tie, Blaisdell and Kaminsky,[10] as nearly as possible. These data are very accurate but their range is too limited to define the slope. The slope selected corresponds to a gas imperfection of 0.27% at the boiling point. The most profitable additional contribution to the thermodynamics of mercury would be a direct determination of the gas imperfection at temperatures appreciably above the boiling point so that pressures considerably above one atmosphere could be used.

The ideal heat of vaporization of liquid mercury is given as a function of temperature by the equation

$$H^\circ_{(g)} - H^\circ_{(l)} = \Delta H_0^\circ + \frac{5}{2}RT - (H^\circ_{(l)} - \mathrm{H}_0^\circ) = \Delta H\,(\text{ideal}) \quad (8)$$

The thermodynamic equation

$$(\partial H/\partial P)_\mathrm{T} = V - T(\partial V/\partial T)_\mathrm{P} \quad (9)$$

may be combined with the equation for gas imperfection and the data of state for the liquid to obtain the actual heat of vaporization of liquid mercury to its equilibrium vapor.

$$\Delta H\,(\text{actual}) = \Delta H(\text{ideal}) + \frac{3b'P}{T^2} + V_{(l)}\,(1 - T\alpha)(1 - P) \quad (10)$$

Values of the actual heat of vaporization are given in Table IV along with values of the vapor pressure calculated by means of the $(F^\circ - H_0^\circ)/T$ function and equation 7.

ΔH(ideal) is identical with ΔH(actual) to within one cal. mole^{-1} up to 500°K. At the boiling point ΔH(ideal) is greater by 10 cal. mole^{-1} and at 750°K. it is 46 cal. mole^{-1} greater. The difference can be calculated by means of equation 10. The volume of the liquid and α, the coefficient of expansion at t° may be obtained from the equation.[2]

$$V_{(l)} = 14.756 + 2.678 \times 10^{-3}t + 1.36 \times 10^{-7}t^2 + 9.8 \times 10^{-11}t^3 + 9.93 \times 10^{-13}t^4 \quad (11)$$

The heat content and entropy of actual mercury gas may be calculated from the equations

$$\frac{H_\mathrm{T} - H_0^\circ}{T} = \frac{5}{2}R + \frac{3bP}{T^3} \quad (12)$$

$$S = \frac{3}{2}R\ln M + \frac{5}{2}R\ln T - R\ln P + \frac{5}{2}R + \frac{2bP}{T^3} - 7.2819 \quad (13)$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

A Study of Refractive Index Increments of Weak Acids and Buffer Mixtures

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A differential refractometer which is suitable for measuring refractive index increments at 1° in the range of $\Delta n = 10^{-3}$ to 5×10^{-3} with a precision of $\Delta n = 1 \times 10^{-6}$ is described. This instrument has been used to measure the refractive index increments of buffers formed by acetic, aspartic and glutamic acids and their sodium salts and of aqueous solutions of monochloroacetic, oxalic and phosphoric acids. The variation of the integral molar increment for a constituent with concentration is discussed for buffers and for aqueous solutions. It is shown that for a restricted concentration range the refractive index increment of a solution may be represented as a summation of products of molar increments and concentrations of the various salts and weak acids at equilibrium.

One of the problems in applying the theory of moving boundary systems formed by weak electrolytes is the prediction of changes in refractive index across boundaries. The present investigation was undertaken because there appears to be no previous work on the problems encountered in buffers. The difference between the refractive index (n) of a solution and that of the solvent (n_0) is a function of the concentrations of the added substances and will be referred to as the refractive index increment. The integral increment for a constituent A in a solvent is defined as

$$\bar{k}_\mathrm{A} = (n - n_0)/\bar{c}_\mathrm{A} \quad (1)$$

where $\bar{c}_\mathrm{A}$ is the molar concentration of A including all ionized and un-ionized forms in the solution. Since we will deal here only with integral increments, the quantity defined by (1) will be referred to simply as the constituent increment.[2] If the solvent is a buffer it is to be understood that the total molar concentrations of the constituents of the buffer are to be held constant.

In general $\bar{k}_\mathrm{A}$ is a function of $\bar{c}_\mathrm{A}$, due to the fact that the relative concentrations of the various forms of the constituent A may vary and that these forms may have integral refractive index increments which are not equal. It is assumed that the increments of the individual species in the solution are additive, as expressed in equation (2).

$$n - n_0 = \sum_i^N k_i c_i \quad (2)$$

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(1) Wisconsin Alumni Research Foundation Research Fellow (1951–1952); Shell Fellow (1952–1953).

(2) The differential constituent increment is defined by

$$\bar{k}_{\mathrm{A},\mathrm{d}} = \partial(n - n_0)/\partial\bar{c}_\mathrm{A}$$

so that

$$\bar{k}_{\mathrm{A},\mathrm{d}} = \bar{k}_{\mathrm{A},\mathrm{i}} + \bar{c}_\mathrm{A}(\partial\bar{k}_{\mathrm{A},\mathrm{i}}/\partial\bar{c}_\mathrm{A})$$

where $\bar{k}_{\mathrm{A},\mathrm{i}}$ is the integral increment.

