[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF WESTERN AUSTRALIA AND OF THE UNIVERSITY OF MALAYA]

The Variation of Equivalent Conductance with Concentration and Temperature

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Recent theoretical extensions of the Onsager conductance equation are tested by comparison with conductance data for sodium chloride, potassium chloride, potassium bromide, potassium iodide and hydrochloric acid over a range of concentration and at temperatures between 5° and 55° or 65°. The new equations are found to represent the experimental data with an average deviation of 0.022% using, in addition to the limiting conductances, only one parameter characteristic of each electrolyte. This parameter, which has the important property of being independent of temperature, is the "distance of closest approach" of the ions.

In two previous communications, the theory of the electrophoretic effect in the diffusion and conductance of strong electrolytes has been examined critically,[1a] and a successful theoretical expression for the variation of transference numbers with concentration[1b] has been developed. In reference 1b Falkenhagen's recent modification of the theory of the relaxation effect[2] was combined with the theory of the electrophoretic effect to yield an expression which for 1:1 electrolytes takes the form[3]

$$\Lambda = \left(\Lambda^0 - \frac{82.5}{\eta(\epsilon T)^{1/2}}\frac{\sqrt{c}}{1+\kappa a}\right)\left(1 + \frac{\Delta X}{X}\right) \qquad (1)$$

where the relaxation effect $\Delta X/X$ is given by Falkenhagen's expression. Ignoring the slight effect of the modified distribution function used by Falkenhagen (which will make an inappreciable difference below 0.1 M), his expression may be simplified for a 1:1 electrolyte to

$$\frac{\Delta X}{X} = -\frac{\mathbf{e}^2}{3\epsilon kT}(0.2929\kappa)\frac{e^{0.2929\kappa a} - 1}{0.2929\kappa a(1+\kappa a)} \qquad (2)$$

For values of κa less than about 0.3, this equation 2 approximates closely (on expanding the exponential) to the result

$$\frac{\Delta X}{X} = -\frac{\mathbf{e}^2}{3\epsilon kT} \times \frac{0.2929\kappa}{1+\kappa a} \qquad (3)$$

which differs from Onsager's limiting formula[4] only by the factor $1/(1 + \kappa a)$. On substituting equation 3 in equation 1 and neglecting the second order cross-product term, one obtains for a 1:1 electrolyte

$$\Lambda = \Lambda^0 - \frac{(B_1\Lambda^0 + B_2)\sqrt{c}}{1 + B\mathring{a}\sqrt{c}} \qquad (4)$$

where

$$\begin{aligned} B_1 &= 8.20 \times 10^5/(\epsilon T)^{3/2} \\ B_2 &= 82.5/[\eta(\epsilon T)^{1/2}] \\ B &= 50.29/(\epsilon T)^{1/2} \end{aligned} \qquad (4a)$$

and $\mathring{a}$ is the distance of closest approach of the ions, expressed in ångströms. Equation 4 will be seen to be identical with that proposed as an empirical modification of the Onsager limiting law by Hasted and Ritson,[5] and differs from the limiting formula only by the factor $1/(1 + \kappa a)$, just as in the case of the formula for the activity coefficient. It is easily shown that errors involved in the approximation from equation 2 to equation 3, and from equations 3 and 1 to equation 4, are proportional to $c/(1 + B\mathring{a}\sqrt{c})^2$. Also, by differentiating equation 4 partially with respect to $\mathring{a}$, one finds that

$$\frac{\partial \Lambda}{\partial \mathring{a}} \propto \frac{c}{(1 + B\mathring{a}\sqrt{c})^2}$$

It follows that the effect of these approximations can be accurately compensated by a small change in the value of $\mathring{a}$; and since this is a disposable parameter of the theory, equation 4 should be capable of representing the conductivities of fully-ionized 1:1 electrolytes with good accuracy up to moderate concentrations.

