Based upon an early heat of combustion for *t*-butyl alcohol obtained by Zubow-Swietoslawski, Parks and Huffman give for the enthalpy and free energy of formation of *t*-butyl alcohol(l) at 25° the values −89,410 and −47,500 cal. mole^{-1}, respectively.[11] From the enthalpies of formation of isobutene(g) (−4.04 kcal.)[12] and water(l) (−68.32 kcal.)[13] which must certainly be reliable, one obtains for the standard enthalpy change of reaction 3, ΔH°_{298}, the value −17.05 kcal. mole^{-1}. This result is 4.5 kcal. less than the value of ΔH°_{298} reported above, and indicates that the heat of combustion of *t*-butyl alcohol is too low (*ca.* 0.7%) by about this amount. On the basis of the data presented above, the enthalpy of formation of *t*-butyl alcohol(l) is −85.0 kcal. mole^{-1} at 25°. This value is 5.4 kcal. more negative than the value given by Parks and Huffman for *n*-butyl alcohol.[11]

From the free energies of formation of isobutene(l) (+13.88 kcal.)[12] and of water(l) (−56.69 kcal.),[13] and ΔF°_{298} of reaction 3, one obtains for the free energy of formation of *t*-butyl alcohol(l) at 25° the value −44.1 kcal. mole^{-1}. This is 3.8 kcal. more negative than the value for the free energy of formation at 25° of *n*-butyl alcohol given by Parks and Huffman.[11]

The standard entropy change accompanying reaction 3 may be obtained from the values of ΔF°_{298} and ΔH°_{298} given above. The result (which is unlikely to be in error more than 1.5 e.u.) is

$$\Delta S^\circ_{298} = -37.9 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad \text{(reaction 3)}$$

Third Law entropies may also be used to calculate ΔS°_{298}. From the entropies of the substances involved (isobutene(g)S°_{298} = 70.2 e.u.[12]; water(l), ΔS°_{298} = 16.7[13] e.u.; *t*-butyl alcohol(l), S°_{298} = 45.3 e.u.[11]), one obtains for ΔS°_{298} the figure −41.7 cal. deg.$^{-1}$ mole^{-1}. The agreement between the two values for ΔS°_{298} is rather disappointing.[14]

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[11] Ref. 10, p. 109.

[12] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Penna., 1953, p. 475.

[13] Ref. 12, p. 464.

[14] The two values may be brought into agreement if we take ΔS°_{298} = −39.4 e.u., and use for isobutene the experimental value of S°_{298} = 69.0 e.u. given by S. S. Todd and G. S. Parks, THIS JOURNAL, **58**, 134 (1936), and the value 46.3 e.u. for S°_{298} for *t*-butyl alcohol(l), which is within the limits of error given by Parks for the value quoted above.

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The Formation of Silicon Monosulfide[1]

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During the course of the preparation of silicon disulfide by direct synthesis, as described by Gabriel and Alvarez-Tostado,[3] it was found that a major product of the reaction was silicon monosulfide. Similar results were obtained, but to a lesser extent, by the use of Malatesta's[4] method. In both cases the initial reaction product was white to gray, indicating the presence of SiS_2, whereas the sublimed product was yellow, and red to black, these being known modifications of SiS. The composition of this colored sublimate was confirmed by chemical analysis. The failure to observe the characteristic color of SiS in the crude reaction mixture suggested that the formation of the monosulfide was due to subsequent reaction between SiS_2 and excess Si, analogous to the formation of SiO from SiO_2 and Si. The possibility of this reaction occurring has been suggested by Kohlmeyer and Retzlaff.[5]

In order to demonstrate that SiS may be formed in this way, pure SiS_2 was intimately mixed with excess Si and heated under vacuum to 850°. The reaction was quantitative and the product consisted entirely of SiS. It was further shown that the monosulfide was not formed in the original reaction between silicon and sulfur at atmospheric pressure and that the monosulfide which later appeared was entirely due to the high temperature reaction under vacuum. Reactions were run between silicon and sulfur with the atomic ratio S/Si varying from 1.0 to 2.0, and in all cases the only initial product was SiS_2. This was demonstrated by the fact that the crude reaction mixture did not evolve hydrogen upon treatment with dilute NaOH. The monosulfide reacts quantitatively with aqueous NaOH according to the equation

$$SiS + 2OH^- + H_2O \longrightarrow SiO_3^{=} + H_2 + H_2S$$

The number of moles of H_2 evolved per formula weight of SiS in two determinations was 1.01 and 0.98.

