

4. By making assumptions applicable in this case an equation, based on Langmuir's adsorption theory, is developed; this equation is in agreement with the experimental results. The essential assumption made is that of three-point contact between the germane molecule and the germanium surface.

5. The temperature coefficient and the heat of activation have been determined. The significance of this energy term has been discussed in the light of the proposed theory.

6. A discussion of the validity of the assumptions made and of similar work in this field concludes the article.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A STUDY OF VAN DER WAALS FORCES BETWEEN TETRAHALIDE MOLECULES

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The theoretical and experimental investigations of the general problem of solubility conducted by the senior author and collaborators during a period of years have made evident the importance of a more accurate knowledge than we now possess of intermolecular forces between like and unlike molecules in the simplest possible cases, where the molecules are non-polar and where the molecular field, as shown by recent applications of wave mechanics, is spherical. While the noble gases are theoretically satisfactory for such an investigation, we selected the tetrahalides as practically far more suitable. They are not only available in large quantities, but their molecular volumes and intermolecular forces represent a wide range of variation. We are making a systematic study of certain properties of six tetrahalides and their solutions. The properties thus far measured are the expansion on mixing and the thermal pressure coefficient, $(\partial p/\partial T)_V$, from which can be calculated the important quantity, $(\partial E/\partial V)_T$. There is now under way, as a further part of the general program, a study of the activities of the same substances in their binary solutions.

Preparation and Purification of Materials.—Stock U. S. P. carbon tetrachloride, about 1500 cc., was shaken with c. p. sodium hydroxide sticks, and a small quantity of distilled water for two days. The liquid was then decanted, filtered, and the process repeated. After standing in contact with phosphorus pentoxide overnight, it was distilled from fresh phosphorus pentoxide. The distilling apparatus was of Pyrex glass, with all connections fused, except the connection to the receiving flask, which was a cork covered with tin foil, and the cork holding the thermometer, inserted in the distilling flask, which was also covered with tin foil. The first and last portions of the distillate were discarded, although the boiling point rose only 0.08° during the entire run. The fraction retained boiled at 76.37 to 76.43° (754 mm.). The purified material was kept in the dark, in a Pyrex flask, with a tin foil-covered stopper.

Baker and Adamson stannic chloride, colorless and free from sediment, was filtered through glass wool into a Pyrex distilling apparatus, with all joints fused. The distilling flask contained phosphorus pentoxide, and the receiving flask was connected through a phosphorus pentoxide tube to the atmosphere, or to a vacuum pump. The thermometer was hung from a glass hook inside the neck of the distilling flask, so that there would be no possibility of moisture entering the apparatus. Stannic chloride proved to be the most difficult material to obtain absolutely anhydrous, as it forms a hydrate which is extraordinarily stable at temperatures up nearly to the boiling point of water. To remove all water, and any traces of hydrochloric acid resulting from hydrolysis, the liquid was refluxed for several hours, not allowing any appreciable amount to distil into the condenser. The distilling flask was then cooled, and the apparatus partially evacuated, while the condenser, connecting tubes and receiving flask were flamed. This was repeated three times. Finally, the liquid was distilled, discarding the first portion by keeping the receiving flask heated to a higher temperature than the boiling point. The middle portion was distilled slowly and showed a boiling point of 114.0 to 114.1° at 760 mm. The receiving flask was then sealed off. To ensure keeping the liquid dry, the receiving flask was equipped with a device which enabled the flask to be sealed on to another apparatus for removing a part of the liquid, and subsequently to be sealed off again, without allowing access of moisture.

Kahlbaum's silicon tetrachloride was treated in the same manner as the stannic chloride, and showed a boiling point of 57.50-57.55° at 755 mm.

Kahlbaum's titanium tetrachloride, treated in the same way, showed a boiling point of 135.6-135.8° at 758 mm. Silicon tetrabromide was prepared from amorphous silicon. This was placed in a long combustion tube in a furnace. Connections for introducing dry nitrogen and bromine were fused to one end of the tube, and a receiving flask and drying tube to the other end. Air and moisture were removed by heating the tube gently, while a current of dry nitrogen was passed through. The temperature was then raised to just below a red heat, while dry bromine was passed through slowly in a current of nitrogen. The silicon tetrabromide collected in the receiving flask, which was cooled with water. In spite of precautions taken to ensure the absence of oxygen, the silicon in time became covered with a white coating, which stopped the reaction. Three runs gave approximately 500 cc. of silicon bromide. This was heated, while connected to a vacuum, to remove excess bromine, and mercury was then added to remove the last traces. It was then purified in the same manner as stannic chloride and showed a boiling point of 152.8-152.9° at 758 mm.

To prepare stannic bromide, lead-free tin was placed in a large distilling flask, sealed to a condenser and receiving flask, and also to a tube leading to a flask of dry bromine. After thorough drying of the system, dry bromine was slowly distilled onto the tin, while the neck of the distilling flask was kept cold by a jet of air cooled to -50°. The reaction was started by slightly warming the tin, and kept at a convenient speed by regulating the flow of bromine. The addition of bromine was continued until there was only a slight amount of tin left in the flask. The product was then purified in the same way as the stannic chloride. It boiled at 203.3-203.4° at 760 mm. The liquid was almost colorless, and solidified at 33.0° to a clear colorless solid. It was stored in contact with lead-free tin foil.

