the very small $(3.0 \pm 2.0 \text{ cc.})$ apparent orientation polarization observed. Although a small dipole moment is entirely possible from the data, no reasonable structure has been proposed for this substance for which one would predict an electric moment of the magnitude 0.5 D. Most of the structures proposed recently for nitrogen tetrasulfide such as the cradle form of the eight-membered ring favored by Lu and Donohue,¹ or the closely related ring structure proposed by Hassel and Viervoll,² would be non-polar; on the other hand a branched chain structure with several multiple bonds, such as that of Ruff and Geisel,¹⁶ would probably have a considerably larger moment. We favor the idea that nitrogen tetrasulfide is nonpolar but shows an an abnormally large atomic polarization (about $0.15 MR_D$).

Phosphorus sesquisulfide was assigned a structure in which sulfur atoms are inserted between three of the six P–P bonds of the P₄ molecule, \angle PSP = 100° and P-S = 2.15 Å. The P-S bond moment is not known but if we use the observed moment of P_4S_3 and the above data, a value P-S = 0.56 Dis calculated which is close to the 0.40 D predicted from electronegativity differences¹⁷ and, along with the agreement between observed and calculated molar refractions, lends some support to the structure of Hassel and Petterson.

The electric moment of S(CN)2 indicates that it is a bent molecule and, choosing $\angle CSC = 105^{\circ}$ (as in dimethyl sulfide¹⁸), the ŠCN bond moment is found to be 2.28 in good agreement with the vector sum, 2.12, of the C-S and CN moments.

(16) O. Ruff and E. Geisel, Ber., 37, 1573 (1904).

(17) 1, Pauling, "Nature of the Chemical Bond," Second Edition, Cornell University Press, Ithaca, N. Y., 1940.

(18) L. Brockway and H. C. Jenkins, THIS JOURNAL, 58, 2036 (1936).

We assume that $Se_3(CN)_2$ has a straight chain structure analogous to the trisulfides¹⁹ with bond angles \angle Se–Se–Se, \angle Se–Se–C = 105° and dihedral angles $\phi_1(\text{Se-Se-Se-C}_1)$ and $\phi_2(\text{Se-Se-Se-C}_{II}) =$ 90°. The electric moments of the three isomers (see ref. (20)) of Se₃(CN)₂ are then calculated to be $1.45 \ (\phi_1 = 90^\circ, \phi_2 = 270^\circ), 1.45 \ (\phi_1 = 270^\circ, \phi_2 = 90^\circ)$ and $5.09 \ (\phi_1 = \phi_2 = 90^\circ)$, using a value 2.6 D for the Se-CN bond moment (slightly larger than observed above for the SCN bond moment);

on the other hand $\mu = 3.64 D$ would be predicted for free rotation about all single bonds of the molecule. The observed value could be accounted for about equally well by assuming free rotation or by postulating a mixture of isomers resulting from hindered rotation.

The mean electric moment of perchloromethyl mercaptan in the two solvents studied is 0.62 D. Since the Cl_3 -C bond moment (0.8) and the C-S bond moment (0.88) are nearly equal and opposite, the S-Cl bond moment derived from our results is 0.62 D. This is close to both the value 0.45observed previously7 and the value 0.5 predicted from electronegativity differences.17 The moment of S₂Cl₂ calculated for a linear chain molecule using S–C1 = 0.62 D, \angle SSC1 = 105° , and dihedral angle C1–S–S–C1 = 90° , is 0.85 D; this agrees fairly well with the values 0.92,²¹ 1.0^{22} and 0.95^{23} reported previously but not with the value 1.6 reported by Smyth, et al.⁹

(19) J. Donohue and V. Schomaker, J. Chem. Phys., 16, 92 (1948). (20) C. C. Woodrow, M. Carmack and J. G. Miller, ibid., 19, 951 (1951).

(21) G. Scheibe and O. Stoll, Ber., 71B, 1571 (1938).