The structure of SiS in the solid state is not known and the product may possibly be a disproportionated intimate mixture of SiS_2 and finely divided silicon. X-Ray spectrograms of both the yellow and red forms failed to resolve this question, as amorphous patterns were obtained in both cases.

Sublimation of the sulfides was carried out by placing the crude products of direct synthesis in a large porcelain boat and heating under vacuum in a sublimation tube constructed of 38 mm. o.d. clear quartz and Vycor. The quartz section was one foot long and one foot of Vycor was fused to the quartz at either end. The heating unit was a Hoskins electric furnace.

The test for the presence of SiS in the solid products was carried out by the addition of 0.05 *N* NaOH to the solid under vacuum. H_2S and water vapor were condensed at −196° and any increase in pressure in the system was attributed to the presence of H_2. Under these conditions SiS gave a strong positive test, whereas the initial product of reaction between Si and S gave negative tests.

The preparation of pure SiS_2 was most conveniently accomplished by the reaction between Al_2S_3 and SiO_2.[6] The reaction of the product with finely divided Si resulted in the formation of SiS. *Anal.* Calcd. for SiS: Si, 46.7; S, 53.3. Found: Si, 45.3, 45.0; S, 54.5, 54.5.

Analysis of the sulfides was carried out by decomposing the sample in concentrated HNO_3, filtering off silica and then precipitating barium sulfate. Quantitative determination of the number of Si–Si bonds in SiS was carried out by the measurement of the volume of H_2 evolved upon decomposition of samples in 1 *N* NaOH. Samples were prepared by adding the finely ground powder to weighed, thin-walled

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[1] From part of a thesis presented by W. J. Bernard to the Department of Chemistry, M. I. T., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] National Science Fellow, 1953–1954.

[3] H. Gabriel and C. Alvarez-Tostado, THIS JOURNAL, **74**, 262 (1952).

[4] L. Malatesta, *Gazz. chim. ital.*, **78**, 702 (1948).

[5] E. J. Kohlmeyer and H. W. Retzlaff, *Z. anorg. Chem.*, **261**, 248 (1950).

[6] E. Tiede and M. Thimann, *Ber.* **59**, 1703 (1926).

glass bulbs, this operation being carried out in an inert atmosphere.

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The Conductance and Viscosity of Highly Concentrated Aqueous Solutions of Hydrazinium Chloride and Hydrazinium Nitrate

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Since the properties of salt solutions at concentrations higher than those corresponding to saturation at room temperature have been but little investigated, it seemed worthwhile to measure some of the properties of solutions of salts having sufficiently low melting points that the observations could be made up to 100% salt at moderately elevated temperatures. In an earlier publication,[1] measurements of the viscosity and electrical conductance of solutions of tetrabutylammonium picrate in butyl alcohol over the complete concentration range, 0–100% salt, were reported. It was shown that the salt behaved as if incompletely dissociated in dilute solution but, judging from the behavior of the conductance–viscosity product, became fully dissociated at very high salt concentrations. As the extent to which the conductance–viscosity product may be relied on as a measure of the degree of dissociation is questionable, it appeared desirable to have measurements on aqueous solutions of uni-univalent salts in which little or no ion pair formation is expected. Hydrazinium chloride, N_2H_5Cl, and hydrazinium nitrate $N_2H_5NO_3$, were found to be suitable salts for this purpose. Measurements of the density, viscosity and conductance were made on solutions up to 100% salt for hydrazinium chloride at 95° and for hydrazinium nitrate at 75°. Since it was thought that the temperature coefficients of conductance and viscosity might be of interest, measurements were made at 25° with both salts up to approximate saturation, and with the chloride at several other temperatures.

C. A. Kraus[2] has recently reviewed previous measurements of conductance and viscosity in concentrated aqueous solutions of uni-univalent salts. The salt concentration, however, did not exceed 60 mole % in any of these solutions. The four salts, silver nitrate, ammonium nitrate, cesium formate and potassium formate discussed by Kraus showed, with increasing salt concentration, an initial sharp drop in the conductance–viscosity product followed by a leveling off or flat minimum. The measurements reported here confirm the existence of the minimum and show that at still higher concentrations the conductance–viscosity product increases smoothly to its limiting value at 100% salt.

