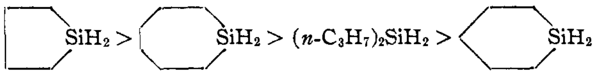
activation would be expected to be greater for III, both because the free energy of activation is greater and because of the postulated additional strain in the transition state. However, this result was not expected for the five-membered ring II. A consideration of the relative entropies of activation for the three compounds shows that it is the very large relative entropy of activation for II which overwhelms the effect of the increased heat of activation and causes II to react faster than the straight-chain compound I. The entropy of activation for III is also greater than that for the standard compound I, but in this case the heat of activation predominates so that III reacts more slowly than I. The high entropies of activation probably indicate that in this reaction compounds II and III have greater freedom of motion and a larger number of degrees of freedom in their transitions states than in the ground states. It would be of interest to compare these results with those for a reaction of ordinary carbocyclic rings, proceeding by a bimolecular displacement mechanism, but apparently no such study has been published.

Some experiments were also carried out to determine rates of hydrolysis of linear and cyclic difunctional silanes (R_2SiH_2). Theoretically it should be possible to determine the rates of hydrolysis of each of the two hydrogen atoms by a process entirely analogous to that used in radiochemistry to analyze curves representing two simultaneous first-order decay reactions. In practice, however, it was found that the first hydrogen is removed so rapidly that no estimate of the rate could be made. Approximate rates were obtained for the removal of the second hydrogen atom. The reactivity of the compounds tested decreased in the order



The order is thus the same as that observed with the monofunctional cyclic silanes. It is interesting that the order of reactivity of cyclic silanes as a function of ring size follows the same order observed for carbocyclic compounds in several different reactions.[3–5] If the assumptions made above about the conformations of silicon-containing rings are valid, then these experiments provide additional confirmation of the I-strain theory[1–3] and indicate that it may be extended to reactions occurring at elements other than carbon. In any case, it seems that the factors which operate to cause activation and deactivation of carbocyclic rings of certain sizes also operate to cause quite similar effects among cyclic organosilicon compounds.

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NOTES

Thermodynamic Functions of the Chlorofluoromethanes

By L. F. Albright, W. C. Galegar and K. K. Innes

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Two recent studies of chlorofluoromethanes have made it possible to refine the thermodynamic calculations by Gelles and Pitzer[1] for these compounds. Claassen[2] combined his measurements of the Raman spectra of the gases with the infrared data of Plyler and Benedict[3] to estimate what he considers to be the best values of the fundamental frequencies. Thirteen of the frequencies, whose values are less than 800 cm.$^{-1}$, differ by more than 5 cm.$^{-1}$ and four by greater than 20 cm.$^{-1}$ from the values reported by Plyler and Benedict and used by Gelles and Pitzer. Masi[4] measured the heat capacity of gaseous CCl_2F_2 and reported derived values for the ideal gas, which he claims are accurate to within 0.15% at temperatures from -30 to 90°. His results are about 0.7% higher than values calculated using the rigid-rotator, harmonic-oscillator approximation. The difference was attributed to a shift of one frequency (later verified by Claassen[2]) and to the effect of anharmonicity. Masi included approximate values for the anharmonicity contribution. These values became appreciable at higher temperatures.

McCullough and co-workers[5] have presented empirical equations for correlating anharmonicity contributions for various thermodynamic functions. These equations are used in the present study.

The thermodynamic functions of chlorofluoromethanes were calculated assuming a rigid-rotator and harmonic-oscillator in the usual manner at temperatures from 100 to 1000°K. Calculations were made using the products of the moments of inertia presented by Gelles and Pitzer,[1] fundamental frequencies given by Claassen,[2] and tables of the vibrational contributions to various thermodynamic functions as presented by Taylor and Glasstone.[6] The experimental heat capacity values for CCl_2F_2 were subtracted from the calculated ones. The differences were assumed to be caused by anhar-

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(1) E. Gelles and K. S. Pitzer, This Journal, **75**, 5259 (1953).