(22) Y. Morino and S. Mizushima, Sci. Papers Inst. Phys. Chem. Research (Tokyo), 32, 220 (1937).

(23) Computed from the data of Lowry and Jessop, ref. 8.

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[CONTRIBUTION FROM INSTITUTION OF CHEMISTRY, UNIVERSITY OF HELSINKI]

A Differential Potentiometric Method of Measuring Acid and Base Dissociation Constants

By S. Kilpi

RECEIVED NOVEMBER 30, 1951

The differential potentiometric determination of acid and base dissociation constants, as described some time ago by the author, is compared with a fundamentally similar method recently described by Grunwald.¹ It is now shown that the most exact results are obtained from measurements of the buffer capacity at the inflection point of the titration curve. These measurements and the calculation of the dissociation constants are explained.

Measurement of buffer capacity or potential jump to determine the dissociation of acids and bases has been used repeatedly in this Laboratory since 1935 both in aqueous,^{35,6,7,8ab} ethanolic⁴ and acetic

(1) E. Grunwald, This JOURNAL, 73, 4934 (1951).

(2) Fr. I., Hahn and R. Klockmann, Z. physik. Chem., [A] 146,

(2) FT. L. Hann and K. KICKMAIN, J. Phys. Lett. 11, 121, 373 (1930).
(3) S. Kilpi, *ibid.*, (a) **173**, 223 (1935); (b) **173**, 427 (1935); (c) **175**, 239 (1935).
Cf. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, 1939, p. 309.
(1) MacInnes, T. Wardib, Cham. **177**, 427 (1936).

(4) S. Kilpi and H. Varsila, Z. physik. Chem., 177, 427 (1936).

(5) S. Kilpi (a) Suomen Kemistilehti, 9, 7 (1936); (b) Z. physik. Chem., [A] 177, 116 (1926); (e) [A] 177, 442 (1936); (d) 187, 276 (1940); (e) Ann. Acad. Sci. Fenn., Ser. [A] 57, 10 (1941).

(6) Y. Hentola, Kemian Keskusliiton julkaisuja, 13, 2 (1946).

(7) D. D. van Slyke, J. Biol. Chem., 52, 525 (1922); &. S. Kilpi, refs, 35, e.

acid⁵ solutions. The idea of this method was, however, first presented by Hahn and Klockmann² in 1930.

Grunwald¹ has recently presented a modified version of the differential method whose development, while in principle the same as mine, differs from it in some important respects. Because of the great practicability of the differential method, I consider it justifiable to compare these two modifications with each other.

Grunwald deals only with the dissociation of univalent acids and bases. On the other hand,

(8) S. Kilpi and A. Meretoja, Z. physik, Chem., (a) 179, 371 (1936); (b) 180, 264 (1937); (c) 180, 464 (1937); (d) Suomen Kemistilehti. [B] 18, 11 (1945); (e) R. Nüsänen, ibid., [B] 21, 5 (1948).

I have derived the general equations suitable for all possible cases in which the pH change (the buffer capacity), when an acid or base is added, reaches a maximum (a minimum).^{3c} These equations can be used as such for instance, for the determination of the dissociation constants of polybasic acids.⁶ This is due to the fact that my derivation is based on van Slyke's general equation

$$P = \frac{d[B]}{d\rho H} = -\frac{d[A]}{d\rho H} = 2.303 \left\{ \sum_{i} \frac{K_{i}C_{i}[H^{+}]}{(K_{i} + [H^{+}])^{2}} + [H^{+}] + [OH^{-}] \right\}$$
(1)

where the symbols in brackets are concentrations, K_i concentration dissociation constants and C_i stoichiometric concentrations of the acids present. [B] and [A] are the respective stoichiometric concentrations of the strong acid and base added. In the case of a univalent acid, we obtain