We now proceed to a comprehensive test of equation 4. For this purpose we shall use modern measurements on a number of aqueous 1:1 electrolytes *over a wide range of temperatures;* because of the substantial temperature dependence of the viscosity of water, the validity of equation 4 is best tested over a range of temperature as well as of concentration. The most comprehensive study of the variation of conductivity with temperature and concentration is that of Owen and Sweeton[6] on hydrochloric acid solutions at 10° intervals from 5° to 65°; they gave unsmoothed experimental results for concentrations from about 0.001 M up to 0.08 M, and smoothed results at rounded higher concentrations. Here we shall use only their unsmoothed results. The next most thorough investigation is that of Owen and Zeldes[7] on potassium iodide solutions up from 0.001 M to 0.018 M and from 5° to 55°; again the unsmoothed data are available. Gordon and co-workers[8] have studied potassium chloride, potassium bromide and sodium chloride solutions from 0.0005 M to 0.01 M and from 15° to 45°, and their work has been supplemented by Owen and Zeldes[7] who made measurements on potassium chloride and bromide at 5°, 25° and 55°. For these five electrolytes we therefore have accurate data for a large part of the liquid–water range. In addition, there are the extremely careful measurements of Shedlovsky,[9] at 25° only. Because there are minor variations of opinion about the correct value of the limiting

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[1] (a) R. H. Stokes, THIS JOURNAL, **75**, 4563 (1953); (b) **76**, 1988 (1954).

[2] H. Falkenhagen, M. Leist and G. Kelbg, *Ann. Physik*, [6] **11**, 51 (1952).

[3] The notation is that of references 1a and 1b.

[4] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

[5] D. M. Hasted and J. B. Ritson, *J. Chem. Phys.*, **16**, 11 (1948).

[6] B. B. Owen and F. H. Sweeton, THIS JOURNAL, **63**, 2811 (1941).

[7] B. B. Owen and H. Zeldes, *J. Chem. Phys.*, **18**, 1083 (1950).

[8] G. C. Benson and A. R. Gordon, *ibid.*, **13**, 473 (1945); R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

[9] T. Shedlovsky, *ibid.*, **54**, 1411 (1932) (the values reported in this paper have been converted to the Jones and Bradshaw standard).

conductivity Λ^0 for some salts, we shall not use the values given by the authors referred to, but instead rearrange equation 4 to read

$$\Lambda^0 = \Lambda + \frac{B_1\Lambda + B_2}{1 + (B\mathring{a} - B_1)\sqrt{c}}\sqrt{c} \qquad (5)$$

Table I

Values of the Theoretical Constants in Equations 4, 5, and 6 for Aqueous Solutions of 1:1 Electrolytes

Computed with dielectric constants from ref. 10, viscosities from ref. 11, proton charge = 4.803 × 10^{-10} e.s.u., ice-point = 273.16, and Boltzmann's constant = 1.3804 × 10^{-16} erg molecule^{-1} deg.$^{-1}$.

Temp., °C.	B_1	B_2	B
5	0.2212	35.1_1	0.3249
15	.2249	46.9_8	.3267
25	.2289	60.3_0	.3286
35	.2333	75.0_9	.3307
45	.2381	91.2_1	.3330
55	.2432	106.8	.3353
65	.2487	127.3	.3379