(2) H. H. Claassen, *J. Chem. Phys.*, **22**, 50 (1954).

(3) E. K. Plyler and W. S. Benedict, *J. Research Natl. Bur. Standards*, **47**, 202 (1951).

(4) J. F. Masi, This Journal, **74**, 4738 (1952).

(5) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and G. Waddington, *ibid.*, **76**, 2661 (1954).

(6) H. S. Taylor and S. Glasstone, "A Treatise on Physical Chemistry," Vol. I, D. Van Nostrand Co., New York, N. Y., 1942, p. 655.

monicity and were correlated by the equation[5]

$$C^\circ(\text{anh}) = z\{C^\circ/R\}\{[3(C^\circ/R)/U] - [1 + 2/U][(H^\circ - H_0^\circ)/RT]\}$$

to obtain the constants $z = 0.1573$ and $\mu = 300$ cm.$^{-1}$ in $U = hc\nu/kT$. Here, C°/R and $(H^\circ - H_0^\circ)/RT$ are values for the harmonic oscillator whose frequency is μ. At the suggestion of Dr. D. W. Scott,[7] z was assumed to be the same for all five chlorofluoromethanes and a proportionality constant was assumed between ν and the sums of the fundamental frequencies. Using values of ν determined in this manner and equations[5] for S^0(anh) and $(H^\circ - H_0^\circ)/T$(anh), anharmonicity contributions were calculated over the desired temperature range. These contributions were added to those of the harmonic-oscillator approximation with the results shown in Tables I–V. The heat capacity values due to anharmonicity are shown in Table VI.

TABLE I

THERMODYNAMIC PROPERTIES OF CCl_4

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
100	11.36	8.85	48.19	57.04
150	14.44	10.23	52.03	62.27
200	16.79	11.59	55.16	66.75
250	18.62	12.81	57.89	70.70
300	20.08	13.91	60.34	74.25
400	22.04	15.71	64.58	80.29
500	23.28	17.10	68.23	85.33
600	24.07	18.22	71.46	89.68
700	24.61	19.08	74.33	93.41
800	25.00	19.80	76.92	96.72
900	25.29	20.40	79.33	99.73
1000	25.52	20.90	81.48	102.38

TABLE II

THERMODYNAMIC PROPERTIES OF CCl_3F

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
100	10.37	8.54	49.91	58.45
150	13.15	9.63	53.57	63.20
200	15.46	10.80	56.49	67.29
250	17.31	11.92	59.03	70.95
300	18.81	12.95	61.30	74.25
400	20.99	14.71	65.27	79.98
500	22.43	16.12	68.72	84.84
600	23.35	17.25	71.76	89.01
700	24.01	18.19	74.50	92.69
800	24.49	18.94	76.96	95.90
900	24.87	19.58	79.24	98.82
1000	25.16	20.12	81.37	101.49

TABLE III

THERMODYNAMIC PROPERTIES OF CCl_2F_2

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
100	9.49	8.28	49.36	57.64
150	11.83	9.06	52.85	61.91
200	14.05	10.05	55.59	64.65
250	15.90	11.04	57.95	68.99
300	17.45	11.98	60.04	72.02
400	19.81	13.66	63.72	77.38
500	21.44	15.07	66.93	82.00
600	22.58	16.23	69.78	86.01
700	23.38	17.20	72.36	89.56
800	23.97	18.02	74.72	92.74
900	24.41	18.70	76.87	95.57
1000	24.74	19.30	78.89	98.19

TABLE IV

THERMODYNAMIC PROPERTIES OF $CClF_3$

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
100	8.80	8.11	47.18	55.29
150	10.69	8.63	50.57	59.20
200	12.71	9.41	53.15	62.56
250	14.53	10.26	55.34	65.60
300	16.13	11.10	57.28	68.38
400	18.66	12.68	60.70	73.38
500	20.49	14.09	63.69	77.78
600	21.79	15.26	66.35	81.61
700	22.73	16.27	68.78	85.05
700	23.42	17.10	71.02	88.12
900	23.94	17.84	73.05	90.89
1000	24.35	18.48	74.98	93.46

