few wave numbers apart.

The present code has already been applied to the study of the planar and nonplanar vibrations of a large number of ethylenes. Other SEAC codes have been developed and used successfully for the calculation of the matrix products and reciprocals involved in statistical and least-squares techniques for finding best sets of force constants. Details of all these applications will be published later.

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<sup>1</sup> SEAC is the designation for the National Bureau of Standards Eastern Automatic Computer. See: Natl. Bur. Standards Tech. News Bull. **34**, 121 (1950); Proc. Inst. Radio Engrs. **41**, 1300 (1953). See also: "The Incorporation of Sub-Routines into a Complete Problem on the NBS Eastern Automatic Computer," Math. Tables and Other Aids to Computation **4**, 164 (1950).

<sup>2</sup> E. B. Wilson, Jr., J. Chem. Phys. **7**, 1047 (1939); **9**, 76 (1941).

<sup>3</sup> P. Torkington, J. Chem. Phys. **17**, 1026 (1949).

<sup>4</sup> W. M. Kincaid, Quart. Appl. Math. **5**, 320 (1947).

## Erratum: Studies by Infrared Spectra on the Initiation Process in Autoxidation of Methyl Linolenate

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PAGE 952, third paragraph, line 15, "These unstable peroxides" should read: "These unstable hydroperoxides" and line 19 "structure of the peroxides," : "structure of the hydroperoxides."

This paragraph should also include: "1. These results along with the infrared absorption by hydroxyl group of hydroxylinolenate at  $2.94\mu$  indicate that methyl linolenate forms monomeric monohydroperoxide at the initial stage of autoxidation. 2. Oxygen-free nitrogen was bubbled through all the samples as a measure of precaution against further oxidation, wherever it was necessary."