$$P = 2.303 \left\{ \frac{K_{\rm A} C[{\rm H^+}]}{(K_{\rm A} + [{\rm H^+}])^2} + [{\rm H^+}] \right\}$$
(2)

when the dissociation constants $K_{\rm A}$ are determined from the equivalent point on back titration. Equation (2) corresponds to Grunwald's equation (4). The inflection point on the titration curve is more advantageous for the determinations of the dissociation constant than the equivalence point used by Grunwald. These two points do not generally agree.^{8a, p. 279} In the inflection point of the titration curve on back titration^{3c,8a}

$$[\mathrm{H}^{+}]_{\mathrm{i}} = \sqrt{K_{\mathrm{A}}C\frac{1-K_{\mathrm{A}}/[\mathrm{H}^{+}]}{(1+K_{\mathrm{A}}/[\mathrm{H}^{+}])^{3}}} \qquad (3)$$

The buffer capacity P at the inflection point can be measured. It is thus possible, using the iterative method,^{8a} simply to calculate the value of the dissociation constant by means of equations (2) and (3), just as by Grunwald's equation (4) and (5).

In the approximations it is advantageous to use the expansions

$$P_{i} = 4.606 \sqrt{K_{\Lambda}C} \left\{ 1 - \frac{K_{\Lambda}}{[H^{+}]} + \frac{3}{2} \left(\frac{K_{\Lambda}}{[H^{+}]} \right)^{2} - \cdots \right\}$$
(2')

$$[\mathrm{H}^+] = \sqrt{K_{\mathrm{A}}C} \left\{ 1 - 2 \frac{K_{\mathrm{A}}}{[\mathrm{H}^+]} + \frac{5}{2} \frac{K_{\mathrm{A}}}{[\mathrm{H}^+]} - \cdots \right\}$$
(3')

$$P_{1} = 4.606 \sqrt{K_{A}C} \left\{ 1 - \sqrt{\frac{K_{A}}{C}} - \frac{1}{2} \frac{K_{A}}{C} + \cdots \right\}$$
(2') and (3').

where in the estimation of the first approximation the terms containing $K_{\Lambda}/[\text{H}^+]$ or K_{Λ}/C as factor are neglected.

At equivalence point, in the approximation the following equation can be used

$$P_{\bullet} = 4.606 \sqrt{K_{A}C} \left\{ 1 - \sqrt{\frac{K_{A}}{C}} + \frac{5K_{A}}{8C} - + \cdots \right\}$$
(4)

The accuracy obtained by this method depends in the first place on the experimental determination of the buffer capacity P_i at the inflection point. This quantity has been calculated graphically^{8a} and lately by means of the equations^{8e}

$$D = \Delta_m + \frac{1}{6} \left\{ (\Delta_m - \Delta_1) + (\Delta_m - \Delta_2) - \frac{1}{2} \frac{(\Delta_m - \Delta_1)(\Delta_m - \Delta_2)}{(\Delta_m - \Delta_1) + (\Delta_m - \Delta_2)} \right\}$$
(5)

and

$$P_{\rm i} = \Delta V n / V_{\rm i} D$$

where Δ_1 , Δ_m and Δ_2 are three successive changes of pH (Δ_m the greatest), each corresponding to an equal addition of ΔV ml. of a *n*- normal reagent. V_i is the volume of the solution at the inflection point in ml. It may be shown that when $\Delta V < 0.2\%$ of the volume V_i the error due to the change in volume is negligible.^{8a}

Grunwald determines the quantity $(d\rho H/d\epsilon)_{\epsilon=1}$ (ϵ the degree of neutralization), which corresponds to the quantity P_e of our method, in a quite different way. He determines first an approximate value, assuming that the ρ H is a linear function of ϵ . Then he multiplies this value by a factor f_c , which is determined by a graphical method. Grunwald's method has been planned for a potentioneter of inferior accuracy (the accuracy of Grunwald's potentioneter was 0.3–0.6 mv.), in which case the curvature of the titration curve at the inflection is not very distinct. In Table I we see that the curvature of the titration curve at the inflection point appears even according to Grunwald's data.