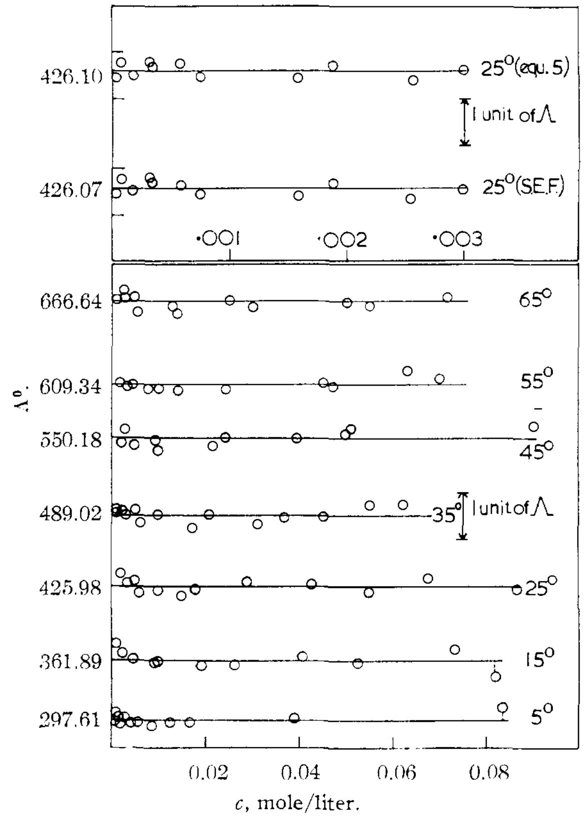

Fig. 1.—Deviation plots for the limiting equivalent conductances of hydrochloric acid at various temperatures: upper two curves from data of Shedlovsky,[12] others from data of Owen and Sweeton.[6] The Λ^0 values, plotted as circles of radius 0.1 equivalent conductance units, were computed from equation 5 with $\mathring{a}$ = 4.3 in all cases, except for the set marked 25° (S.E.F.), where the Shedlovsky extrapolation function (eq. 6) was used. The vertical scale is constant throughout the figure, and is indicated by arrowheads. The horizontal lines represent the mean values of Λ^0 for each set of results.

In this form, once the value of the single parameter $\mathring{a}$ is decided upon, a value of Λ^0 can be calculated from each individual measurement; the constancy of Λ^0 at all concentrations is the criterion of the correctness of the $\mathring{a}$ value. The theoretical constants B_1, B_2 and B are computed by equations 4a using Wyman's[10] values of the dielectric constant and Bingham and Jackson's[11] for the viscosity of water, and are given in Table I. The hydrochloric acid data are in many ways the most suitable for testing the equation; in particular, since the ionization of water and carbonic acid is suppressed by this solute, the solvent corrections are negligible so that results for even extremely dilute solutions may be used with complete confidence. Therefore we shall first compare equation 5 with the conventional Shedlovsky[12] extrapolation formula

$$\Lambda^0 = \Lambda^{0\prime} + bc = \Lambda + \frac{B_1\Lambda + B_2}{1 - B_1\sqrt{c}}\sqrt{c} + bc \qquad (6)$$

where b is an empirical constant, using Shedlovsky's 11 measurements between 0.000028 and 0.003 M HCl at 25°. We find with the value b = 235 determined by the method of least squares

$$\left.\begin{array}{l}\Lambda^0 = 426.10 \pm 0.14 \text{ (eq. 5, } \mathring{a} = 4.3) \\ \text{and} \\ \Lambda^0 = 426.07 \pm 0.14 \text{ (eq. 6, } b = 235)\end{array}\right\} \qquad (7)$$

It will be noted that we are unable to confirm exactly the value 426.16 obtained from equation 6 by Shedlovsky, but in view of the experimental scatter of about ±0.03% in the data (shown graphically in the upper two curves of Fig. 1) the difference of 0.007% between the Λ^0 results in 7 cannot be called significant. It thus appears that equation 5 is valid within experimental error up to 0.003 M. Next, let us see how it fits the data at higher concentrations; for this purpose we apply it first to the data of Owen and Sweeton at 25°, which extend from 0.001 to 0.086 M. The same value $\mathring{a}$ = 4.3 gives from their results

$$\Lambda^0 = 425.98 \pm 0.13 \quad (\text{eq. 5, } \mathring{a} = 4.3)$$

The Shedlovsky equation 6 on the other hand gives from these results

$$\Lambda^0 = 426.29 \pm 0.17 \quad (\text{eq. 6, } b = 168.8)$$

the constant b = 168.8 being again determined by least squares. The use of equation 6 over this range, therefore, gives a result 0.052% high, if that from the more dilute solutions be taken as correct, while the present equation 5 gives a result 0.028% low. The mean deviation from equation 5 is also somewhat lower than that from equation 6. The present theoretical equation therefore compares very favorably with the empirical one of Shedlovsky.

On extending the tests to other temperatures and solutes, a very interesting result emerges: *the value of $\mathring{a}$ is constant for each solute at all temperatures from 5° to 65°.* This gives very strong support to equation 5 since it indicates that $\mathring{a}$ is a real molecular parameter and not merely a carry-all for all manner of deviations, unlike the parameter b of equation 6, which varies widely with temperature.

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(10) J. Wyman, Jr., and E. N. Ingalls, This Journal, **60**, 1182 (1938).

(11) E. C. Bingham and R. F. Jackson, *Bull. Bur. Standards*, **14**, 59 (1918).