In this equation, c_i represents the molar concentration of the ith species (for example, undissociated acid, dissociated acid or salt) and k_i s the integral increment of that particular species, which is assumed to be constant in the concentration range of interest. In equation (2) the bar is omitted above k's and c's since they refer to individual species in the solution rather than constituents. In the case of a non-electrolyte or a salt of a strong acid and a strong base it is not necessary to distinguish between these two types of increments. In addition to using equation (2) to represent the refractive index increments of buffers it will be used to interpret the dependence of the constituent increment, $\bar{k}_A$, upon the constituent concentration, $\bar{c}_A$.

Equation (2) represents the first approximation to the refractive index increment for a solution and such a relationship will be especially good over a restricted range of concentrations. To achieve a higher degree of accuracy terms in further powers of the concentrations could be added. The linear approximation will be much better in the case of non-electrolytes than for electrolytes.[3]

The assumption involved in equation (2) may be clarified by considering a buffer consisting of a weak acid HA and a salt NaA. The refractive index increment for the solution may be represented as a surface in a three dimensional figure of $n - n_0$ *versus* (HA) and (NaA). It is assumed that this surface may be considered a plane in the range of HA and NaA concentrations of interest. The intersection of this surface with a vertical plane parallel to the (NaA) axis at a concentration of HA in the range of interest is a straight line with a slope of k_{NaA}. The intersection of the surface with a vertical plane parallel to the (HA) axis is a straight line of slope k_{HA}. The constants k_{NaA} and k_{HA} do not necessarily have the values which would be obtained from refractive index measurements on solutions of the single solutes. In the absence of added HA the partial hydrolysis of NaA will affect the refractive index, and in the absence of NaA, the ionization of HA will affect the refractive index as will be discussed later in this paper.

Equation (2) will be used to calculate the variation with concentration of the constituent increment of a weak acid when it is dissolved in (a) a buffer and (b) in water. In the first case an acid-base reaction occurs so that the characteristics of the buffer components are also involved, and in the second case the characteristics of the ionized acid are involved.

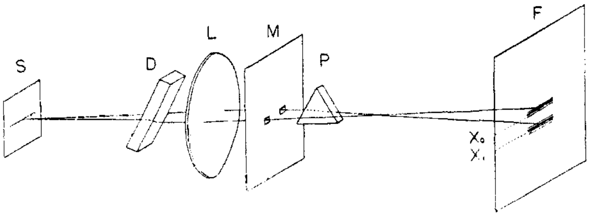

Fig. 1.—Differential refractometer: S, Gaertner precision slit (20 × 0.02 mm.); L, lens; D, deflecting plate; M, mask; P, 60° hollow prism cell; F, focal plane. The distance from the prism cell to the photographic plate is 250 cm.

The Differential Refractometer.—The elements of a schlieren optical system have been adapted for the measurement of refractive index differences at 1°. The apparatus is similar to that described by Longsworth[4] except that the photographic plate is placed in the focal plane of the schlieren lens. The optical arrangement is illustrated in Fig. 1 except for the source of illumination of the horizontal slit S (an H-4 mercury lamp, condensing lens and Wratten No. 77A filter isolating the 546.1 mμ mercury line) and the thermostat in which the prismatic cell P is immersed. Part of the light from the illuminated horizontal slit passes through a glass deflecting plate D which displaces that part of the light which passes through the reference slit and forms the slit image at x_0 in the focal plane F of the schlieren lens. Light passing through the other slit in mask M is deflected by the 60° prism cell P[5] and forms the slit image at x_1. Because of the deflecting plate these two images do not overlap, even when the cell is filled with distilled water. The slits in mask M are sufficiently narrow ($^1/_8 \times {}^1/_8$ inches) so that the secondary maxima in the diffraction patterns are quite prominent. The use of such a mask also has the advantage that only a small area of the faces of the cell is used and distortions due to imperfections over the whole face are diminished. The slit image at x_0 is a reference position with respect to which the position of the deflected image at x_1 may be measured with a comparator. This distance is measured for the cell filled with distilled water as well as with dilute aqueous solutions. The net displacement $(x_1 - x_0)_{soln} - (x_1 - x_0)_{H_2O}$ should be a linear function of the refractive index increment of the solution $(n_{soln} - n_{H_2O})$ for small increments. In this case the relation may be written

$$\Delta n = n_{soln} - n_{H_2O} = C\{(x_1 - x_0)_{soln} - (x_1 - x_0)_{H_2O}\} \quad (3)$$

Refractive index increment data of Gosting and Morris[3] for sucrose solutions have been used to calibrate the refractometer. Their values are for 1° and the mercury green line (λ 546.1 mμ). For concentrations less than 4 g./100 ml. of solution, the specific refractive index increment is given with an average uncertainty of 0.1%. By use of these data, it has been found in several different calibration experiments for Δn less than 0.005 that $C = (339.3 \pm 0.3) \times 10^{-6}$ mm.$^{-1}$. The temperature of the thermostat was regulated at 1.0 ± 0.1°.