		Table I		
$\Delta v \times 10^{2}$, m1.	pH + const. obsd.	ΔøH	pH + const. caled.	ΔpH
4.133	0.65	0.08	0.638	0.066
4.004	. 57	.065	.572	.068
3.875	.505	.065	. 504	.069
4.133	.44	.075	.435	.077
4.133	.365	.085	.358	.077
4.004	.280	.075	.281	.075
3.875	.205	.065	.206	.070
4.133	.140	.070	.136	.072
3.875	.070	.070	.064	.064
	.00		.00	

However, it is not so distinct as in the curve calculated by using the value 1.89×10^{-5} of the concentration dissociation constant obtained in the titration in question. The volume increments ΔV of the reagent added, which vary somewhat and thus make the observation of the maximum pH change more difficult, have been calculated according to his values.

With a more accurate potentiometer the maximum appears so distinctly that our method, described above, is more appropriate and also simpler to use. In this Laboratory we have also successfully applied this same method to pH change

TABLE II									
According to Kilpi-Meretoja ⁸			According to Grunwald ¹						
C_{i}	$\times I 104$	$\stackrel{K_{ m A}}{ imes 10^5}$	$K_{A,O} \times 10^{6}$	Ce	$\times 10^{4}$	$\stackrel{K_{\mathrm{A}}}{ imes 10^5}$	$K_{A,O} \times 10^{5}$		
$\begin{array}{c} 0.0_3982\\ .0_3985\\ .0_3984\\ .0_21969\\ .0_24878\\ .0_24932\\ .0_24932\\ .0_24941\\ .0_2998\\ .01989\\ .01989\end{array}$	3.61 3.10 3.17 3.76 5.95 8.40 40.80 44.1 42.9		1.744 1.749 1.762 1.771 1.747 1.774 1.750 1.759 1.736	0.021315 .021927 .023172 .02422 .0521 Mean	14.78 21.58 36.5 45.1 55.4 1 value	2.07	1.81 1.70 1.80 1.63 1.73 0.067		
. 04983 . 09804 . 1862 Mea	42.3 42.1 46.8 n value 1	$2.015 \\ 2.01 \\ 2.03 \\ 1.754 \pm$	1.756 1.747 1.753 0.012						

measurements made with a glass electrode and a potentiometer (radiometer) of inferior accuracy (0.3 to 0.6 mv.)

In Table II Grunwald's values at low ionic strength have been compared with our values. Here C_i and C_e are the stoichiometric concentrations of acetic acid at the inflection point and equivalent point, respectively. I is the ionic strength of the solution. Our values deviate from each other much less than those of Grunwald, owing partly to the somewhat greater accuracy of the potentiometer used by us. For the thermodynamic constant our values give 1.754×10^{-5} in perfect agreement with the value of Harned and Ehlers⁹ $1.753 \times 10^{-5} (20^{\circ}).$

Because this differential method is based on the measurement of small potential differences, great accuracy of the potentiometer is essential. On the other hand the accurate measurement of the small potential jumps is possible because the uncontrolled factors, which often disturb the potentiometric measurements, very largely cancel each other out in a differential method in which the measurements are carried out under constant conditions.

(9) H. S. Harned and R. W. Ehlers, THIS JOURNAL, 54, 1350 (1932); 55, 652 (1933).

Our measurements given here were made with a potentiometer of the Cambridge Instrument Co., slidewire-type, graduated in 0.2-mv. intervals and with an accuracy of 0.1 mv. We have since used the Vernier potentiometer of the Cambridge Instrument Co., graduated on 0.01-mv. intervals and a potentiometer of Leeds–Northrup graduated on 0.05-mv. intervals and with an accuracy of 0.01mv. Now the error due to the potential measurement is of the same order of magnitude as the other experimental errors.^{8a,e}

Next to the potential jumps, the accuracy in measuring the volume increment of the reagent added is important. With our drop method,^{5b,p,126} if a micro-buret is used, an accuracy of 0.001 ml. may easily be reached. An accuracy of 0.0002 ml. may be attained with micrometer pipets. This corresponds to the accuracy obtained with the accurate potentiometers described.

