rine. The results are given in Table IA. The average value of $-22{,}130$ calories agrees very well with that of $-22{,}120$ calories given by Rossini[8] when corrected to the same temperature.

Six runs were made on the reaction of diborane with chlorine, and the results are given in Table IB. The average value for the heat of reaction from these runs is -342.4 kcal. per mole of diborane with a maximum deviation from the average value of 1.5%. When corrected to 25° by heat capacity data this becomes -343.0 kcal.

Figure 1 is offered as proof that the products of the reaction are boron trichloride and hydrogen chloride. It gives the infrared spectra of diborane, boron trichloride and the calorimeter exit gases. From the intensities of absorption of the various peaks, it is found that boron trichloride is present in the exit gases to the extent of about 150 mm. and diborane about 15 mm. The peaks at 3.4 and 3.6 μ are due to hydrogen chloride and indicate a partial pressure of about 450 mm. Since no extraneous peaks are present, it is doubtful if any side reactions have taken place. The absence of chlorine in the exit gases was shown by ultraviolet absorption spectra.

If one takes the heats of formation of diborane,[7] boron trichloride,[10] and hydrogen chloride to be -7.5, $+94.5$ and $+22.06$, respectively, the heat of reaction may be calculated to be -328.9 kcal. This is lower than the observed value by 4% and is considerably greater than our experimental error which is estimated to be about 1%. If one takes the heat of formation of diborane to be -7.5, one may calculate that the heat of formation of boron trichloride is 102 kcal. This is fairly close to the value of 104 recommended by Roth.[5] On the other hand, if we take the heat of formation of boron trichloride to be 94.5 kcal., then one may calculate the heat of formation of diborane to be -22 kcal. This is in fairly good agreement with the values recommended by Roth[5] and Eggersgluess.[6] The existing data on the heats of formation of these compounds are not consistent.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Sulfur and Selenium Compounds

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The electric moments and molecular refractions of nitrogen tetrasulfide, phosphorus sesquisulfide, cyanogen sulfide cyanogen triselenide and perchloromethyl mercaptan have been measured in solution in non-polar solvents at 25°. Some conclusions concerning the structures of these molecules are drawn from the data.

The structure of nitrogen tetrasulfide, N_4S_4, has been the subject of extensive research[1-4] but is still uncertain. Several of the proposed structures would have zero dipole moment but the compound has been reported[4] to have a dipole moment of 0.72 *D* in benzene solution. Since small dipole moments are occasionally reported for non-polar compounds as a result of solvent effects, or of errors, it appeared worthwhile to redetermine the dipole moment and molecular refraction of N_4S_4 in both benzene and carbon bisulfide solution. A reasonable structure for phosphorus sesquisulfide, P_4S_3, has been proposed by Hassel and Petterson[5] on the basis of an electron diffraction investigation; we have measured the electric moment of P_4S_3 and find that it is consistent with their results. No physical measurements have been reported previously on cyanogen sulfide, $S(CN)_2$, or cyanogen triselenide, $Se_3(CN)_2$; we have measured the dipole moments to obtain some information concerning their structures.

An estimated value 0.45 *D* for the S–Cl bond moment is obtained from the $\angle$ Cl–S–Cl = 102° found by electron diffraction[6] and the dipole moment calculated by Smith[7] from an early measurement of the molar polarization.[8] Some doubt has been thrown on this value by the large electric moment reported for sulfur monochloride S_2Cl_2, by Smyth, *et al.*,[9] so we have obtained an independent estimate of the S–Cl bond moment by measuring the electric moment of perchloromethyl mercaptan, Cl_3–C–S–Cl.

Experimental Part

Materials. Benzene.—C.P. thiophene-free benzene was purified by drying over sodium and distilling before use, d^{25}_4 0.87344, $n^{25}\text{D}$ 1.4979.

Carbon Tetrachloride.—This was prepared according to the recommendations of Fieser[10] by treatment of C.P. carbon tetrachloride with concd. potassium hydroxide solution and alcohol, water, concd. sulfuric acid, water and anhydrous calcium chloride, in turn, d^{25}_4 1.58427, $n^{25}\text{D}$ 1.4573.