A photograph of the slit images is shown in Fig. 2. In determining the displacement of the slit image, it has been the practice to locate for each diffraction envelope the center of the secondary band which lies next to the lower side of the central band.[6] The displacement can be determined within ± 0.003 mm. when several measurements are made on the photograph for each of two or more fillings of the prismatic cell. In the experiments reported, $x_1 - x_0$ was in the range of 2 to 15 mm. so that the error in measurement was always less than 0.15%. A mask with a straight edge aligned vertically was placed just in front of the photographic plate so that it cut off one end of each of the slit images. The photographic plates were lined up with the

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(3) For example, in the case of potassium chloride at 0.5° $\Delta n/c = 0.011405 - 0.00100\sqrt{c}$ over the concentration range 0.1 to 1.0 N (G. E. Perlman and L. G. Longsworth, THIS JOURNAL, **70**, 2719 (1948)). The increments for non-electrolytes on a weight per volume basis are more nearly constant. For sucrose at 1° the value of $(\Delta n/\Delta c) \times 10^6$ for $\Delta c = 0.5$ g./100 ml. is 1467.4 ± 1.3 for concentrations from 0.5 to 4.5 g./100 ml. (L. J. Gosting and M. S. Morris, *ibid.*, **71**, 1998 (1949)).

(4) L. G. Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

(5) Pyrocell Manufacturing Co., 207 East 84th St., New York 28, N. Y.

(6) A number of experiments were performed using two double slits in mask M so as to obtain two Rayleigh interference patterns at F. This principle is utilized in the differential refractometer of Cecil and Ogston, *J. Sci. Instruments*, **28**, 253 (1951). It was found, however, that the displacement of a given fringe might be different from that of the diffraction envelope, so that there was a shifting of the fringes with respect to the envelope which made it difficult to identify the correct fringe. This phenomenon is a result of the fact that displacement of the diffraction envelope depends upon the prism angle while the displacement of a fringe depends upon the difference in optical path at the two levels in the prism. In the case of our prism it was also found that the Rayleigh pattern was not normal because the diffraction envelopes from the two slits did not exactly superimpose.

comparator axis by use of these ends of the slit images. Periodically $(x_1 - x_0)_{H_2O}$, the displacement of the image when the cell was filled with doubly-distilled water, was redetermined.

Solutions.—In determining integral refractive index increments, measurements have been made on solutions containing acetic, aspartic and glutamic acids and their sodium salts. These solutions were prepared by dissolving known amounts of the acids and of sodium hydroxide in volumetric flasks which had been calibrated at 1°. Hence, the concentrations are for that temperature. Acetic acid and sodium hydroxide were delivered from calibrated pipets. The sodium hydroxide had been standardized against potassium acid phthalate, and the acetic acid solution had been standardized against the sodium hydroxide. Quantities of aspartic and glutamic acids were weighed directly in the volumetric flasks. These reagents, which were supplied by the Eastman Kodak Company and the Pfanstiehl Company, respectively, were twice recrystallized from water and dried at 110° for 36 hours before use.

Refractive index measurements were also made for solutions of monochloroacetic, phosphoric and oxalic acids. Concentrations of oxalic acid solutions were determined by dissolving accurately weighed quantities of the acid and diluting to the mark in volumetric flasks. Concentrations of chloroacetic and phosphoric acid solutions were determined by titrating aliquots of each solution with standard sodium hydroxide with the use of phenolphthalein as an indicator. In the case of phosphoric acid, two equivalents of acid were titrated in the method described by Kolthoff and Sandell.[7] The concentrations which were calculated were for 1°.

Refractive Index Increments of Buffers.—Measurements of refractive index increments were made using simple buffer solutions containing a single weak acid and its sodium salt.

TABLE I

REFRACTIVE INDEX INCREMENTS OF ACETATE BUFFERS AT 1° FOR 546.1 mμ

(NaOAc)	(HOAc)	$10^6\ \Delta n$ (obsd.)	$10^6\ \Delta n$ (calcd.)	Deviation, %
0.1023	0.2041	2277	2276	+0.04
.1361	.2719	3028	3029	− .03
.1362	.2213	2778	2779	− .04
.1363	.1703	2528	2527	+ .04
.1705	.2379	3280	3284	− .12
			Mean	0.05

TABLE II

REFRACTIVE INDEX INCREMENTS OF ASPARTATE BUFFERS AT 1° FOR 546.1 mμ

(NaAsp)	(HAsp)	$10^6\ \Delta n$ (obsd.)	$10^6\ \Delta n$ (calcd.)	Deviation, %
0.03400	0.03036	1708	1709	−0.06
.03406	.03725	1872	1871	+0.06
.06812	.03436	2812	2812	0
.06815	.02900	2689	2689	0
.06820	.02391	2572	2572	0
			Mean	0.02

TABLE III

REFRACTIVE INDEX INCREMENTS OF GLUTAMATE BUFFERS AT 1° FOR 546.1 mμ

(NaGlut)	(HGlut)	$10^6\ \Delta n$ (obsd.)	$10^6\ \Delta n$ (calcd.)	Deviation, %
0.03400	0.02664	1791	1790	+0.06
.03406	.03228	1936	1938	− .10
.06812	.02874	2948	2950	− .07
.06815	.02812	2939	2935	+ .14
.06820	.02122	2763	2758	+ .18
.10227	.02871	4049	4056	− .17
			Mean	0.12