These technical improvements are important in the studies on the dissociation constants in mixtures of electrolytes being made in this Laboratory. Further, we are investigating the dissociation of bases in acetic acid solutions by means of our method described above.

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[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. VIII. Zirconium(IV)Complexes with 2-Nitroso-1-naphthol^{1a}

By HANS B. JONASSEN AND WINSTON R. DEMONSABERT^{1b} **Received January 2, 1952**

The complexes formed between 2-nitroso-1-naphthol and zirconium(IV) have been investigated in mixtures of water and ethanol and water and dioxane in the absence and presence of HClO₄. It has been found that in the absence of HClO₄ a one-to-one complex forms, whereas in solutions 3 M or larger in HClO₄ and 3×10^{-3} M Zr(IV) a one-to-four complex is formed. The pK instability values have been determined: for the one-to-one complex in ethanol-water it is 3.7 and for the one-to-four complex in 50% dioxane-water it is 11.6.

Introduction

Distribution studies by Connick and McVey² show that Zr^{+4} or $(ZrOH)^{+3}$ ions are present in 2 Mperchloric acid and low zirconium(IV) ion concentration. Connick and Reas³ report the formation of zirconium polymers at zirconium ion concentrations of $2 \times 10^{-3} M$ in 2 M HClO₄ and $2 \times 10^{-4} M$ in 1 M HClO₄ solutions.

Thamer and Voigt⁴ have investigated zirconium chloranilate complexes in 1 M and 2 M HClO₄ solutions and find evidence to support a one-to-one and a one-to-two monomeric complex.

Bellucci and Savoia⁵ reported that 1-nitroso-2naphthol precipitates zirconium(IV) in acid solution forming $ZrO(C_{10}H_6(NO)O)_2$ and that the

(1) (a) Presented before the Division of Physical and Inorganic Chemistry at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March 23-27, 1952. (b) Department of Chemistry, Loyola University of the South, New Orleans, Louisiana.

(2) R. E. Connick and W. H. McVey, THIS JOURNAL, 71, 3182 (1949).

(5) I. Bellucci and G. Savoia, Atti congr. nucl. chim. para applicate, 483 (1023)

isomeric 2-nitroso-1-naphthol behaves in a similar manner. The composition and stability of the 2-nitroso-1-naphthol zirconium(IV) complex is only a matter of conjecture.⁶ Its study in aqueous, alcoholic and dioxane media in the absence and presence of perchloric acid was initiated in order to determine their possible effects on these zirconium complexes.

Experimental

Zirconyl chloride, ZrOCl2·8H2O, obtained from the Fairmount Chemical Company was recrystallized six times from concentrated HCl solutions.

Zirconium tetrachloride, ZrCl4, obtained from the Fairmount Chemical Company, was added directly to the solvent (alcohol, dioxane) and the resulting solution standardized by precipitation of the zirconium with aqueous NH3 and igniting to ZrO₂.

The sodium nitrate solution was prepared from Baker C.P. grain sodium nitrate. 2-Nitroso-1-naphthol, Eastman Chemical Company, was

weighed directly in the preparation of the standard solutions. The Beckman model DU spectrophotometer equipped with 10-mm. Corex cells was used throughout the deter-

⁽³⁾ R. E. Connick and W. H. Reas, *ibid.*, 73, 1171 (1951).

⁽⁴⁾ B. J. Thamer and A. F. Voigt, ibid., 73, 3197 (1951).

⁽⁶⁾ Pritz Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 259.