Carbon Bisulfide.—C.P. carbon bisulfide was shaken with mercury, mercuric chloride solution, potassium permanganate solution, washed, dried and distilled, as outlined by Fieser,[10] d^{25}_4 1.25566, $n^{25}\text{D}$ 1.6239.

Cyanogen Triselenide.—This was prepared by passing chlorine over potassium selenocyanate solution until the reaction was complete.[11] The yellow precipitate was refluxed in chloroform with charcoal and the hot solution filtered. Yellow plates, m.p. 133–134°, crystallized out and were recrystallized from benzene giving orange needles, m.p. 133–134°. The two crystal forms were investigated separately but gave the same molar polarization.

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TABLE I

EMPIRICAL CONSTANTS,[a] MOLAR POLARIZATIONS, MOLAR REFRACTIONS AND DIPOLE MOMENTS[b]

α'	ϵ_{10}	β'	V_{10}	γ'	n_0^2	MR_D	P_2^∞	μ
Cyanogen Triselenide in Benzene								
22.73	2.2725	−2.967	1.14190	0.70	2.2437	41.4 (46.2)	365.1	3.98
Cyanogen Sulfide in Benzene								
11.11	2.2700	−0.402	1.14500	0.09	2.2437	26.0 (18.7)	182.8	2.77
Phosphorus Sesquisulfide in Benzene								
2.52	2.2706	−1.76	1.14500	1.66	2.2428	57.8 (59.3)	71.2	0.81
Nitrogen Tetrasulfide in Benzene (25°)								
1.479	2.2723	−1.60	1.14465	1.12	2.2444	41.4 (42.6)	47.3	0.52
Nitrogen Tetrasulfide in Benzene (45°)								
1.507	2.2334	−1.707	1.17395	—	—	—	47.3	0.56
Nitrogen Tetrasulfide in Carbon Bisulfide								
2.225	2.6294	−0.727	0.79620	0.963	2.6383	40.4 (42.6)	51.0	0.72
Sulfur in Benzene								
2.072	2.2723	−2.03	1.14460	1.817	2.2443	66.6 (62.4)	70.7	0
Perchloromethyl Mercaptan in Benzene								
0.64	2.2716	−1.273	1.14480	0.173	2.2450	35.8 (34.1)	43.2	0.65
Perchloromethyl Mercaptan in Carbon Tetrachloride								
0.56	2.2298	−0.054	0.63120	0.27	2.1237	34.3 (34.1)	40.8	0.56

[a] The observed dielectric constants ϵ_{12}, specific volumes V_{12} and squares of refractive indices n_{12}^2, of the solutions were plotted graphically against mole fraction solute. The points fall, within experimental error, on straight lines with slopes α', β', γ', respectively, and the intercepts at zero mole fraction are ϵ_{10}, V_{10} and n_0^2, respectively. The molar polarizations at infinite dilution P_2^∞ and the dipole moments μ (Debye units), were calculated from these constants. [b] Values in parentheses were calculated from empirical constants.

Cyanogen Sulfide.—Dry silver cyanide was added to sulfur dichloride in carbon bisulfide solution, the mixture filtered, and the filtrate cooled. White crystals of sulfur dicyanide separated on cooling[12] and were sublimed before use.

Phosphorus Sesquisulfide.—Eastman Kodak Co. technical phosphorus sesquisulfide was extracted with carbon bisulfide and the filtered extract evaporated to dryness. This material was placed in water, steam passed through for an hour, the water removed, the product dried and recrystallized from carbon bisulfide, m.p. 172°.

Nitrogen Tetrasulfide.—Ammonia was passed through a solution of sulfur chloride in ether until no more precipitate formed. The crude material was extracted with benzene repeatedly, and the benzene solution evaporated to dryness. After two recrystallizations from benzene deep orange crystals were obtained apparently free of sulfur[13]; the crystals decomposed (163–170°) before melting.

Perchloromethyl Mercaptan.—Eastman Kodak Co. material was fractionated through an efficient packed column, b.p. 50.5° (28 mm.), d^{25}_4 1.6866, n^{25}_D 1.5371.