TABLE V

THERMODYNAMIC PROPERTIES OF CF_4

T, °K.	C_p°	$(H^\circ - H_0^\circ)/T$	$-(F^\circ - H_0^\circ)/T$	S°
100	8.31	8.00	42.75	50.75
150	9.61	8.30	46.04	54.34
200	11.37	8.84	48.50	57.34
250	13.11	9.52	50.54	60.06
300	14.73	10.26	52.34	62.60
400	17.41	11.72	55.49	67.21
500	19.43	13.08	58.26	71.34
600	20.91	14.26	60.76	75.02
700	21.99	15.29	63.03	78.32
800	22.84	16.19	65.13	81.32
900	23.42	16.96	67.09	84.05
1000	23.91	17.64	68.89	86.53

TABLE VI

ANHARMONIC CONTRIBUTION TO HEAT CAPACITY

T, °K.	CCl_4	CCl_3F	CCl_2F_2	$CClF_3$	CF_4
100	0.02	0.01	0.01	0.00	0.00
150	.05	.03	.03	.01	.01
200	.08	.06	.05	.03	.03
250	.11	.09	.07	.05	.04
300	.14	.11	.09	.08	.06
400	.20	.16	.13	.11	.09
500	.25	.21	.17	.15	.13
600	.30	.25	.21	.19	.16
700	.35	.29	.25	.22	.19
800	.40	.34	.29	.25	.22
900	.45	.38	.33	.28	.25
1000	.50	.43	.36	.32	.28

The calculated results based only on the harmonic-oscillator approximation vary in all cases by less than 0.18 cal./deg. mole and in most cases by less than 0.10 cal./deg. mole from the values presented by Gelles and Pitzer.[1] The anharmonicity contributions become appreciable at higher temperatures so that the total values of the various thermodynamic functions differ in such cases by as much as 0.2 to 0.5 cal./deg. mole. The experimental entropy values available for these compounds are all for low temperatures. Within experimental accuracy the comparison with cal-

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(7) D. W. Scott, private communication, 1954.

culated values that was made by Gelles and Pitzer[1] is unaffected.

The anharmonicity calculations are considered to be only approximations. Until more specific heat data and/or anharmonicity constants are experimentally determined, further significant refinements of anharmonicity contributions seem impossible.

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The Coefficient of Linear Thermal Expansion of Tridymite

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The occurrence of two "high-low" inversions in tridymite is well-established and the inversion temperatures have generally been accepted as close to 117 and 163°, respectively,[1] although there have been occasional suggestions that these temperatures may vary significantly.

Mosesman and Pitzer,[2] however, have reported heat content data which indicate the possible existence of a third transition at 223°. Since this transition had not been described previously, and since they were unable to explain it on the basis of possible impurities present in their sample or to interpret it in terms of present knowledge of the crystalline structure of tridymite, they suggested that final acceptance should await further verification. As such transitions are usually accompanied by a change in volume, measurements of thermal expansion offer a possible means of confirmation. Accordingly, a number of measurements of linear expansion, made some years ago during a study of the behavior of silica refractories, have been reexamined for indications of this third transition.

Samples.—Three different samples of silica were examined. Two were purified tridymite, one being the same material used by Mosesman and Pitzer. The third was a silica coke-oven liner which, after long service, had been converted almost entirely to tridymite.

The raw material for the purified tridymite was, in each case, a very pure sample of vein quartz from Lake Toxaway, North Carolina. This material was ground to pass a 60-mesh sieve, was repeatedly washed with hydrochloric acid, and then dried. Analysis with hydrofluoric acid gave 99.99% SiO_2. The residue, when tested with sodium thiocyanate, gave a red coloration indicating the presence of iron.

