per cent. are listed in Table II. The relationship $D_{25}^{W} = (4.515 + 0.134c) \times 10^{-6}$ cm.^{2}/sec. fits the data.

TABLE II

DIFFUSION DATA FOR SILICOTUNGSTIC ACID

Wt. % acid	0	0.964	1.957	4.695	6.192
$D_{25}^{W} \times 10^6$, cm.^{2}/sec.	4.515[a]	4.635	4.769	5.140	5.307

[a] Extrapolated.

It remains to prove the stability of the $SiW_{12}O_{40}^{-4}$ anion in these solutions. Silico-12-tungstic acid is stable at *p*H values more acid than 6, according to the titration data of Malaprade[11], which we have essentially confirmed. Furthermore, we have measured the *p*H of several solutions of the acid in the acetate buffer used in these experiments. If the change of the *p*H of the solution from that of the buffer is attributed to the effect of the liberation of H ions from the silicotungstic acid upon the acetate–acetic acid equilibrium, a simple calculation gives the number, *n*, of such H ions per molecule of the silicotungstic acid. This number is close to 4, as is seen in Table III, in agreement with the above formulation of the anion.

TABLE III

Wt. % $H_4SiW_{12}O_{40}$	*p*H of buffered soln.	*n*[a]
0	4.58	..
1.966	4.49	4
3.122	4.40	4
5.154	4.33	4
8.116	4.28	3

[a] Number of protons ionized per molecule of silicotungstic acid, see text.

We have also performed sedimentation and diffusion experiments with phospho-12-tungstic and phospho-12-molybdic acids in the same acetate buffer.[12] With these acids, however, *p*H measurements on the solutions confirm earlier titration studies[11] in indicating that the acids are decomposed at *p*H 4.58. Ultracentrifuge experiments in solutions sufficiently acid to ensure the stability of the $PW_{12}O_{40}^{-3}$ and $PMo_{12}O_{40}^{-3}$ ions have been impractical because of reaction of the metal in the ultracentrifuge synthetic boundary cells. The experiments with these unstable acids at *p*H 4.58, while not of use for the purposes of this paper, are of interest, however, in connection with the chemistry of these compounds, but this will not be discussed here.

From the constants characterizing the silico-12-tungstic acid, we may calculate the molecular weight of the anhydrous anion $SiW_{12}O_{40}^{-4}$ from the Svedberg equation. The parameter s_0 is the least precise quantity in the equation, and the calculated molecular weight is estimated to have a precision measure of ±3%. The calculated value is 2.91×10^3, and the agreement with the formula weight 2875.1 is excellent. Should it become possible to determine *s* with a precision comparable to that of *D* and $(1 - \bar{V}\rho)$, a still more sensitive test of the Svedberg equation would be possible.

From the friction coefficient per mole, $f = (1 - \bar{V}\rho)/s_0$, and the friction coefficient of the equivalent sphere, $f_0 = 6\pi\eta N(3M\bar{V}/4\pi N)^{1/3}$, where η is the solvent viscosity and N is Avogadro's number, we find that the friction ratio[1] $f/f_0 = 1.0$. Such a value indicates that the solute molecule is indeed effectively spherical and unhydrated in solution. The effective hydrodynamic diameter, *d*, calculated from the relation $d = 2(3M\bar{V}/4\pi N)^{1/3}$, is about 11 Å. On the other hand, X-ray studies of crystalline silico-12-tungstic acid[4] show that the molecule conforms to a cuboöctahedron, which may be considered effectively spherical. The unit cell dimension of the pentahydrate of the acid is 12.1 Å., which is consistent with the hydrodynamic diameter obtained above.

With these results, the Svedberg equation has been subjected to the most critical experimental test as yet applied, so far as we are aware. These results, together with the derivation of the Svedberg equation from irreversible thermodynamics,[13] should help to confirm its general validity in the determination of molecular weights in solution.

Silicotungstic acid, and related substances, may also be of use in calibrating other methods of molecular weight determination, such as light scattering, and as model substances for investigating various problems of molecular hydrodynamic behavior.

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(11) L. Malaprade, *Ann. Chim.*, [10] **11**, 159, 172 (1929).

(12) Unpublished experiments.

(13) G. J. Hooyman, H. Holtan, P. Mazur and S. R. deGroot, *Physica*, **19**, 1095 (1953).

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On the Dielectric Constant of Liquid Hydrogen Cyanide

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The dielectric constant of hydrogen cyanide is noteworthy in that it varies from 206 at −13.3° (m.p.) to 106 at 25.7° (b.p.). Pauling[1] has pointed out that the value at room temperature is about three times larger than expected empirically for a normal liquid with the same molecular dipole moment; for a model of straight chain polymers the factor three is the average degree of polymerization. Coates and Coates[2] in reporting their dielectric constant results further remark that the rapid decrease with temperature indicates a decreasing degree of polymerization at higher temperatures. It is the purpose of this note to present a more quantitative discussion on the basis of the linear chain model and the dielectric constant theory of Kirkwood.[3]

We assume the series of equilibria $(HCN)_n$ +

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(1) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1939, p. 275.

(2) G. E. Coates and J. E. Coates, *J. Chem. Soc.*, 77 (1944).