(12) T. Shedlovsky, This Journal, **54**, 1405 (1932).

The results of our computations are summarized in Table II. The average and maximum deviations from the mean value of Λ^0 are given as percentages to facilitate comparison of the quality of fit for various temperatures and electrolytes. The value of Λ^0 given in the second column is the one computed by equation 5; that in the last column is that given by the authors referred to in column 7, who used in some cases equation 6 and in some cases a further extension of it by the addition of a second empirical term in $c \log c$. Such an equation, containing two empirical constants besides Λ^0, may lead to a slightly better fit, but also involves some risk of over-weighting the more dilute measurements, for which the uncertainty due to solvent corrections is appreciable. This is especially true in cases where only a few measurements are made, as with Owen and Zeldes' work on potassium bromide at 25°. We believe that the Λ^0 values obtained by the present method from equation 5 are preferable to those given in the last column, because: (a) the equation has a sound theoretical basis and (b) the single parameter $\mathring{a}$ for each solute describes the variation of Λ with c at all temperatures.

TABLE II

TESTS OF EQUATION 5: $\Lambda^0 = \Lambda + \dfrac{(B_1\Lambda + B_2)\sqrt{c}}{1 + (B\mathring{a} - B_1)\sqrt{c}}$

O + S, Owen and Sweeton, ref. 6; S, Shedlovsky, ref. 9, converted to Jones and Bradshaw 0.1 demal standard; G, Gordon, *et al.*, ref. 8 (direct current method); O + Z, Owen and Zeldes, ref. 7. Λ° (S.E.F.) denotes the values obtained by the observers named, using the Shedlovsky extrapolation function (eq. 6) or a modification thereof with a further adjustable parameter.

Temp., °C.	Λ^0 mean eq. 5	Mean δ, %	Max. δ, %	Number of points	Range molar	Observer	Λ^0 (S.E.F.)
HCl, $\mathring{a}$ = 4.3 at all temperatures							
5	297.61	0.03	0.09	12	0.001–0.083	O + S	297.6
15	361.89	.04	.09	11	.001– .082	O + S	362.0
25	425.98	.03	.06	12	.002– .086	O + S	426.2
25	426.10	.03	.05	11	.00003– .003	S	426.07[a]
35	489.02	.02	.06	14	.001– .062	O + S	489.2
45	550.18	.02	.05	11	.002– .090	O + S	550.3
55	609.34	.02	.05	11	.002– .070	O + S	609.5
65	666.64	.02	.06	12	.001– .072	O + S	666.8
NaCl, $\mathring{a}$ = 3.8 at all temperatures							
15	101.07	0.04	0.07	5	0.0005–0.01	G	101.18
25	126.45	.005	.01	5	.0005– .01	G	126.45
35	153.76	.01	.02	5	.0005– .01	G	153.75
45	182.64	.005	.01	5	.0005– .01	G	182.65
KCl, $\mathring{a}$ = 3.3 at all temperatures							
5	94.21	0.03	0.06	14	0.001– 0.02	O + Z	94.26
15	120.98	.02	.06	5	.0005– .01	G	121.07
25	149.80	.01	.02	5	.0005– .01	G	149.85
25	149.82	.03	.05	7	.001– .02	O + Z	149.88
35	180.39	.005	.01	5	.0005– .01	G	180.42
45	212.38	.005	.01	5	.0005– .01	G	212.41
55	245.73	.03	.06	12	.002– .02	O + Z	245.69
KBr, $\mathring{a}$ = 3.8 at all temperatures							
5	95.92	0.02	0.04	5	0.001– 0.008	O + Z	96.00
15	122.84	.025	.07	5	.0005– .01	G	122.81
25	151.64	.004	.006	5	.0005– .01	G	151.64
25	151.60	.02	.04	5	.001– .007	O + Z	151.68
35	182.26	.01	.03	5	.0005– .01	G	182.24
45	214.14	.005	.005	5	.0005– .01	G	214.17
55	247.04	.02	.05	7	.001– .013	O + Z	247.15
KI, $\mathring{a}$ = 4.5 at all temperatures							
5	95.25	0.02	0.03	8	0.001–0.018	O + Z	95.32
15	121.78	.02	.03	8	.001– .017	O + Z	121.83
25	150.32	.01	.03	11	.001– .016	O + Z	150.34
25	150.46	.01	.02	4	.0005– .005	G	150.47
35	180.53	.02	.06	8	.001– .018	O + Z	180.60
45	212.06	.04	.05	7	.0016– .017	O + Z	212.13
55	244.65	.02	.05	8	.001– .016	O + Z	244.73

[a] Computed by present authors. Shedlovsky gave 426.16.