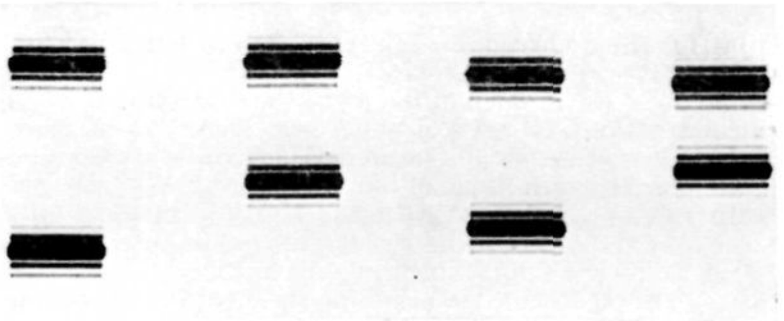

Fig. 2.—Differential refractometer photograph.

The measurements were made in the pH range near the pK of the acid in order to reduce the effect of ionization of the weak acid and hydrolysis of the salt. When this is done, the concentrations of hydrogen and hydroxyl ions are small enough so that the composition of the solution may be represented completely by the concentrations of salt and undissociated acid. In principle, it is necessary to measure Δn for two buffer solutions and to solve the two simultaneous equations for k_{HA} and k_{NaA}

$$\Delta n_1 = (\mathrm{HA})_1 k_{\mathrm{HA}} + (\mathrm{NaA})_1 k_{\mathrm{NaH}} \quad (4)$$

$$\Delta n_2 = (\mathrm{HA})_2 k_{\mathrm{HA}} + (\mathrm{NaA})_2 k_{\mathrm{NaH}} \quad (5)$$

In practice it is better to measure Δn for a large number of solutions and to obtain the k_{HA} and k_{NaA} which best represent these measurements by the least squares treatment. The results of these experiments for acetic, aspartic and glutamic acids are reported in Tables I, II and III. For aspartic and glutamic acids, each of which has three ionizable groups, the measurements are in the range of the second pK; that is, only the monosodium salts of these acids are used. The agreement between the refractive index increments calculated using the k's from the least squares treatment and the refractive index increments measured experimentally is within the experimental uncertainty. Furthermore there is no trend which indicates any dependence of these molar refractive index increments on concentration within the concentration ranges used.

Refractive index increments have also been measured for solutions containing two or three of these weak acids with their sodium salts. The increments have been calculated by the use of the equation

$$\Delta n = (\mathrm{NaOAc})k_{\mathrm{NaOAc}} + (\mathrm{HOAc})k_{\mathrm{HOAc}} + (\mathrm{NaAsp})k_{\mathrm{NaAsp}} + (\mathrm{HAsp})k_{\mathrm{HAsp}} + (\mathrm{NaGlut})k_{\mathrm{NaGlut}} + (\mathrm{HGlut})k_{\mathrm{HGlut}} \quad (6)$$

The integral refractive index increments which were employed in calculating Δn were those obtained from the data in Tables I, II and III and summarized in Table IV. The concentrations of the various salts and weak acids are not known directly from the quantities used in making up the solutions but must be calculated with the aid of the appropriate ionization constants. The following approximation method was used for these calculations. The approach to the problem is to make an approximation for the hydrogen ion concentration; for a particular hydrogen ion concentration, the concentrations of the salt and acid forms may be calculated from the relations

TABLE IV

REFRACTIVE INDEX INCREMENTS (IN L. MOLE^{-1}) FOR WEAK ACIDS AND THEIR SODIUM SALTS AT 1° FOR 546.1 mμ

Obtained by the method of least squares from the data of Tables I, II and III

	k_{HA}	k_{NaA}	$k_{\mathrm{NaA}} - k_{\mathrm{HA}}$
Acetate	0.00497	0.01232	0.00735
Aspartate	.02315	.02960	.00645
Glutamate	.02587	.03239	.00652

$$(\mathrm{NaA}) = K_{\mathrm{HA}}\bar{c}_{\mathrm{A}}/(K_{\mathrm{HA}} + (\mathrm{H}^+)) \quad (7)$$

$$(\mathrm{HA}) = \bar{c}_{\mathrm{A}} - (\mathrm{NaA}) \quad (8)$$

Since the solutions were made up with weak acids and sodium hydroxide the following relation must hold.

$$(\mathrm{NaA}_1) + (\mathrm{NaA}_2) + \ldots + (\mathrm{NaA}_n) = \bar{c}_{\mathrm{Na}} \quad (9)$$

There will be only one hydrogen ion concentration, how-

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[7] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 562.

ever, for which equation (9) will be satisfied. This correct value for the hydrogen ion concentration is arrived at by a series of successive approximations. The ionization constants used in the calculations were the apparent constants calculated from the pH's of buffer solutions at 1° measured with a glass electrode. The ionization constants obtained in an ionic strength range of 0.02 to 0.4 were $K_{\mathrm{HOAc}} = 2.00 \times 10^{-5}$, $K_{\mathrm{HGlut}} = 5.25 \times 10^{-5}$, and $K_{\mathrm{HAsp}} = 11.75 \times 10^{-5}$. Since only the ratios of these constants are important in the calculations, the errors which may be introduced are smaller than might be expected considering the error in the absolute measurements in pH. It is seen from Table V that the agreement between Δn (obsd.) and Δn (calcd.) is good. Undoubtedly the checks are as good as can be expected from a consideration of the uncertainty in the compositions of the solutions.

