for dilute aqueous solutions of all uni-univalent salts (D = dielectric constant; T = absolute temperature).

This equation predicts that the curve should be nearly straight in moderate concentrations, but that the limiting slope at extreme dilutions should be plus infinity.

We have devised a modification of the capillary rise method which has enabled us to measure the surface tension of solutions relative to that of water with greater precision than has hitherto been possible. The data for potassium chloride solutions are shown in the accompanying figure, together with a plot of the Onsager and Samaras equation. At extreme dilutions (less than 0.006 N) the surface tension is less than that of water, whereas above 0.006 N the surface tension is increased and is approximately a linear function of the concentration. These results are not in accord with the Onsager and Samaras equation, especially as to the sign of the limiting slope at extreme dilutions. Similar results have been obtained with potassium sulfate and cesium nitrate solutions. On the other hand, sucrose solutions from 0.0005 to 0.005 mole per liter, inclusive, when measured in the same apparatus, gave an increased surface tension. The effect which causes the diminution of surface tension and therefore, according to the Gibbs Theorem, also causes positive adsorption in the surface layer, is presumably due to an interaction between the polarized water molecules and the ions, which at extreme dilutions tends to force the ions into the surface layer. At higher concentrations the interionic forces predominate and cause negative adsorption and increased surface tension.

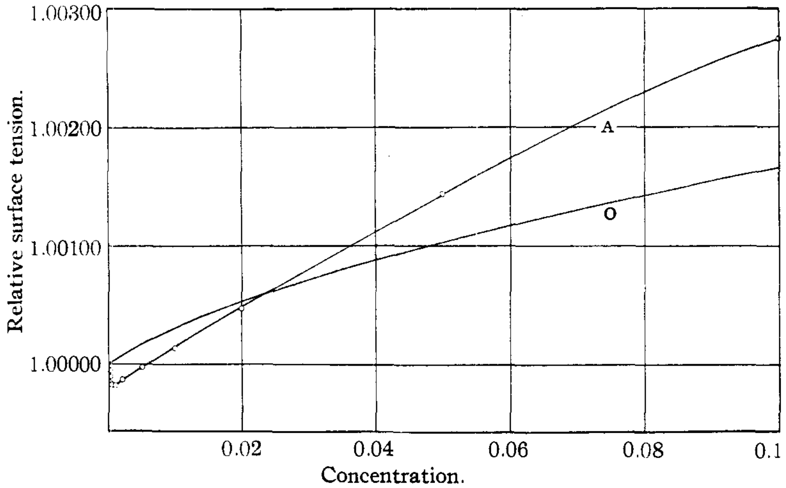

Fig. 1.—A, KCl at 25°; O, Onsager equation for uni-univalent salts.

The work is being continued both experimentally and theoretically to determine the general validity of the phenomenon and the factors which influence it.

MALLINCKRODT LABORATORY GRINNELL JONES
HARVARD UNIVERSITY WENDELL A. RAY
CAMBRIDGE, MASS.

RECEIVED APRIL 18, 1935

THE MOLECULAR STRUCTURE OF GERMANIUM TETRACHLORIDE

Sir:

The electron diffraction investigation of the chlorides of the fourth group elements [L. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934)] has been extended by the study of germanium tetrachloride. Professor L. M. Dennis of Cornell University very kindly supplied a sample of the compound.

The photographs show two distinctive qualitative features: the little hump on the inner edge of the first strong maximum and the sloping shelf on the outside of the second maximum. Both of these characteristics appear in the theoretical intensity curve based upon a regular tetrahedral model included in Fig. 1 of the previous report. Two maxima were observed beyond the limit of the published curve.

The quantitative comparison is given in Table I. The third column gives the indicated values for the observed maxima and minima; the fourth gives the corresponding points on the theoretical curve and the fifth column shows the Ge–Cl interatomic distance. The first two points give values much lower than the average as has always been observed in the case of short distance (about ten centimeters) photographs of relatively large molecules [Ref. 1]. The value which Wierl [*Ann. Physik.*, [5] **8**, 548 (1931)] obtained with photographs covering only half of the present angular range is not altered by this more complete investigation.

Germanium tetrachloride shows about the same deviation (Table II) from additivity of the radii that the silicon and tin chlorides do. The sharp

TABLE I

GERMANIUM TETRACHLORIDE

Three photographs; camera distance, 10.43 cm.; $\lambda = 0.0606$ Å.

