Table V. Compressibility of Isopropyl Alcohol

t, °C.	30.25	40.0	50.4	60.0	70.0
$10^6 K$, Atm.$^{-1}$	120.2	135.0	152.5	175.2	206.6

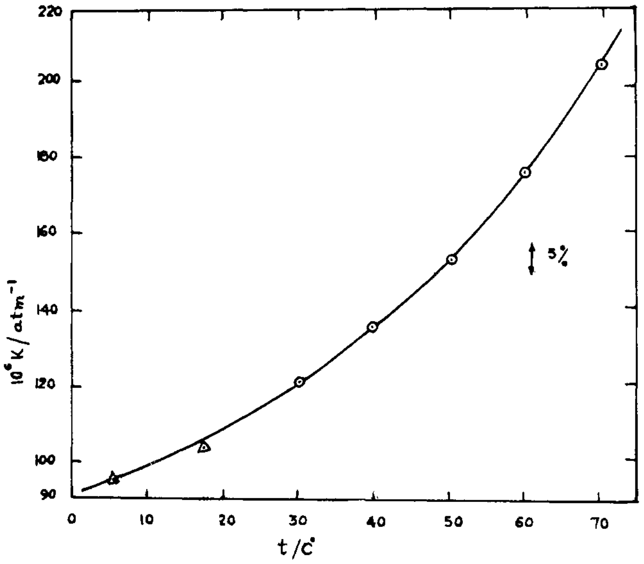

Figure 5. Plot of isothermal compressibility K of isopropyl alcohol against temperature

○ Authors' results

△ Rontgen (*17*).

Freyer (*9*) has calculated the isothermal compressibilities in the range of temperature 0° to 50° C. from the measurement on the velocity of ultrasonic waves in methanol taking into consideration the correction term $T\alpha^2 v/c_p$. The correction terms are of the order of 30%. Tyrer (*18*) has made measurements on the adiabatic compressibility of methanol in the range of temperature 0° to 40° C., and has used them to calculate the isothermal compressibility. His correction terms also are of the order of 30%. Both Freyer and Tyrer's values agree to within 0.5% in the range of temperature common to them. The compressibility of methanol obtained by Philip (*14*) at 27.6° C. is slightly higher (by about 2%) as seen from Figure 3. The authors' observed values in the temperature range of 30° to 60° C. lie on a curve with a larger slope than those of Tyrer and Freyer's results. These two curves intersect at 40° C. At 30° C., the authors' value is less than theirs by 3%, and at 50° C., higher by 6.5%. Both of them are well above the range of experimental errors.

As pointed out earlier, the poor agreement between the present results and the early results of Bridgman is due obviously to the large intervals of pressures (about 500 atm.) used by Bridgman and the difficulties involved in extrapolating them to zero pressures.

The large deviations from Tyrer and Freyer's results are not surprising in view of the fact that measurements were made under adiabatic conditions and the correction terms $T\alpha^2 v/c_p$ which are as large as 30% of K and depend upon the accuracy in the measurement of the parameters α and c_p are involved in the quantity.

Compressibility of Isopropyl Alcohol. Measurements on the isothermal compressibility of isopropyl alcohol have been made at temperatures of 5.65° and 17.85° C. by Rontgen (*17*) within the range of 1.032 to 8.256 kg. per sq. cm. (1 to 8 atm.). However, accurate measurements in the range of temperatures 30° to 70° C. and pressures of 1.032 to 30 kg. per sq. cm. (1 to 29.04 atm.) required for these investigations on the statistical properties of binary liquid mixtures are not readily available. Table V shows the values of K obtained by us in the temperature range of 30° to 70° C. Figure 5 shows the plot of compressibilities of isopropyl alcohol with temperature. Rontgen's observations were made under truly isothermal conditions at temperatures 5.65° and 17.85° C. Within the entire range of measurement, all the observed points lie on a smooth curve with deviations less than the estimated experimental error of 1%.

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Allyl- and Vinyl-Substituted Silazanes

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LITTLE has been published on the preparation and properties of either N-substitued or Si-substituted allyl and vinylsilanes (*1-3, 6-8*). In the course of a study of the synthesis of silazane polymers, a series of allyl and vinylsilazanes and silylamines were prepared and characterized. These compounds, which are reported in Table I, could be prepared readily by methods reported previously (*3*). Yields were usually high except when mixtures of silyl-

