

the very small ( $3.0 \pm 2.0$  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,<sup>1</sup> or the closely related ring structure proposed by Hassel and Viervoll,<sup>2</sup> would be non-polar; on the other hand a branched chain structure with several multiple bonds, such as that of Ruff and Geisel,<sup>16</sup> would probably have a considerably larger moment. We favor the idea that nitrogen tetrasulfide is non-polar but shows an abnormally large atomic polarization (about  $0.15 MRD$ ).

Phosphorus sesquisulfide was assigned a structure in which sulfur atoms are inserted between three of the six P-P bonds of the  $P_4$  molecule,  $\angle PSP = 100^\circ$  and P-S =  $2.15 \text{ \AA}$ . 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 =  $0.56 D$  is calculated which is close to the  $0.40 D$  predicted from electronegativity differences<sup>17</sup> 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 sulfide<sup>18</sup>), the SCN 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) L. 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 trisulfides<sup>19</sup> with bond angles  $\angle Se-Se-Se$ ,  $\angle Se-Se-C = 105^\circ$  and dihedral angles  $\phi_1(Se-Se-Se-C_I)$  and  $\phi_2(Se-Se-Se-C_{II}) = 90^\circ$ . The electric moments of the three isomers (see ref. (20)) of  $Se_3(CN)_2$  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  $0.45$  observed previously<sup>7</sup> and the value  $0.5$  predicted from electronegativity differences.<sup>17</sup> The moment of  $S_2Cl_2$  calculated for a linear chain molecule using S-Cl =  $0.62 D$ ,  $\angle SSCl = 105^\circ$ , and dihedral angle Cl-S-S-Cl =  $90^\circ$ , is  $0.85 D$ ; this agrees fairly well with the values  $0.92$ ,<sup>21</sup>  $1.0$ <sup>22</sup> and  $0.95$ <sup>23</sup> reported previously but not with the value  $1.6$  reported by Smyth, *et al.*<sup>9</sup>

(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

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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.<sup>1</sup> 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,<sup>3b,6,7,8ab</sup> ethanolic<sup>4</sup> and acetic

(1) E. Grunwald, *This Journal*, **73**, 4934 (1951).

(2) Fr. L. Hahn and R. Klockmann, *Z. physik. Chem.*, [A] **146**, 373 (1930). Cf. S. Kilpi, *ibid.*, **173**, 435 (1935).

(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.

(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 (1936); (c) [A] **177**, 442 (1936); (d) **187**, 276 (1940); (e) *Ann. Acad. Sci. Fenn.*, Ser. [A] **57**, 10 (1941).

(6) Y. Heitola, *Kemian Keskuksilaiton julkaisuja*, **13**, 2 (1946).

(7) D. D. van Slyke, *J. Biol. Chem.*, **52**, 525 (1922); cf. S. Kilpi, *ref. 3a, c*.

acid<sup>5</sup> solutions. The idea of this method was, however, first presented by Hahn and Klockmann<sup>2</sup> in 1930.

Grunwald<sup>1</sup> 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. Näsänen, *ibid.*, [B] **21**, 5 (1948).



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  $1.754 \times 10^{-5}$  in perfect agreement with the value of Harned and Ehlers<sup>9</sup>  $1.753 \times 10^{-5}$  (20°).

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 0.01 mv. Now the error due to the potential measurement is of the same order of magnitude as the other experimental errors.<sup>8a,e</sup>

Next to the potential jumps, the accuracy in measuring the volume increment of the reagent added is important. With our drop method,<sup>5b,p.126</sup> 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<sup>1a</sup>

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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  $\text{HClO}_4$ . It has been found that in the absence of  $\text{HClO}_4$  a one-to-one complex forms, whereas in solutions 3  $M$  or larger in  $\text{HClO}_4$  and  $3 \times 10^{-3} M$   $\text{Zr(IV)}$  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 McVey<sup>2</sup> show that  $\text{Zr}^{+4}$  or  $(\text{ZrOH})^{+3}$  ions are present in 2  $M$  perchloric acid and low zirconium(IV) ion concentration. Connick and Reas<sup>3</sup> report the formation of zirconium polymers at zirconium ion concentrations of  $2 \times 10^{-3} M$  in 2  $M$   $\text{HClO}_4$  and  $2 \times 10^{-4} M$  in 1  $M$   $\text{HClO}_4$  solutions.

Thamer and Voigt<sup>4</sup> have investigated zirconium chloranilate complexes in 1  $M$  and 2  $M$   $\text{HClO}_4$  solutions and find evidence to support a one-to-one and a one-to-two monomeric complex.

Bellucci and Savoia<sup>5</sup> reported that 1-nitroso-2-naphthol precipitates zirconium(IV) in acid solution forming  $\text{ZrO}(\text{C}_{10}\text{H}_6(\text{NO})\text{O})_2$  and that the

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.<sup>6</sup> 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,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , obtained from the Fairmount Chemical Company was recrystallized six times from concentrated  $\text{HCl}$  solutions.

Zirconium tetrachloride,  $\text{ZrCl}_4$ , 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  $\text{NH}_3$  and igniting to  $\text{ZrO}_2$ .

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-

(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).

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

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

(5) I. Bellucci and G. Savoia, *Atti congr. naz. chim. para applicate*, 183 (1923).

(6) Fritz Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, p. 253.