Sulfur.—Rhombic sulfur was recrystallized from benzene and carbon bisulfide before use.

Apparatus and Method.—Dielectric constants were measured by a heterodyne-heat method described previously,[14] refractive indices were measured with an Abbé refractometer and densities with a modified Ostwald pycnometer[14]; all measurements were made at 25°, with the exception of one series for nitrogen tetrasulfide in benzene at 45°. Electric moments were calculated from the data by the method of Halverstadt and Kumler.[15] The constants[15] α', β', γ', ϵ_{10}, V_{10} and n_0^2 are shown in Table I along with the calculated values of P_2^∞, MR_D and μ. The probable error in molar polarization is ±0.02 *P*, in most cases, and the probable error in dipole moment about ±0.10 *D*; the errors are somewhat larger for measurements made in carbon bisulfide solution. Duplicate runs were made on nitrogen tetrasulfide in benzene and in carbon bisulfide solutions using material from a different preparation; the dipole moments in each case agreed within ±0.10 *D* and the data given in Table I for these compounds are the mean values.

Molar refractions were calculated from empirical atomic constants, using for S, P, Se and N the values 7.80, 8.98, 11.75 and 2.84, respectively; no multiple bonds were assumed in any case except —C≡N, for which the value 5.46 cc. was used. The agreement between observed and calculated values is good except in the cases of cyanogen sulfide and cyanogen triselenide where the experimental errors were much larger (±0.10 MR_D) than normal (±0.03 MR_D).

Discussion

The dipole moment of nitrogen tetrasulfide in benzene solution reported here, 0.52 *D*, is somewhat lower than the value, 0.72 *D*, reported by Phalnikar and Bhide[4] and also lower than the moment, 0.72 *D*, found in carbon bisulfide solution. Since atomic polarization, which was neglected in the above calculations, becomes of importance when the orientation polarization is small, we have studied solutions of sulfur in benzene by the same technique to obtain an estimate of the atomic polarization in a substance somewhat analogous to nitrogen tetrasulfide. Sulfur is non-polar so the difference, 4.2 cc. or 0.07 MR_D, between the molar polarization and molar refraction of sulfur may be taken as the atomic polarization. Using this figure for nitrogen tetrasulfide, the correction for atomic polarization would be 2.9 cc., so the orientation polarization is reduced to 3.0 cc., a figure only slightly larger than the sum of the errors in P^∞_2 and MR_D. It seems entirely possible that a large molecule such as nitrogen sulfide in which the individual bonds are polar, but the net dipole moment perhaps zero, could show an abnormally large atomic refraction; this would then account for

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[13] H. B. Van Valkenburgh and J. C. Bailar, Jr., THIS JOURNAL, **47**, 2134 (1925).

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the very small (3.0 ± 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,[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 P_4 molecule, ∠ 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 *D* is calculated which is close to the 0.40 *D* predicted from electronegativity differences[17] 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 ∠ CSC = 105° (as in dimethyl sulfide[18]), 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. We assume that $Se_3(CN)_2$ has a straight chain structure analogous to the trisulfides[19] with bond angles ∠ Se–Se–Se, ∠ Se–Se–C = 105° and dihedral angles ϕ_1(Se–Se–Se–C_I) and ϕ_2(Se–Se–Se–C_{II}) = 90°. The electric moments of the three isomers (see ref. (20)) of $Se_3(CN)_2$ are then calculated to be 1.45 (ϕ_1 = 90°, ϕ_2 = 270°), 1.45 (ϕ_1 = 270°, ϕ_2 = 90°) and 5.09 ($\phi_1 = \phi_2$ = 90°), 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 μ = 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[7] and the value 0.5 predicted from electronegativity differences.[17] The moment of S_2Cl_2 calculated for a linear chain molecule using S–Cl = 0.62 *D*, ∠ SSCl = 105°, and dihedral angle Cl–S–S–Cl = 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]

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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

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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,[3b,6,7,8ab] ethanolic[4] and acetic acid[5] solutions. The idea of this method was, however, first presented by Hahn and Klockmann[2] in 1930.

Grunwald[1] 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,

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