with aqueous ammonia afforded a mixture of diaminocyclohexanetetrols which were isolated and separated as the picrates.

The main product from the α-dibromotetrol (α-diamine I) was converted into suitable acyl derivatives and compared with the main product from the β-dibromotetrol (β-diamine I) and its derivatives. Though in many respects similar, the two diamines appear to be different chemical entities. Their N,N′-diacetyl derivatives both consumed two moles of periodate indicating that the parent diamines could be either 1,3- or 1,4-diaminocyclohexanetetrols. Identity with streptamine is excluded in either case by the properties of the acyl derivatives.

In addition both dibromotetrols yielded small amounts of an identical diaminocyclohexanetetrol (diamine II). The N,N′-diacetyl derivative consumed three moles of periodate and hence must carry the acetamido groups in vicinal ring positions.

NEW BRUNSWICK, N. J. RECEIVED OCTOBER 28, 1948

[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Molecular Properties of Liquids. V. Inorganic Halides[1]

BY ALFRED WEISSLER

The relation between sound velocity and molecular structure has been studied[2] in several series of organic liquids, but thus far not in inorganic liquids. A group of compounds which seemed especially suitable for this purpose consists of the Group IV tetrahalides. Their molecules may be considered as approximately spherical, so that they are easier to treat theoretically and thus furnish an approach to a better understanding of the liquid state. Because of this, their physical and thermodynamic properties have been studied for many years by Hildebrand[3] and co-workers.

A two-fold aim motivated the present work: (a) comparison of inorganic and organic liquids with respect to sound velocity, and (b) determining further properties of the interesting tetrahalides referred to above. Several thermodynamic quantities may be calculated from the measured velocity of sound in a liquid.

In addition to CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$ and $SnCl_4$, some of the Group V halides were included here, specifically, PCl_3, PBr_3, $POCl_3$, $AsCl_3$ and $SbCl_5$.

Experimental

The ten liquids were procured from commercial sources. Each was purified by fractional distillation (the fraction retained had a boiling-range of 0.5°) shortly before use, and protected as well as possible from deterioration due to moisture. The liquids were handled only under conditions of low atmospheric humidity.

Sound velocities at 30° were measured by means of the three-megacycle ultrasonic interferometer already described,[2] which requires only 10 ml. of sample. In order to minimize contamination of these reactive liquids, all interior surfaces were gold-plated and the usual nickel diaphragm at the floor of the cell was replaced by tantalum.

Densities, heat capacities and coefficients of thermal expansion at 30° were obtained from the "International Critical Tables" and Landolt–Börnstein tables.

Results and Discussion

The velocity of sound in each of these inorganic halides is given in Table I; the probable accuracy is ±0.1%. These values lie in the range from about 760 to 1000 meters per second, which is somewhat lower than for most other liquids, including the organic halides. Figure 1 shows that no regular change of sound velocity in the tetrachlorides occurs as the atomic number of the central atom increases. In the Group V halides also, there is no consistent trend with molecular weight.

Molar Sound Velocity.—Because it is an additive function[4,5] of the chemical bonds in the molecule, the molar sound velocity is useful in correlating molecular structure with sound velocity. It is defined, so as to be empirically almost temperature-independent, as the molar volume times the cube root of sound velocity.[6]

From the values of molar sound velocity listed in Table I, the bond increment characteristic of each bond present in these compounds was obtained by simple arithmetic. For example, the value for $SiCl_4$ was divided by 4 in order to find the Si–Cl increment, while that for PBr_3 was divided by 3 to get the P–Br increment. Table II contains the figures so derived, which again fail to vary regularly with atomic number of the central atom, in either Group IV or Group V.

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[1] The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the Navy service at large. Article not copyrighted.

[2] Weissler, THIS JOURNAL, **71**, 93 (1949); **71**, 419 (1949); and references contained therein.

[3] Hildebrand, *J. Chem. Phys.*, **15**, 727 (1947).

[4] Lagemann and Dunbar, *J. Phys. Chem.*, **49**, 434 (1945).

[5] See, however, Lagemann, Evans and McMillan, THIS JOURNAL, **70**, 2996 (1948), who studied a large number of organic halides and concluded that molar sound velocity is not strictly additive, but rather highly constitutive.

[6] Rao, *J. Chem. Phys.*, **9**, 688 (1941).