TABLE V

COMPARISON OF CALCULATED AND OBSERVED VALUES FOR Δn FOR SOLUTIONS CONTAINING MORE THAN ONE WEAK ACID

(NaOH)	(HOAc)	(HGlut)	(HAsp)	10^6 Δn (obsd.)	10^6 Δn (calcd.)	Deviation, %
0.05450	0	0.04961	0.05229	2852	2847	+0.18
.06813	0.2002	.03243	.05339	3534	3537	− .08
.1000	.2000	.02000	.02000	2686	2685	+ .03
.1000	.2000	.04000	.04000	3653	3649	+ .11
.1022	.1502	.07132	0	3309	3306	+ .09
.1022	.2002	.03029	.03186	3236	3227	+ .28
.1022	.2002	.04459	.02858	3521	3524	− .09
.1022	.2002	0	.08155	3585	3586	− .03
						Mean 0.11

Constituent Increments of Weak Acids in a Buffer Solvent.—The difference between the refractive index of a buffer and a solution of a weak acid in that buffer may be used to calculate an integral refractive index increment for the weak acid constituent. Since chemical reaction will, in general, occur between the added weak acid and the salt of the buffer, the increment determined in this manner will also depend on the properties of the buffer.

Longsworth[8] has measured the changes in refractive index which occur when aspartic and glutamic acids are dissolved in an acetate buffer solvent. He reported the increment for 0.04 molal weak acid in 0.1 N sodium acetate buffer solvent of pH 4.6 at 1°. To a first approximation his solutions may be represented as: (a) 0.2 M HOAc, 0.1 M NaOH; (b) 0.2 M HOAc, 0.1 M NaOH, 0.04 M HGlut; (c) 0.2 M HOAc, 0.1 M NaOH, 0.04 M HAsp. Longsworth measured the difference in optical path between the buffer and the solution containing added weak acid by an interference method at 1°. He found that with a 2.5-cm. path and using mercury green light that the increment for 0.04 molal glutamic acid is 46.2 fringes and for aspartic acid of the same concentration, 40.8 fringes. Thus the molal increments for the weak acid constituents are

$$\bar{k}_{\mathrm{Glut}} = \frac{(46.2)(5.46 \times 10^{-5})}{(2.5)(0.04)} = 0.0252$$

$$\bar{k}_{\mathrm{Asp}} = \frac{(40.8)(5.46 \times 10^{-5})}{(2.5)(0.04)} = 0.0223$$

It is noteworthy that the constituent increment $\bar{k}$ for a weak acid will, in general, depend upon the constituent concentration of weak acid in a buffer of fixed composition. The refractive indices of the buffer (n') and the buffer solution containing added weak acid (n) are

$$n' = n_{\mathrm{H_2O}} + (\mathrm{NaB})'k_{\mathrm{NaB}} + (\mathrm{HB})'k_{\mathrm{HB}} \quad (10)$$

$$n = n_{\mathrm{H_2O}} + (\mathrm{NaB})k_{\mathrm{NaB}} + (\mathrm{HB})k_{\mathrm{HB}} + (\mathrm{NaA})k_{\mathrm{NaA}} + (\mathrm{HA})k_{\mathrm{HA}} \quad (11)$$

Furthermore

$$(\mathrm{NaA}) + (\mathrm{HA}) = \bar{c}_{\mathrm{A}}$$

$$(\mathrm{NaA}) = (\mathrm{NaB})' - (\mathrm{NaB}) = (\mathrm{HB}) - (\mathrm{HB})'$$

Hence

$$n - n' = -(\mathrm{NaA})k_{\mathrm{NaB}} + (\mathrm{NaA})k_{\mathrm{HB}} + (\mathrm{NaA})k_{\mathrm{NaA}} + \{c_{\mathrm{A}} - (\mathrm{NaA})\, k_{\mathrm{HA}}\} \quad (12)$$

$$\frac{n - n'}{\bar{c}_{\mathrm{A}}} = \bar{k}_{\mathrm{A}} = k_{\mathrm{HA}} + \frac{(\mathrm{NaA})}{\bar{c}_{\mathrm{A}}}\{(k_{\mathrm{NaA}} - k_{\mathrm{HA}}) - (k_{\mathrm{NaB}} - k_{\mathrm{HB}})\} \quad (13)$$

$$\bar{k}_{\mathrm{A}} = k_{\mathrm{HA}} + \frac{K_{\mathrm{HA}}}{K_{\mathrm{HA}} + (\mathrm{H}^+)}\{(k_{\mathrm{NaA}} - k_{\mathrm{HA}}) - (k_{\mathrm{NaB}} - k_{\mathrm{HB}})\} \quad (14)$$

The quantity in braces may be considered to be the change in integral increment for the reaction which occurs when HA is added to the buffer. The quantity $K_{\mathrm{HA}}/(K_{\mathrm{HA}} + (\mathrm{H}^+))$ is the fraction of added acid which is converted to the salt form by reaction with the buffer.