For the first preparation, this purified quartz was mixed with purified sodium tungstate in the proportion of 6 silica to 1 Na_2WO_4 by weight. The mixture was ground in an agate mortar to pass 200-mesh screen. It was then placed in a platinum cone, which was covered with platinum foil resting on two porcelain rods, set in a magnesia block into which a noble metal thermocouple had been inserted. This assembly was then heated in a furnace provided with silicon carbide heating elements for 24 hours at 1250°. On removal from the furnace, a piece of the sintered mass was cut off for the preparation of specimens for the dilatometer. The remainder was washed repeatedly with hot water to remove the flux. A second set of interferometer specimens was then prepared from this material and was further treated successively with boiling water, hydrochloric acid, ammonium hydroxide and boiling water, and was then carefully dried. Analysis showed 98.7% silica and examination under the petrographic microscope indicated complete conversion to tridymite. The residual mass was ground in an agate mortar to pass through a 400-mesh screen and was given the same series of washings as before. It was this finely ground material which was used by Anderson[3] and by Mosesman and Pitzer in their specific heat measurements.

Another sample was prepared by heating the purified quartz and sodium tungstate in the same proportions for 27 hours at 1300°. The cooled sinter was boiled in 1:1 HCl for 2 hours, was left overnight in a constant-boiling mixture of HCl, was then repeatedly washed in boiling distilled water and was finally dried. Specimens for the dilatometer were then prepared from the dried material. Examination under the microscope showed complete conversion to tridymite.

A fourth set of specimens was cut from the center of a silica coke-oven liner which, as a result of long service at high temperature, had been converted almost completely to tridymite. This liner has been described elsewhere.[4]

Apparatus.—The measurements were made by means of an interferometric dilatometer which has already been described.[5] The specimens for each sample were in the form of three small pyramids, about 3 mm. in height, which were placed between the silica plates of the interferometer. The observations were plotted on a large scale as increase in length per unit length against temperature.

Since these measurements were made with the temperature increasing at a constant rate of 3° per minute, and since the specimens were not good thermal conductors and, moreover, were not of identical shape, there were inevitably small temperature differences among them. The evidence indicates that this difference was usually less than 0.3°. The specimens therefore transformed in succession at intervals of a few seconds, rather than simultaneously. This made it difficult to obtain precise measurements within a degree or so of the transition temperatures, with the result that the several length–temperature curves did not coincide but were displaced relative to each other. There was, however, substantial agreement in the slope of the curves, as read from the plot by means of an optical tangent meter. Accordingly, the results are reported in the form of instantaneous coefficients as a function of temperature.

Results

The composite data for all three types of specimen are presented in Fig. 1. For all specimens, the values of the coefficient, at or just above room temperature, clustered in the range 23 to 26 $\times 10^{-6}$, and then increased sharply to the inversion temperature. In all specimens, the first inversion appeared to be complete within a degree of 117°.

The coefficient for the intermediate form was, for all specimens, close to 45 $\times 10^{-6}$, and again increased rapidly as the inversion temperature was approached. The second inversion appeared to be complete within a degree of 163°.

Above the second transition, the coefficient for each set of samples was, within the error of measurement, constant over the range 163 to 210°. There was, however, some variation in the magnitude of the coefficient in this range. Thus, the specimens cut from the coke-oven brick gave 45 $\times 10^{-6}$, and a second run on the sample which still contained the flux gave 65 $\times 10^{-6}$, whereas for five

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(1) R. B. Sosman, "The Properties of Silica," Chemical Catalog Co., New York, N. Y., 1927, pp. 124, 125.

(2) A. Mosesman and K. S. Pitzer, THIS JOURNAL, **63**, 2348 (1941).

(3) C. T. Anderson, *ibid.*, **58**, 568 (1936).

(4) J. B. Austin and R. H. Pierce, *J. Amer. Ceramic Soc.*, **16**, 102 (1933).

(5) J. B. Austin and R. H. H. Pierce, THIS JOURNAL, **55**, 661 (1933).