TABLE I

PROPERTIES OF INORGANIC HALIDES AT 30°

Compound	Sound velocity, meters/sec.	Density, g./ml.	Molar sound velocity	Adiabatic compressibility (10^{-12} cm.^{2}/dyne)	Coefficient of thermal expansion	Heat capacity, joule/g.	Isothermal compressibility (10^{-12} cm.^{2}/dyne)	Ratio of specific heats	Thermal pressure coefficient, 10^6 dyne/cm.^{2} deg.	Energy-volume coefficient, 10^6 dyne/cm.^{2}
CCl_4	905.8	1.5746	945.4	77.40	1.240×10^{-3}	0.866	111.6	1.44	11.11	3367
$SiCl_4$	766.2	1.4622	1063.2	116.50	1.438	.837	167.7	1.44	8.57	2598
$TiCl_4$	977.5	1.7078	1102.6	61.28	1.045	.804	85.4	1.39	12.24	3708
$GeCl_4$	768.6	1.8533	1059.8	91.34	1.273	.699[a]	129.3	1.42	9.85	2984
$SnCl_4$	782.3	2.2004	1090.9	74.26	1.178	.619	105.2	1.42	11.20	3394
PCl_3	944.1	1.5567	831.3	72.07	1.207	.876	104.4	1.45	11.56	3504
PBr_3	916.7	2.8513	922.4	41.74	0.858					
$POCl_3$	969.3	1.6564	916.5	64.26						
$AsCl_3$	1006.7	2.1392	884.5	46.13	1.040	.737	66.9	1.45	15.55	4712
$SbCl_5$	912.3	2.331	1244.3	51.54						

[a] Estimated by interpolation.

Compressibility.—The adiabatic compressibility K_{ad} is related to the velocity of sound v and the density d by the equation

$$K_{ad} = 1/v^2d \qquad (1)$$

Adiabatic compressibilities computed from (1) are listed in Table I. $SiCl_4$ is by far the most compressible of these liquids, in agreement with its known low boiling point and low internal pressure, while PBr_3 is the least compressible.

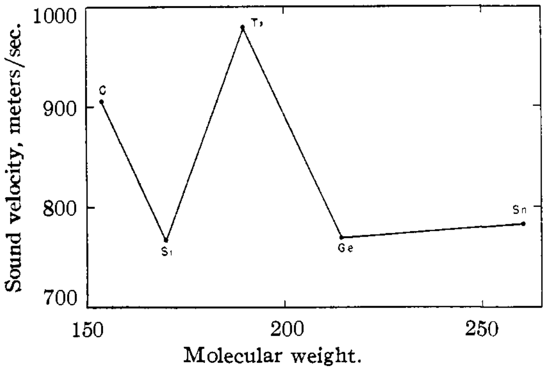

Fig. 1.—Sound velocity in liquid tetrachlorides.

A plot of K_{ad} for the tetrachlorides (solid line, Fig. 2) shows an irregular variation with molecular weight. This is in sharp contrast to the organic halides (for example, methylene chloride, bromide, and iodide) where each increase in molecular weight causes a considerable decrease in compressibility.[5,7]

Freezing points of the tetrachlorides are also plotted in Fig. 2 (broken line) using an inverted temperature scale. The remarkable similarity between the two curves suggests that the same forces which determine compressibility also fix the freezing temperature, for each of these liquids. This may be thought of in the following way. The greater the space between molecules, the greater the compressibility—also, the greater the cooling necessary to bring the molecules sufficiently close together so that their mutual attractive forces become strong enough to freeze the molecules into the solid lattice.

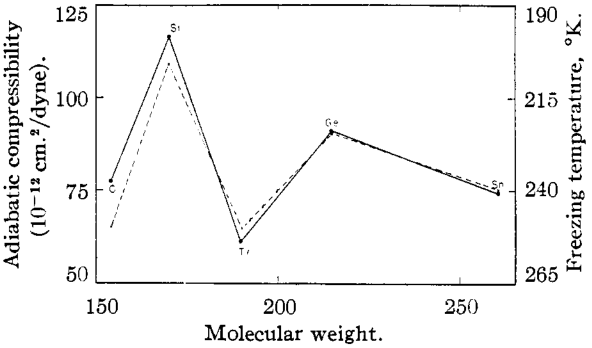

Fig. 2.—Adiabatic compressibility (solid line) and freezing temperature (broken line) of liquid tetrachlorides.

From the adiabatic compressibility plus the heat capacity c_p, coefficient of thermal expansion α, temperature T, and density d, the isothermal compressibility may be calculated using the equation

$$K_{is} = K_{ad} + T\,\alpha^2/c_pd \qquad (2)$$

Table I gives the values (where available) for c_p, d, and α, as well as the isothermal compressibilities calculated therefrom for seven of the liquids.

Of thermodynamic interest is the fact that the ratio of isothermal to adiabatic compressibility is equal to the ratio of specific heats γ. The values for γ shown in Table I are as usual considerably higher than those for the same molecules in the gaseous state: thus, 1.44 for liquid CCl_4 compared to 1.18 (theoretical) for the gas. For $TiCl_4$, γ is appreciably lower than for the other tetrahalides, possibly as a result of the greater ionic character of its bonds.