The hydrogen ion concentration of the solution depends upon the amount of weak acid HA which has been added to a fixed quantity of buffer. If the difference between the integral refractive index increments of salt and acid forms is not the same value for both the weak acid and the buffer, $\bar{k}_{\mathrm{A}}$ is a function of the concentration of the weak acid. Substituting values for refractive index increments, which are given in Table IV, and the appropriate equilibrium constants, the following equations are obtained

$$\bar{k}_{\mathrm{Glut}} = 0.02587 - \frac{0.00436}{5.25 + 10^5(\mathrm{H}^+)} \quad (15)$$

$$\bar{k}_{\mathrm{Asp}} = 0.02315 - \frac{0.01058}{11.75 + 10^5(\mathrm{H}^+)} \quad (16)$$

By use of the method which has been described the hydrogen ion concentrations of solutions (b) and (c) have been calculated. These values are $(\mathrm{H}^+) = 3.30 \times 10^{-5}$ for (b) and $(\mathrm{H}^+) = 3.75 \times 10^{-5}$ for (c). Substituting these values in equations (15) and (16), respectively, it follows that $\bar{k}_{\mathrm{Glut}} = 0.02536$ and $\bar{k}_{\mathrm{Asp}} = 0.02247$. These calculated values for a weak acid concentration of 0.04 M are in good agreement with the experimental results of Longsworth. The difference between these computed values and the experimental values may be due to the fact that the constituent increments were calculated for solutions not identical with those used by Longsworth.

If the constituent increment were determined at a weak acid concentration less than 0.04 M, it would be expected that a lower value for the increment would be obtained. This is due to the fact that the hydrogen ion concentration diminishes with decreasing concentration of aspartic acid or glutamic acid in a fixed quantity of acetate buffer, and the effect of this change is seen in equations (15) or (16). If the weak acid concentration were made infinitesimally small, the hydrogen ion concentration would be that of the buffer solution,

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(8) L. G. Longsworth, *Anal. Chem.*, **23**, 346 (1951).

namely, $(H^+) = 2.00 \times 10^{-5}$. Hence, it would be expected that $\bar{k}_{\mathrm{Glut}}$ and $\bar{k}_{\mathrm{Asp}}$ should approach limits of 0.02527 and 0.02238, respectively, as the weak acid concentration approaches zero.

Effect of Ionization on Refractive Index Increment.—If a weak acid is dissolved in a solution of its salt or in a solution of a strong acid, ionization is repressed so that the increment for the undissociated weak acid may be obtained, but if the weak acid is simply dissolved in water ionization occurs and the measured increment is not that of the undissociated acid. Consider a solution which contains the acid HA. The integral increment for the undissociated acid is designated k_{HA}. If it were completely ionized, the integral increment could be designated as $k_{\mathrm{H^+A^-}}$. At intermediate stages of ionization, the result obtained by dividing the measured increment by the molar concentration would be between k_{HA} and $k_{\mathrm{H^+A^-}}$. Let $\bar{c}$ moles of the weak acid be contained in a liter of aqueous solution. If α is the fraction which is ionized, then $(\mathrm{HA}) = (1 - \alpha)c$ and $(\mathrm{H^+A^-}) = \alpha\bar{c}$. Provided that the increment is linear in the concentration of each form, the refractive index of the solution would be

$$n_{\mathrm{soln}} = n_{\mathrm{H_2O}} + (1 - \alpha)\bar{c}k_{\mathrm{HA}} + \alpha\bar{c}k_{\mathrm{H^+A^-}} \quad (17)$$

Hence, the constituent increment $\Delta n/\bar{c}$ is

$$\bar{k}_{\mathrm{A}} = k_{\mathrm{HA}} + (k_{\mathrm{H^+A^-}} - k_{\mathrm{HA}})\alpha \quad (18)$$

Then the constituent increment should be a linear function of the degree of ionization, except in the special case when $k_{\mathrm{H^+A^-}} = k_{\mathrm{HA}}$.

The applicability of equation (18) has been tested by measuring the refractive index increments of solutions of monochloroacetic acid and solutions of phosphoric acid. The degree of ionization was calculated by use of the equation $\alpha^2 c/(1 - \alpha) = K$. Although phosphoric acid is tribasic, only the first ionization had to be considered. The value of K for each acid was obtained from the equation $\log K = -A^*/T + D^* - C^*T$. The appropriate values of the constants A^*, D^* and C^* are listed by Harned and Owen.[9] Computation of the constants for monochloroacetic (HM) and phosphoric (HP) acids at 1° yields $K_{\mathrm{HM}} = 1.525 \times 10^{-3}$ and $K_{(1)\mathrm{HP}} = 8.734 \times 10^{-3}$, respectively. Plots of constituent increment against α for these acids are shown in Fig. 3. The least squares treatment has been used to obtain the theoretical lines. For monochloroacetic acid, the experimental data fit the equation $\bar{k} = 0.01017 + 0.00530\alpha$ with a mean percentage deviation of 0.08%. For phosphoric acid, the equation $\bar{k} = 0.00860 + 0.00738\alpha$ is obeyed with a mean percentage deviation of 0.12%. The interpretation of the constants in these two equations is that $k_{\mathrm{HM}} = 0.01017$, $k_{\mathrm{H^+M^-}} = 0.01547$, $k_{\mathrm{H_3PO_4}} = 0.00860$, and $k_{\mathrm{H^+H_2PO_4^-}} = 0.01598$.