Table I. Properties of Allyl- and Vinylsilazanes and Silylamines

	Method of Preparation	Yield, %	B.P., °C. (mm.)	n^t_D	d^t	Analyses Calcd. N	Analyses Calcd. Si	Analyses Found N	Analyses Found Si
$Me_2(CH_2:CH)SiNHMe$	Aminolysis of $Me_2(CH_2:CH)SiCl$	31	93°(atm.)	1.4131(26°)	0.772(26°)	12.16	24.37	12.11	23.91
$Me(CH_2CH)Si(NHMe)_2$[a]	Aminolysis of $Me(CH_2:CH)SiCl_2$	21	65–66° (78)	1.4318(27°)					
$MeN[SiMe(CH:CH_2)NHMe]_2$[b]	Aminolysis of $Me(CH_2:CH)SiCl_2$	11	86° (11)	1.4571(24°)		18.31	24.48	18.11	24.66
$[Me_2(CH_2:CH)Si]_2NH$	Ammonolysis of $Me_2(CH_2:CH)SiCl$	77	95° (84)	1.4362(28°)	0.825(28°)	7.55	30.30	7.50	30.15
$[Me_2(CH_2:CH)Si]_2NMe$	$Me_2(CH_2:CH)SiNHMe$ heated to 155° with $(NH_4)_2SO_4$	65	110° (83)	1.4457(27°)	0.839(27°)	7.02	28.17	7.24	27.93
$[Me(CH_2:CH)SiNH]_3$[c]	Ammonolysis of $Me(CH_2:CH)SiCl_2$	27	122–124° (20)	1.4779(27°)	0.964(27°)	16.44	32.98	16.52	32.79
$[Me(CH_2:CH)SiNMe]_3$	$Me(CH_2:CH)Si(NHMe)_2$ heated to 180° with $(NH_4)_2SO_4$	76	110–113° (4)	1.4783(27°)		14.12	28.31	13.82	28.40
$Me_2(CH_2:CHCH_2)SiNHMe$	Aminolysis of $Me_2(CH_2:CHCH_2)SiCl$	77	64° (98)	1.4250(26°)	0.794(26°)	10.84	21.73	10.88	21.65
$Me(CH_2:CHCH_2)Si(NHMe)_2$[d]	Aminolysis of $Me(CH_2:CHCH_2)SiCl_2$	47	84–87° (80)	1.4409(25°)		19.41	19.47	19.00	19.53
$[Me_2(CH_2:CHCH_2)Si]_2NH$	Ammonolysis of $Me_2(CH_2:CHCH_2)SiCl$	85	113–115° (45)	1.4481(27°)	0.833(27°)	6.56	26.32	6.59	26.17
$[Me_2(CH_2:CHCH_2)Si]_2NMe$	$Me_2(CH_3CH:CH)SiNHMe$ heated to 170° with $(NH_4)_2SO_4$	73	128–130° (45)	1.4580(26°)	0.852(26°)	6.16	24.69	6.44	25.06
$(Me_3Si)_2NCH_2CH:CH_2$[e]	Reference (*1*)	39	176–177° (atm.)	1.4372(27°)					
$[Me(CH_2:CHCH_2)SiNMe]_3$	$Me(CH_2:CHCH_2)Si(NHMe)_2$ heated to 145° with $(NH_4)_2SO_4$	71	99–104° (0.2)	1.4888(23°)		12.37	24.81	12.50	24.60

[a] Reported, b.p. 131° (743.5 mm.), n^{20}_D 1.4360, d^{20} 0.8432; Reference (*5*). [b] Reported, b.p. 79.5° (1.5 mm.), n^{20}_D 1.4665, d^{20} 0.9100; Reference (*5*). [c] Reported, b.p. 100° (7 mm.), n^{20}_D 1.4810, d^{20} 0.9673; References (*2* and *3*). B.p. 63–5° (1 mm.), n^{20}_D 1.482, d^{20} 0.9662; Reference (*4*). [d] Reported, b.p. 155° (752), n^{20}_D 1.4450, d^{20} 0.8525, Reference (*5*). [e] Reported, b.p. 179° (741 mm.), n^{25}_D 1.4363, d^{25} 0.820; Reference (*1*).

Table II. Stability of Silazanes Heated at 139° C. with 1% Di-*tert*-butylperoxide

Monomer	Viscosity Ratio, Viscosity at t_{22} Hours/Viscosity at t_0 Hours	Monomer Recovered, %
$(Me_3Si)_2NCH_2CH:CH_2$	1.0	75
$[Me_2(CH_2:CHCH_2)Si]_2NH$	1.3	75
$[Me_2(CH_2:CHCH_2)SI]_2NMe$	1.5	. .
$[Me_2(CH_2:CH)Si]_2NH$	95	25
$[Me_2(CH_2:CH)Si]_2NMe$	36	31
$[Me_2(CH_2:CH)Si]_2O$	∞ (gel)	. .

amines and silazanes were obtained, and there appeared to be little or no loss of product through allyl or vinyl polymerization, even at high temperatures.

Infrared spectra of the compounds were determined with a Beckman Infracord Spectrophotometer, but no unexpected features were observed. The C=C stretching frequency was found at 1575–1590 cm.$^{-1}$ in the vinylsilazane and silylamine compounds and at 1630–1645 cm.$^{-1}$ in the allylsilazane and silylamines. The shift to lower frequencies in the vinyl compounds is consistent with results reported for other functional vinyl-substituted derivatives (*5*), and the presence of a conjugated vinylsilazane linkage apparently does not alter this shift.

The resistance of allyl- and vinyl-substituted silazanes to radical initiated reaction was demonstrated by a procedure similar to one described by Mixer and Bailey (*4*), and the results are reported in Table II. Changes in viscosity of the silazanes heated at 139° C. with di-*tert*-butylperoxide were determined as a function of time. Under these conditions, 1,3-divinyltetramethyldisiloxane formed a gel within the specified time period, but the corresponding allylsilazane did not polymerize and could be recovered from the mixture. Surprisingly, the vinyl derivatives were somewhat more reactive than the allyl derivatives and did polymerize to some extent, which is the reverse of the order of reactivity reported for vinyl and allylsiloxanes.

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