Thermal Pressure and Energy–Volume Coefficients.—The thermal pressure coefficient $(\partial P/\partial T)_V$ is related to the isothermal compressi-

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(7) Bergmann, "Der Ultraschall," 3rd ed., Edwards Brothers, Ann Arbor, Mich., 1944, p. 183.

bility in that their product is equal to the coefficient of thermal expansion[8]

$$\left(\frac{\partial P}{\partial T}\right)_V \bullet \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{-1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad (3)$$

Values for $(\partial P/\partial T)_V$ computed from this equation are listed in Table I, which shows that $SiCl_4$ has the lowest and $AsCl_3$ the highest. Comparison with the thermal pressure coefficients previously obtained by direct measurement[9] for four of these liquids indicates fairly good agreement; uncertainty in the specific heats probably accounts for much of whatever differences exist.

A thermodynamic equation of state applicable to all substances is

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \qquad (4)$$

which makes it possible to calculate the important coefficient for the variation of energy with volume, $(\partial E/\partial V)_T$. For a liquid, this quantity is also called the internal pressure (dimensions of energy/volume are equivalent to pressure) because it is a measure of the attractions and repulsions of the molecules. These energy–volume coefficients obtained from equation (4), taking P as atmospheric pressure (1.013×10^6 dynes/cm.^{2}), are given in Table I. Again there is no monotonic variation with molecular weight.

Estimation of Heat Capacity.—The heat capacity c_P may be estimated by means of equation (2), if the other quantities are known. This may be illustrated in the case of PBr_3. Assuming as an approximation that γ for this compound is 1.45, the same as for PCl_3 and $AsCl_3$, we find that the heat capacity at 30° is 0.417 joule/gram, with a presumable accuracy of a few per cent.

TABLE II

BOND INCREMENTS FOR MOLAR SOUND VELOCITY

Bond	Increment	Bond	Increment
C–Cl	236	P–Cl	277
Si–Cl	266	P–Br	307
Ti–Cl	276	P=O	85
Ge–Cl	265	As–Cl	295
Sn–Cl	273	Sb–Cl	249

Acknowledgment.—It is a pleasure to acknowledge the many helpful suggestions made by Dr. G. R. Ringo during the course of this work.

Summary

The velocity of sound at 30° in ten inorganic halides has been determined; on the average, it is lower than in the organic halides. Such properties as compressibility, ratio of specific heats, and the energy–volume coefficient have been computed from the sound velocities. There is no systematic variation with molecular weight in any of these properties.

RECEIVED OCTOBER 29, 1948

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[8] Westwater, Frantz and Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

[9] Hildebrand and Carter, THIS JOURNAL, **54**, 3592 (1932).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Resolution of the Dissociation Constants of Citric Acid at 0 to 50°, and Determination of Certain Related Thermodynamic Functions[1]

BY ROGER G. BATES AND GLADYS D. PINCHING

The development of exact electromotive-force methods[2,3] has brought about a considerable extension of our knowledge of the thermodynamics of weak electrolytes in recent years. In general, these experimental procedures, based upon electromotive-force measurements of cells without liquid junction, have been applied only to systems the composition of which can be completely expressed in terms of stoichiometric concentrations, the water equilibrium, and a single step in the dissociation of the weak electrolyte. If two or more acids or acidic groups are partially neutralized in the same range of hydrogen-ion concentrations, as is often the case with organic polybasic acids, the composition of the mixture may be quite difficult to establish. For this reason little attention has been directed to the resolution, by thermodynamic methods, of the dissociation constants of dibasic acids for which K_1/K_2 is less than 1000.

Separation of the constants for three overlapping equilibria is even more laborious. For citric acid, K_1/K_2 and K_2/K_3 are both about 44 at 25°. Existing values[4,5,6] of the thermodynamic constants for this acid were derived from electromotive-force measurements of cells with liquid junction. The analysis of the data rests in each instance upon a computation of the hydrogen-ion concentration or activity. Consequently, an assumption regarding the potential at the liquid junction must be introduced.

In spite of the interest that attaches to the thermodynamics of such a three-step dissociation process, no determination of the constants of a tribasic acid, with or without overlapping, has

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[1] Presented before the Physical and Inorganic Division at the September, 1947, meeting of the American Chemical Society at New York City.

[2] H. S. Harned and B. B. Owen, THIS JOURNAL, **52**, 5079 (1930).

[3] H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932).

[4] H. S. Simms, *J. Phys. Chem.*, **32**, 1121 (1928).

[5] I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, **47**, 558 (1928).

[6] N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, No. 1 (1929).