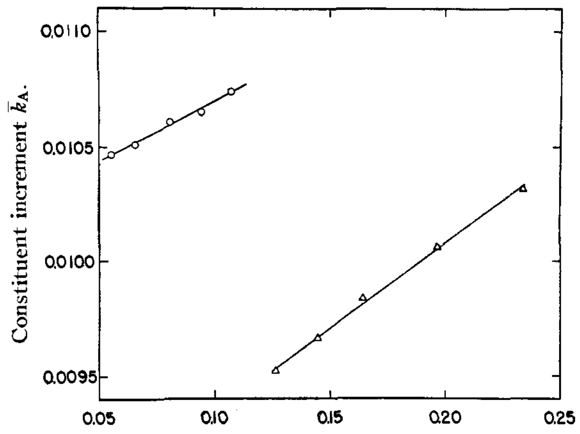

Fig. 3.—Variation of constituent increments for phosphoric acid (Δ) and chloroacetic acid (O) with degree of ionization (α) in water at 1°.

For acetic acid the dependence of the constituent increment is far less pronounced than it is for chloroacetic acid due to the fact that acetic acid is considerably weaker as an acid. However, it has been possible to demonstrate that the constituent increment does increase with dilution. For example, when the constituent concentration of acetate, $\bar{c}_{\mathrm{OAc}}$, is 0.6, the constituent increment for acetate, $\bar{k}_{\mathrm{OAc}}$, is 0.00498; at $\bar{c}_{\mathrm{OAc}} = 0.1$, $\bar{k}_{\mathrm{OAc}} = 0.00501$. From these measurements and others with solutions containing only acetic acid, it appears that the data are represented best by values of $k_{\mathrm{HOAc}} = 0.00495$ and $k_{\mathrm{H^+OAc^-}} = 0.0096$. It will be recalled that a value of 0.00497 was obtained for the integral increment for undissociated HOAc in a buffer, in which NaOAc represses ionization. The difference between these two values for the integral increment of un-ionized acetic acid is just a little larger than the experimental error which suggests that there may be an effect of ionic strength on the increment. The increment for un-ionized weak acid may also be measured by adding it to a solution of a strong acid which represses ionization. A number of measurements of the increment of acetic acid in 0.1 *M* hydrochloric acid yielded an average value of $k_{\mathrm{HOAc}} = 0.00496$, in very good agreement with the value obtained in acetate buffers of 0.1–0.17 ionic strength. It is of interest to compare the value of the integral increment for dissociated acetic acid calculated from equation (18) with that calculated with the following equation based upon the assumption of the additivity of integral increments for individual ion species.

$$k_{\mathrm{H^+OAc^-}} = k_{\mathrm{NaOAc}} + k_{\mathrm{HCl}} - k_{\mathrm{NaCl}} \quad (19)$$

The increments for 0.1 *N* solutions of sodium acetate, hydrochloric acid and sodium chloride have been measured at 1° and 546.1 mμ, and the values of the integral increments are 0.01232 (from Table IV), 0.00896 and 0.01123, respectively. Thus equation (19) leads to a value of 0.01005 in comparison with 0.0096 obtained from equation (18). This agreement is considered to be satisfactory at the present time in view of the difficulty in accurately determining the slope of a plot of $\bar{k}_{\mathrm{HOAc}}$ *versus* α.

For acetic, chloroacetic and phosphoric acids, it has been shown that the difference in integral increment for completely ionized and completely un-ionized forms of the acid lies in the range 0.004–0.008. Assuming a difference $k_{\mathrm{H^+Asp^-}} - k_{\mathrm{HAsp}} =$

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[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 583.

0.006, it is possible to estimate the error which would have been encountered in measuring the integral increment for aspartic acid by ignoring the effect of ionization. If $\bar{c}_{\text{Asp}} = 0.03$, the degree of ionization is approximately $\sqrt{K/c} = \sqrt{11.75 \times 10^{-5}/0.03} = 0.063$. In this case the percentage error would be 1.6%. For glutamic acid, the percentage error would undoubtedly be smaller, since glutamic is a weaker acid and has a larger integral increment. Yet, in both cases the probable error arising from the omission of ionization considerations would be less than the error encountered in the experimental method.