(3) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

HCN = $(HCN)_{n+1}$ with the same equilibrium constant

$$K = C_{n+1}/C_nC_1 \qquad (1)$$

for all, where C_n is the concentration of n-mer. If C_0 is the gross concentration as monomer, one obtains the well-known equilibrium expression

$$C_1/(1 - KC_1)^2 = C_0 \qquad (2)$$

The dielectric constant ϵ in Kirkwood's theory is related to the dipole moment μ_0 of the free molecule by the expression

$$\epsilon = \epsilon_\infty + \frac{3\epsilon}{2\epsilon + \epsilon_\infty}\left(\frac{\epsilon_\infty + 2}{3}\right)^2 \frac{4\pi N}{3kTV} g\mu_0^2 \qquad (3)$$

where ϵ_∞ is the dielectric constant for induced polarization, N, kT and V have their usual meaning, and the factor $g\mu = g(\epsilon_\infty + 2)\mu_0/3$ is the average moment of the single molecule and its local environment. In the simplified model, this is the average over values $n\mu$, for each molecule of an n-unit straight chain, weighted by the number nC_n of such molecules. This gives

$$g\mu = (\mu/C_0)\sum_{n=1}^{\infty} n^2C_n = \mu\frac{1 + KC_1}{1 - KC_1}$$

on using (1) for the C_n. From eq. 2, one then has

$$KC_0 = (g^2 - 1)/4 \qquad (4)$$

From this result, equilibrium constants KC_0 can be calculated for "experimental" correlation factors g obtained by using measured values of dielectric constant and dipole moment in eq. 3. Using μ_0 = 2.96 debye and dielectric constant data from reference 2 gives the values in Table I.

TABLE I

DIELECTRIC CONSTANT AND ASSOCIATION PARAMETERS

t, °C.	−13.3 (f.p.)	−5	5	15	25.7 (b.p.)
ϵ	205.5	173.7	144.8	123.5	105.7
g^a	4.04	3.52	3.04	2.68	2.38
KC_0	15.6	11.4	8.26	6.20	4.65

[a] Calculated using ϵ_∞ = 1.60 and molar volume V = 39.8 cm.^{3}.

The model may be tested by a rate plot of log KC_0 *versus* reciprocal temperature, which should give a straight line with a reasonable heat of association from the slope. This plot is shown in Fig. 1, and the slope of the straight line corresponds to the figure ΔH = −4.6 kcal./mole. This is interestingly close to the values 3.3 and 4.4 kcal./mole deduced by Long, Hildebrand and Morrell[4] for dimer and trimer formation in the vapor phase. The results are, however, not immediately comparable because of the difference in molecular environment and our simplifying assumption of identical equilibrium expressions for all degrees of association. Such refinements as including a distinct constant for dimers, which have been made in analyzing infrared absorption of alcohol solutions,[5] hardly seem warranted in view of the other approximations in the dielectric constant expression (3) and association model employed.

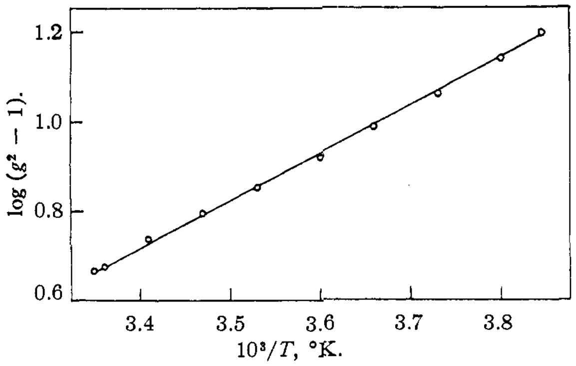

Fig. 1.—Correlation function from eq. 4 as a function of reciprocal temperature.

The temperature dependence of the dielectric constant is thus satisfactorily represented by the model, which is naturally inferred from the known arrangement of parallel linear chains in the solid. The regular arrangement of chains in the solid is not expected or assumed for the liquid; rather, the treatment is a simplified representation of fluctuating directed coördinations by hydrogen bonds of otherwise randomly oriented molecules. A similar discussion of hydrogen bonding in pure alcohols by an extension of Oster and Kirkwood's development[6] to include finite extent of molecular correlation gives a simple basis for understanding variations in the magnitude and temperature dependences of the dielectric constants for different aliphatic alcohols. This analysis will be presented elsewhere.

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[4] R. W. Long, J. H. Hildebrand and W. E. Morrell, THIS JOURNAL, **65**, 182 (1943).

[5] N. D. Coggeshall and E. L. Saier, *ibid.*, **73**, 5414 (1951).

[6] G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 175 (1943).

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Methods of Obtaining Rate Constants for Reactions of Half Order and of Mixed Half Plus First Order Followed Manometrically

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In the course of manometric studies of the rates of the thermal decomposition of benzenediazonium salts in methanolic solutions in the presence of acetate buffers, complex pressure–time curves were obtained.[1] Most of these reactions proved to be of half order, of first order, or of mixed half plus first order. A number of methods of treating these data were investigated from the standpoint of convenience, accuracy and evidence of correctness of the assumed kinetic order. The most reliable method was found to be the least squares procedure. Useful first approximations to the constants of reactions of mixed half plus first order can be obtained graphically.

Equation 1 is the differential expression for a reaction of mixed half plus first order.

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[1] D. F. DeTar and M. N. Turetzky, in preparation.