Max.	Min.	$\frac{4\pi \sin \Theta/2}{\lambda}$	x	a = Ge–Cl
1		4.088	8.17	(2.000)
	2	5.305	10.65	(2.008)
2		6.273	13.22	2.108
	3	8.598	17.82	2.074
3		9.750	20.29	2.080
	4	11.07	22.76	2.056
4		12.75	27.33	2.143
	5	14.24	29.82	2.094
5		15.46	32.20	2.082
	6	17.02	36.86	2.164
6		18.51	39.35	2.123
			Average	2.103

Ge–Cl = 2.10 ± 0.03 Å.
(Wierl, 2.10 ± 0.05 Å.)

TABLE II

Bond	Observed distance	Radius sum	Difference
C–Cl	1.76	1.76	0.00
Si–Cl	2.02	2.16	.14
Ge–Cl	2.10	2.21	.11
Sn–Cl	2.29	2.39	.10

distinction between these three and carbon tetrachloride can scarcely be explained on the basis of gradations in electronegativity of the central atoms. It seems probable that there is some essential difference in the character of the bond, such as the formation of double electron pair bonds as discussed in the previous report.

Studies of the tetramethyl compound are being made in the further investigation of this point.

GATES CHEMICAL LABORATORY L. BROCKWAY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

RECEIVED APRIL 1, 1935

OCCURRENCE OF ANABASINE IN NICOTIANA GLAUCA R. GRAH. (SOLANACEAE)

Sir:

Beta-pyridyl-α'-piperidine, $C_{10}H_{14}N_2$, isomeric with nicotine, was shown by Orechoff and Menschikoff [*Ber.*, **64**, 266 (1931)] to be present in the plant *Anabasis aphylla* L. (Chenopodiaceae) and was named "anabasine." Pictet and Rotschy had previously [*ibid.*, **34**, 696 (1901)] reported β-pyridyl-α'-piperidine, which they called "nicotimine," to be present in tobacco in a ratio of 1 part of nicotimine to 200 parts of nicotine. Later work has shown that Pictet and Rotschy did not isolate the proper compound, but recently Ehrenstein [*Arch. Pharm.*, **269**, 627 (1931)] has apparently isolated the alkaloid anabasine from tobacco.

Schmuck [Krasnodar (U. S. S. R.) State Inst. Tobacco Invest., *Bull.* **109**, 24 (1934)] stated that the alkaloid of *Nicotiana glauca* R. Grah. was not nicotine, but no identification was made. A sample of *Nicotiana glauca* roots was sent to this Laboratory by Mr. B. McKinney of the Tempe, Ariz., station of the Division of Truck Crop and Garden Insect Investigations of this Bureau. When examined it was found to contain about 1% of anabasine. A sample of the whole plant was later received from the same source and the identity confirmed by botanists of this Department. Further examination of samples of dried leaves from plants grown from seeds on the Arlington Experiment Farm by the Bureau of Plant Industry showed that they also contained anabasine. It is doubtful that nicotine is present except possibly in a trace.

The anabasine isolated was a liquid alkaloid boiling at 281° (537.8°F.) (corr.), which was soluble in water in all proportions and formed a picrate whose melting point of 212–213° (413.6–415.4°F.) was unchanged by admixture with picrate of anabasine prepared from commercial anabasine sulfate. The optical rotation $[\alpha]^{20}_D$ was $-9.1°$, instead of $-82.2°$ reported by Orechoff and Menschikoff, or $-59.66°$ reported by Nelson [THIS JOURNAL, **56**, 1989 (1934)]. Dehydrogenation by palladium black produced α,β-dipyridyl, which was formed into the dipicrate and the monopicrate, comparing closely with known samples of these picrates in appearance and melting points.

The principal method used to extract the anabasine was to digest the material with warm 1% hydrochloric acid, filter, make alkaline and extract with ether. When the alkaline solution was distilled, ammonia and pyridine were found in the first part of the distillate but nicotine was not detected. The removal of the anabasine by further distillation was incomplete.

Nicotiana glauca grows wild in various parts of the Southwest, particularly in California. It is the first species of plant in this country found to contain anabasine as the principal alkaloid. A study of certain other species of *Nicotiana* should prove of interest as their alkaloids have not been definitely determined.

Anabasine is a promising contact insecticide,