Experimental

The hydrazinium salts were prepared by adding a slight excess of hydrazine hydrate to a mixture of five volumes of methanol to one of concentrated acid. The salts precipitated on cooling and were recrystallized from methanol and dried in vacuum at room temperature. $N_2H_5 \cdot NO_3$ melted at 70.5°, N_2H_5Cl at 92.0°.

The conductance bridge and viscometers were those previously described.[1] Densities were measured with a 5-ml. pycnometer, except for that of the pure chloride which, because the salt crystallized in the pycnometer so rapidly, was obtained by dropping a calibrated bulb with a capillary outlet into the fused salt, drawing out air in a vacuum, and then letting in air to force the liquid into the bulb.

As the conductances were much greater than those encountered in the butanol solutions, a new cell was constructed. The cell consisted of two 1.5-cm. electrode chambers, equipped with 1-cm. platinum electrodes, connected by about 7 cm. of 1-mm. capillary tubing. The cell constant, determined with the "one demal" potassium chloride solution of Jones and Bradshaw[3] was 276.4. Bright platinum electrodes were employed because platinum black catalyzes decomposition of the hydrazinium salts. The solutions appeared to be perfectly stable with the bright elec-

TABLE I

Mole % salt	Density	c	Λ	$\eta \times 10^3$	$\Lambda\eta$
$N_2H_5 \cdot Cl$ at 25°					
0.35	1.001	0.1896	107.2	8.99	0.962
2.85	1.035	1.516	87.3	9.24	.811
8.07	1.092	3.990	69.8	10.74	.740
11.29	1.120	5.338	60.2	11.96	.720
15.03	1.149	6.743	50.5	13.90	.702
20.50	1.182	8.542	37.6	19.20	.722
28.20	1.224	10.70	26.3	29.00	.764
$N_2H_5 \cdot Cl$ at 95°					
0.35	0.968	0.183	284.0	3.04	0.863
2.85	0.998	1.463	208.4	3.40	.710
8.07	1.052	3.845	155.6	4.15	.662
11.29	1.082	5.151	131.8	4.90	.646
15.03	1.110	6.613	111.5	5.60	.625
20.50	1.149	8.282	88.30	7.03	.621
28.20	1.186	10.39	64.07	9.89	.634
38.40	1.227	12.60	43.90	15.50	.685
50.65	1.266	14.63	28.00	26.83	.742
59.97	1.293	16.02	19.50	40.08	.782
69.80	1.313	17.20	13.37	62.5	.837
81.30	1.334	18.35	8.65	103.8	.899
91.50	1.352	19.25	5.78	162.2	.940
100.00	1.363	19.89	4.10	234.4	.960
$N_2H_5 \cdot NO_3$ at 25°					
0.23	1.002	0.125	103.6	8.95	0.927
0.98	1.018	0.529	88.1	8.92	.786
2.10	1.040	1.058	79.8	9.08	.724
4.25	1.083	2.167	67.3	9.51	.640
9.23	1.163	4.226	50.4	11.57	.583
15.8	1.242	6.51	36.34	15.80	.574
27.2	1.340	9.36	22.10	27.54	.609
38.7	1.403	11.25	14.55	44.37	.646
$N_2H_5 \cdot NO_3$ at 75°					
2.1	1.017	1.070	160.4	4.04	0.648
4.8	1.063	2.239	130.9	4.47	.585
7.5	1.113	3.511	108.3	5.12	.554
11.2	1.160	4.882	88.83	6.06	.538
15.9	1.215	6.390	71.05	7.63	542
22.9	1.277	8.194	53.78	10.43	.562
30.7	1.334	9.863	40.40	14.15	.572
43.3	1.402	11.83	27.02	22.8	.616
63.5	1.472	13.96	15.39	43.0	.662
78.2	1.510	15.08	10.42	65.0	.678
100.0	1.549	16.29	6.12	115.1	.705

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[1] R. P. Seward, THIS JOURNAL, **73**, 515 (1951).

[2] C. A. Kraus, *J. Phys. Chem.*, **58**, 673 (1954).

[3] G. Jones and B. C. Bradshaw, THIS JOURNAL, **55**, 1780 (1933).