

The viscosity of iodine must be of the same order of magnitude as that of bromine and the same holds for solutions in the two solvents. The concentrations at which the minimum conductance appears would seem to indicate a dielectric constant markedly higher than that of bromine at 25°. In benzene (D . const. = 2.28), the conductance minimum for a strong salt lies at $1 \times 10^{-5} N$; for anisole ($D = 4.29$), it lies at 1×10^{-3} and for ethylene bromide ($D = 4.76$), it lies at $5 \times 10^{-3} N$. On this basis, the dielectric constant of liquid iodine at 140°C. might be expected to lie in the neighborhood of 5.0.

In any case, we cannot escape the conclusion that potassium iodide in iodine solution is very measurably dissociated into free ions at low concentrations and highly dissociated at higher concentrations. If we may be permitted to repeat, to gain an understanding of concentrated electrolytic solutions, we shall have to consider them from the point of view of solutions of solvent in salt. In solvents of low dielectric constant, the state of the system is determined by the charged ions of the electrolyte; the lower the dielectric constant, the lower the concentration down to which the ions are the dominant factor.

¹ Darby, Edward H., *J. Am. Chem. Soc.*, **40**, 348 (1918).

² Terwogt, P. C., *Z. anorg. Chem.*, **47**, 203 (1905).

³ Scott, A., *J. Chem. Soc.*, **103**, 347 (1913).

⁴ Strong, L. E., and Kraus, C. A., *J. Am. Chem. Soc.*, **72**, 166 (1950).

⁵ Seward, R. P., *Ibid.*, **73**, 515 (1951).

⁶ Lewis, G. N., and Wheeler, P., *Proc. Am. Acad.*, **41**, 419 (1906).

VELOCITY ULTRACENTRIFUGATION OF HETEROPOLY ACIDS

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This communication is concerned with some preliminary velocity ultracentrifuge experiments which we have performed with 12-tungsto-silicic acid and some other heteropoly acid salts. It was suggested to us by Professor L. Pauling that because of their large densities these compounds might sediment at measurable rates in the ultracentrifuge despite their relatively low molecular weights. Upon investigation it was found that not only were the sedimentation constants (s) easily measurable, but diffusion constants (D) could be determined from the same sedimentation diagrams. In combination with partial specific volume (\bar{V}) determinations, it was possible to calculate molecular weights for the anions in question by means of the familiar Svedberg rate sedimentation equation:¹

$M = RTs/D(1 - \bar{V}d)$. To our knowledge, no ionically dispersed inorganic salt has previously been studied in the velocity ultracentrifuge, and a molecular weight determined from combined measurements of its sedimentation and diffusion constants.

In order to determine the weights of the anions, the compounds were investigated in buffered solutions of fairly large ionic strengths. The

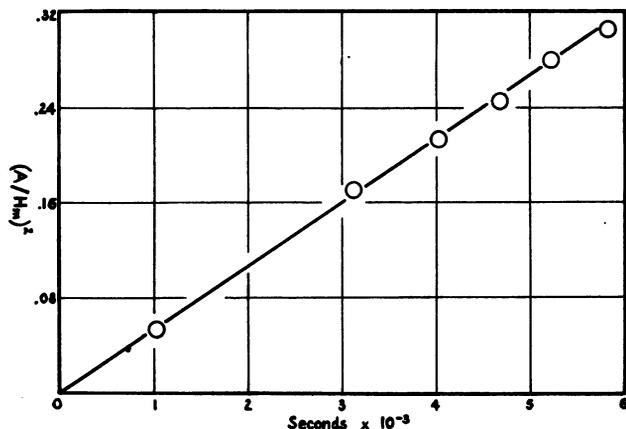


FIGURE 1

A plot of diffusion data obtained during the sedimentation of 12-tungsto-silicic acid.

TABLE 1

PHYSICAL CONSTANTS OF HETEROPOLY ACIDS AND SALTS^a

COMPOUND ^b	BUFFER	SOLUTE CONC., G./100 ML.	\bar{V}	$\frac{w}{520} \times$ 10^{13} , SEC.	$\frac{D_w}{10^6}$, CM. ² / SEC.	M_{formula}^c		
						HYD.	UNHYD.	$M_{\text{sed.}}$
<i>a</i>	NaAc-HAc, pH 5.23, μ 0.2	1.20	0.2524	3.8	4.4	3307	2875	2800
<i>b</i>	NH ₄ Ac, 0.50%, pH 7.0	1.40	0.2846	3.5	3.5	6204	5340	3400
<i>b</i>	KH phthalate-HCl, pH 2.8, μ 0.1	1.39	0.2743	3.6	4.0	6204	5340	3000
<i>c</i>	KH phthalate-HCl, pH 2.8, μ 0.1	2.04	0.3225	3.4	4.1	2742	2346	3000

^a All sedimentation experiments performed at 53,220 r. p. m.

^b See text.