It is possible, at least in principle, to calculate the ionization constant for a weak acid from the variation of its constituent refractive index increment with concentration. For each concentration equation (18) relates the constituent increment $(n - n_0)/c$ to three unknown quantities k_{HA}, $k_{\text{H}^+\text{A}^-}$ and α. The ionization constant K may be considered as a third unknown in place of α, inasmuch as the two quantities are related by the equation $\alpha = (-K + \sqrt{K^2 + 4Kc})/2c$. Hence, it is possible to calculate K from measurements of $n - n_0$ at three concentrations. For oxalic acid, an ionization constant $K_1 = 0.12 \pm 0.02$ at 1° has been calculated in this manner. There is considerable uncertainty in this value of K because it is necessary in solving the three simultaneous equations to use the small differences between the constituent increments at the three concentrations. These small differences are subject to comparatively large errors which are reflected in the calculated value of the ionization constant. In general, this fact presents a serious limitation to the determination of ionization constants by this method.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Isopropylgermanium Halides, Oxides and Hydroxide; Grignard Reaction

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In contrast with the known reaction $4\ n\text{-PrMgBr} + \text{GeBr}_4 = n\text{-Pr}_4\text{Ge} + 4\text{MgBr}_2$, an excess of isopropylmagnesium bromide (or chloride) furnishes only partial substitution products $i\text{-PrMgBr} + \text{GeBr}_4 \rightarrow \text{MgBr}_2 + i\text{-Pr}_2\text{GeBr}_2 + i\text{-Pr}_3\text{GeBr}$ and also furnishes a polymeric solid, essentially $(i\text{-PrGe})_n$. The hydrolysis of $i\text{-Pr}_3\text{GeBr}$ produces $i\text{-Pr}_3\text{GeOH}$, rather than the expected $(i\text{-Pr}_3\text{Ge})_2\text{O}$, which results in reaction of the bromide with silver carbonate in dry hexane. Only one form of $(i\text{-Pr}_2\text{GeO})_3$ is now known. Steric effects may explain differences between n-propylgermanium and isopropylgermanium derivatives, and also differences in their formation through the Grignard reaction. New compounds include the following: $i\text{-Pr}_3\text{GeOH}$, $i\text{-Pr}_3\text{GeF}$, $i\text{-Pr}_3\text{GeCl}$, $i\text{-Pr}_3\text{GeBr}$, $i\text{-Pr}_3\text{GeI}$, $i\text{-Pr}_3\text{Ge(NCS)}$ and $(i\text{-Pr}_3\text{Ge})_2\text{O}$; $(i\text{-Pr}_2\text{GeO})_3$, $i\text{-Pr}_2\text{GeF}_2$, $i\text{-Pr}_2\text{GeCl}_2$, $i\text{-Pr}_2\text{GeBr}_2$ and $i\text{-Pr}_2\text{GeI}_2$.

Previous results with tri-n-propylgermanium[1] and di-n-propylgermanium[2] halides and oxides laid the groundwork for an investigation of diisopropylgermanium and triisopropylgermanium halides and oxides. One of the main purposes of this paper was to evaluate the steric factor of two or more isopropyl groups in germanium compounds; germanium lies between tin, which offers no steric troubles, and silicon, which offers definite steric limitations. Difficulties with diisopropyldichlorosilane and triisopropylchlorosilane, as well as failure to obtain tetraisopropylsilane,[3] evidently were due to steric factors. Isopropylgermanium trichloride[4] offered no unusual problem in the synthesis, yet the corresponding isopropyltrichlorosilane and aniline[5] reacted quite slowly, requiring a large excess of aniline and standing for several days for completion of the reaction.

Some salient difficulties with di- and triisopropylgermanium compounds and some differences from the corresponding n-propylgermanium analogs are listed in the following sentences. First, an excess of isopropylmagnesium halide and a smaller amount of germanium tetrahalide produced a mixture of diisopropylgermanium dihalide and triisopropylgermanium halide, also an unexpected, difficultly-redissolvable solid polymer, essentially $(i\text{-PrGe})_n$; tetraisopropylgermanium was absent. Second, the hydrolysis of triisopropylgermanium bromide furnished only triisopropylgermanium hydroxide (which lost water slowly below 200°), unlike the hydrolysis of a tri-n-propylgermanium halide, probably $2\ n\text{-Pr}_3\text{GeBr} + 2\ \text{H}_2\text{O} = 2\ n\text{-Pr}_3\text{GeOH}$ and then $2\ n\text{-Pr}_3\text{GeOH} = (n\text{-Pr}_3\text{Ge})_2\text{O} + \text{H}_2\text{O}$. Third, only one crystalline form of trimeric diisopropylgermanium oxide appeared; this may be due either to steric factors or to a melting point above room temperature. Fourth, esterification with organic acids such as acetic gave impure products; in the successful preparation of triisopropylgermanium acetate (to be reported later separately) esterification with acetic acid cannot be the process. This is unlike the reactions with halogen acids reported herein. Fifth, antimony trifluoride fluorinated diisopropylgermanium dibromide completely and rapidly, while it fluorinated triisopropylgermanium bromide only slightly in an apparently novel approach to the separation problem. Sixth, as expected, the more compact isopropylgermanium compounds generally had lower boiling points and often had higher melting points

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[1] H. H. Anderson, THIS JOURNAL, **73**, 5440 (1951).

[2] H. H. Anderson, *ibid.*, **74**, 2370 (1952).

[3] C. D. Hurd and W. A. Yarnall, *ibid.*, **71**, 755 (1949). Grignard method. For more successful lithium method see H. Gilman and R. W. Clark, *ibid.*, **69**, 1499 (1947).

[4] E. G. Rochow, R. Didtschenko and R. C. West, Jr., *ibid.*, **73**, 5486 (1951).

[5] H. H. Anderson, *ibid.*, **73**, 2351 (1951).