We have used in each case *all* of the measurements in the original papers, except for three results above 0.02 M for potassium chloride, one at 5° and two at 55°. The total number of individual measurements used in compiling Table II is 258; equation 5 represents these with an over-all average deviation of 0.022% and a maximum deviation of 0.09%, using, besides the Λ^0 values given, only the parameters $\mathring{a}$, which are constant from 5° to 55° for the salts and from 5° to 65° for hydrochloric acid.

The values of the ion-size parameter $\mathring{a}$ required for the conductivity equation are of the same order as those used in the Debye–Hückel expression for the activity coefficient. It has been remarked by various writers that the nature of the activity coefficient data does not permit an unambiguous evaluation of the ion size parameter: the reason for this is that for accurate representation of the activity coefficient a further adjustable parameter (usually occurring in a term linear in the concentration) has to be introduced to allow for short-range ion–solvent interactions. The resulting elasticity of the two-parameter equation for the activity coefficient means that very slight variations in the experimental figures can appreciably alter the value of the parameter $\mathring{a}$. The following comparison of the $\mathring{a}$ values given by different authors demonstrates this point.

TABLE III

$\mathring{a}$ VALUES BY VARIOUS METHODS

	a	*b*	*c*	*d*	*e*	*f*
HCl	4.3	4.4	4.84	4.47	4.4	4.3
NaCl	3.8	5.2	3.97	3.97	4.0	4.0
KCl	3.3	(3.7)	3.63	3.63	4.6	3.8
KBr	3.8	...	3.84	3.85	...	3.84
KI	4.5	...	4.20	4.16	...	3.94

[a] Conductivity, this research. [b] Transport numbers, R. H. Stokes, THIS JOURNAL, **76**, 1988 (1954). [c] Activity coefficients, R. H. Stokes and R. A. Robinson, *ibid.*, **70**, 1870 (1948) (by the one-parameter equation). [d] Activity coefficients, ref. *c* (by the two-parameter equation). [e] Activity coefficients below 0.1 M: T. Shedlovsky, THIS JOURNAL, **72**, 3680 (1950). [f] Activity coefficients above 0.1 M: H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 381 (from the Hückel equation).

The rather large difference between the conductivity and transport number values for $\mathring{a}$ in sodium chloride is puzzling, though it must be remembered that the conductivity value may be slightly influenced by the neglect of viscosity effects which probably cancel from the transport number formulas (ref. *b* to Table III).

We have commented above on the questionable value of the term in $c \log c$ which has been introduced into several recent empirical modifications of the Onsager limiting formula for the conductance. The following theoretical justification for omitting such a term may be of interest: In a previous paper[2] the electrophoretic terms were shown to take the form of a series

$$\sum_n A_n \frac{(z_1^n - z_2^n)^2}{\mathring{a}^n (z_1 - z_2)}$$

the coefficient A_n being a known but complicated function of the index n and the concentration, and z_1 and z_2 being the *algebraic* valences of the cation and anion, respectively. In the present paper, we have used only the first-order term ($n = 1$) of this series: the justification for this was given in reference (1). The second-order term ($n = 2$) is proportional to

$$\frac{(z_1^2 - z_2^2)^2}{a^2(z_1 - z_2)} (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2 Ei(2\kappa a)$$

Now for values of (κa) small compared to unity, $Ei(2\kappa a)$ is proportional to $\log c$, and $(\kappa a)^2\left(\frac{e^{\kappa a}}{1 + \kappa a}\right)^2$ is proportional to c, so that the term in $c \log c$ arises from this second-order electrophoretic correction at low concentrations. However, *for a symmetrical electrolyte* the valence-factor $(z_1^2 - z_2^2)^2/(z_1 - z_2)$ vanishes identically in the second-order term (and indeed in all even-order terms); hence there can be no term in $c \log c$ in the conductance equation in this case. Such a term is, however, possibly justifiable for unsymmetrical valence-type electrolytes, and certainly appears in the *diffusion* coefficient for the symmetrical case.[1a]

We are indebted to Dr. J. N. Agar of the University of Cambridge for drawing our attention to Falkenhagen's treatment[2] of the relaxation effect.