^c For anions.

ultracentrifuge used in these studies has been briefly described.² It employs a cylindrical lens schlieren optical system. In all experiments, the schlieren patterns were symmetrical, and values of s were readily determined from the position of the maximum ordinate of the peak as a function of time. D was calculated from the same patterns by the area-maximum ordinate method.³ In figure 1 is plotted $(A/H_m)^2$ against t for a series of

different exposures in a representative experiment, where A is the area in cm.,² H_m is the maximum ordinate in cm. of the sedimenting peak, and t is the time in seconds after full rotor speed was attained. A straight line passing through the origin is obtained, which is one important criterion for a satisfactory diffusion experiment.⁴ Values of \bar{V} were calculated by the method of Kraemer⁵ from density measurements on solutions of the crystalline hydrated compounds. The molecular weights which we have obtained should therefore best be compared with the molecular weights expected for the hydrated anions, assuming that the water of hydration in the crystal remains largely bound to the sedimenting anions. While there is some uncertainty about \bar{V} , as much as a 10% error in \bar{V} results in an error of only 3% in the calculated molecular weight for these compounds.

Three compounds were studied: compound *a*, 12-tungsto-silicic acid, $H_4SiW_{12}O_{40} \cdot 24H_2O$, whose structure has been determined by x-ray diffraction;^{6,7} compound *b*, reported to be ammonium 11-tungsto-manganate, $(NH_4)_8H_2[Mn_2W_{22}O_{74}] \cdot 48H_2O$;⁸ and compound *c*, which has been described by Rogers⁹ as $13(NH_4)_2O \cdot 2P_2O_5 \cdot 8V_2O_5 \cdot 34WO_3 \cdot 86H_2O$. Analyses indicate that this substance could probably be better represented as $(NH_4)_7[PV_4W_8O_{40}] \cdot 22H_2O$, as suggested by Dr. Pauling, and be regarded as a member of the 12-series of heteropoly compounds in which one third of the tungsten atoms have been replaced by vanadium. In table 1 are summarized the results obtained with these compounds. Within the experimental errors (largely in the diffusion constants), the calculated molecular weight of the hydrated anion $[SiW_{12}O_{40}]^{-4} \cdot 24H_2O$ agrees with the formula weight. In the case of compound *b*, the molecular weight found indicates that the probable molecular weight is one half of its formula weight. For compound *c*, a molecular weight of about 3000 for the hydrated anion is in agreement with the above suggested formulation, $[PV_4W_8O_{40}]^{-7} \cdot 22H_2O$.

Further studies of similar compounds are contemplated. In particular, it should be possible to obtain more accurate diffusion constants for these substances from measurements independent of the ultracentrifuge. These data, combined with appropriate sedimentation constants, would then provide a sensitive test of the adequacy of the Svedberg equation as applied to these small molecules. (The radii of these anions are about 7A.)

Furthermore, the compounds should be useful as standards for calibration of velocity ultracentrifuges, and as model systems for the study of a variety of hydrodynamic problems.

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† Contribution No. 1698.

¹ Svedberg, T., and Pedersen, K. O., *The Ultracentrifuge*, Oxford University Press, London, 1940.

² Singer, S. J., and Campbell, D. H., *J. Am. Chem. Soc.*, **74**, 1794 (1952).

³ Lamm, O., *Nova Acta Reg. Soc. Sci. Upsal.*, **10**, No. 6 (1937).

- ⁴ Longworth, L. G., *Ann. N. Y. Acad. Sci.*, **41**, 269 (1941).
⁵ Reference 1, p. 58.
⁶ Keggins, J. F., *Proc. Roy. Soc.*, **144A**, 75 (1934).
⁷ Signer, R., and Gross, H., *Helv. Chim. Acta*, **17**, 1076 (1934).
⁸ Mair, J. A., and Waugh, J. L. T., *J. Chem. Soc.*, **152**, 2372 (1950).
⁹ Rogers, A., *J. Am. Chem. Soc.*, **25**, 299 (1903).

ON VARIATIONS OF THE GEOMAGNETIC FIELD, FLUID
MOTIONS, AND THE RATE OF THE EARTH'S ROTATION

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Introduction.—Brouwer¹ has recently estimated the changes in the yearly rate of the earth's rotation since 1820. He found considerable systematic fluctuations over periods of time as short as about 50 years. These fluctuations were unexplained, though it was suggested that they are of geophysical origin.

The changes in angular momentum in the atmosphere, oceans, crust and mantle are either too small or take place too slowly to explain the major part of the observed non-seasonal changes in rate of rotation. These conclusions are also presented in a valuable paper by Walter Munk and Roger Revelle given at the spring meeting of the American Geophysical Union in 1952, at which time the present paper was read. It is understood their paper will appear in the *Monthly Notices* of the Royal Astronomical Society.

It is the purpose of the present paper to compare Brouwer's results with changes with time in the westward drift of fluid moving near the surface of the earth's central core, as inferred from the westward drift of the earth's eccentric dipole field of terrestrial magnetism.² Also discussed, as a check, are the effects of variation in the northerly drift of fluid in the core. The latter are less accurately inferred from the geomagnetic data, and would affect the position of the north pole, which as it moves gives a variation of latitude upon the spinning earth.

Motion of Geomagnetic Field.—It is of interest to derive the position of this eccentric dipole relative to the earth's surface as a function of time, supposing this dominant simple feature of the earth's field to indicate some corresponding broad scale feature of the fluid motion of the earth's central core. For instance, at the earth's surface the field of the eccentric dipole may be regarded as that due to a simple spherical electric current sheet flowing in the outer part of the core. Motion of the dipole about