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The Ionization Potentials of Substituted Acetylenes by Electron Impact

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The ionization potentials of acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 3-methyl-1-butyne, vinylacetylene and diacetylene were determined by the electron impact method. The values obtained (in e.v.) are 11.46, 10.48, 10.34, 9.85, 10.39, 10.35, 9.90 and *ca.* 10.9. The value for propyne is in serious diagreement with that obtained spectroscopically (11.30 e.v.). Possible sources for this discrepancy are discussed.

In the course of some electron impact studies being carried on in this Laboratory, we attempted to check the performance of our instrument by measuring the ionization potential of propyne, the value of which had presumably been well-established at 11.30 e.v. by the spectroscopic measurements of Price and Walsh.[1] Much to our surprise, we obtained almost a volt lower than this, and since we doubted that our instrument could be that much in error, we became somewhat suspicious of the published value. Since the only compounds in the acetylene series for which ionization potentials have been measured are acetylene itself, propyne and diacetylene, we decided to make the study described here. The compounds investigated were acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 3-methyl-1-butyne and vinylacetylene.

Experimental

The measurements were made using the apparatus and technique which has been described previously.[2] The vanishing current method was used in determining threshold voltages, and the electron voltage-scale calibrating gas (Kr) was introduced into the apparatus along with the gases under investigation. The temperature of the ion source was maintained at 190 ± 10° for all measurements except those on vinylacetylene, for which compound, because of its instability, no external heat was applied to the ion source. Under these conditions the ion source temperature was 100 ± 10° as a result of heating by the filament. A reproduction of the ionization efficiency curves for acetylene and propyne is given in Fig. 1.

Commercial acetylene was purified from acetone by freezing with Dry Ice. Its mass spectrum showed no peaks which could not be assigned to acetylene. The propyne was made by the Farchan Research Laboratories, Cleveland, Ohio, and was kindly supplied us by Mr. George Toups of these laboratories. The only really objectionable impurity that it could contain would be its isomer, allene, which, because of its quite low ionization potential (10.19 e.v. by ultraviolet spectroscopy[3]; 10.0 e.v. by electron impact[4]), could lead to erroneously low results if present in the propyne to any significant extent. The mass spectrum of the propyne sample was obtained and showed no extraneous peaks, but it could not be used to detect the presence of allene impurity. Consequently, the infrared spectrum of the sample was very kindly obtained for us by Dr. S. H. Hastings of these laboratories, and from the essential absence of the characteristic bands to be ascribed to 1,2-diolefins, it was estimated that the allene content of the sample was less than 0.07%, surely a negligible amount. The 1-butyne and 2-butyne were N.B.S. Standard Samples with purities of 99.87 and 99.93 mole per cent. The pentynes were obtained from Shell Development Company, and were submitted to infrared analysis, which showed the 1,2-diolefin content to be of the order of 1%. The vinylacetylene was made by the du Pont Company of Louisville, Kentucky, and was used without further treatment. Its mass spectrum indicated that no significant impurities were present.

Results

The results of this study are listed in the second column of Table I. The uncertainties given are the average deviations from average for the five replicate determinations made on each substance. These five measurements were not done consecutively but rather were spaced out over the whole course of the work. It is felt that in this way the effect of short term peculiarities in the operation of the mass spectrometer is minimized and that the replicate determinations constitute individual measurements to a greater extent than would be the case were the determinations done consecutively. Since the ionization potential of acetylene is well-established, measurements on this compound were made mostly as a check on the accuracy of the apparatus and technique. The good agreement of

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(1) W. C. Price and A. D. Walsh, *Trans. Faraday Soc.*, **41**, 381 (1945).

(2) F. H. Field, *Rev. Sci. Instruments*, submitted for publication.

(3) L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 899 (1952).

(4) J. Delfosse and W. Bleakney, *Phys. Rev.*, **56**, 256 (1939).