The expansion on mixing was determined in a dilatometer designed by the senior author and illustrated in Fig. 1. The two liquids were in their respective bulbs, separated by mercury. The reversed pear shape of the bulbs permitted a variation in the proportions of the two liquids by increasing the volume of mercury. The capillaries were calibrated by determining the weight of a thread of mercury required to fill them, and tested for uniformity by running a short thread of mercury along them.

Before making a determination, the apparatus was dried by passing a current of dried air through it. The liquids were introduced while the apparatus was placed in a box dried with phosphorus pentoxide, and in such a way that contact with air was avoided as much as possible. The amounts of the liquids used were determined by weighing the apparatus after the addition of each.

After the apparatus had been filled, rubber tubes connected to calcium chloride tubes were placed over the ends of the capillaries, and the apparatus immersed to the bottoms of the capillaries in a thermostat. After the levels of the liquids in the capillaries had become constant, they were read on the graduations, and the apparatus tilted

to allow the liquids to mix. As soon as the levels had come to equilibrium, readings were again taken, and the tube again tilted. This was repeated until further mixing caused no change in the levels.

All determinations were made at $25.000 \pm 0.001^\circ$, except those involving stannic bromide, which were made at $35.000 \pm 0.005^\circ$.

In the case of the mixtures of carbon tetrachloride with titanium tetrachloride and with stannic chloride, after the determination of the expansion on mixing, the temperature of the thermostat was raised to $30.000 \pm 0.002^\circ$, and the expansion of the mixture determined. The accuracy of the results is not as great as

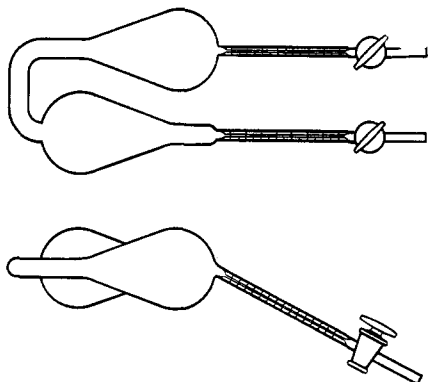


Fig. 1.

for the expansion on mixing, as corrections must be applied for the expansion of the Pyrex apparatus and of the mercury.

The expansion of the mixture of carbon and tin tetrachlorides, which showed the largest expansion, was determined at three compositions, to test the form of the function; the expansions of the others were determined at approximately 50 mole per cent. Biron¹ has used for the relation between expansion and composition the formula $\Delta V/V = k N_1 N_2$, where

TABLE I
EXPANSION ON MIXING

$t = 25^\circ$ except for solutions containing SnBr_4 , where $t = 35^\circ$

Solution	Mole fractions	100 $\Delta V/V$ observed	100 $\Delta V/V$ calcd. at 50 mole per cent.	$k = \frac{\Delta V}{V N_1 N_2} \times 10^5$
$\text{CCl}_4\text{-SiCl}_4$	0.511-0.489	0.014	0.014	56
$\text{CCl}_4\text{-TiCl}_4$.513- .487	.083	.083	340
$\text{CCl}_4\text{-SnCl}_4$.636- .364	.374		1617
$\text{CCl}_4\text{-SnCl}_4$.445- .555	.403	.408	1633
$\text{CCl}_4\text{-SnCl}_4$.247- .753	.303		1630
$\text{CCl}_4\text{-SiBr}_4$.612- .388	.175	.184	732
$\text{CCl}_4\text{-SnBr}_4$.533- .467	.220	.221	884
$\text{SiCl}_4\text{-SnBr}_4$.509- .491	.111	.111	444
$\text{SiBr}_4\text{-SnBr}_4$.487- .513	.093	.093	372

¹ Biron, *J. Russ. Phys.-Chem. Soc.*, 41, 569 (1909).

N_1 and N_2 are the respective mole fractions. It should be noted that $N_1 + N_2 = 1$, but both letters are retained for the sake of symmetry.

Table I summarizes the results. The close agreement of the three values of k for the mixture above mentioned shows the validity of the Biron relation. If k is given the value 0.01632, the calculated and observed values of $100 \Delta V/V$ for the three mixtures agree as follows: 0.374–0.377, 0.403–0.403, 0.303–0.303. A discussion of the relation of these expansions to the properties of the pure substances will be deferred until later.

The coefficient of expansion was determined for two mixtures, carbon tetrachloride with titanium tetrachloride and with stannic chloride. This was used as a check on the calculation of the volumes of the same solutions at 30° from the known volumes of the pure liquids at 30° by assuming that the same per cent. expansion had taken place on mixing as was found at 25° .

The following results were obtained

	Obs.	Calcd.
$\text{CCl}_4\text{-TiCl}_4$	0.00115	0.001133
$\text{CCl}_4\text{-SnCl}_4$.001205	.001202

The agreement is so good that we felt justified in calculating the molal volumes and coefficients of expansion of the other mixtures on the assumption that at each temperature the liquids mixed with the same per cent. increase in volume as was found at 25° . The expansion should probably be smaller at increased temperatures but, as the expansion is so small in any case, it was felt that no significant error would be introduced by taking the same value at all temperatures between 20 and 40° .

The apparatus and procedure for the determination of the thermal pressure, $(\partial p/\partial T)_V$, was substantially that of Westwater, Frantz and Hildebrand² except that all of the containing bulbs were shorter, 10 cm., and wider, 3 cm., instead of 45 cm. and 1.5 cm., respectively, as in the earlier work. This increased the accuracy of the correction for the pressure of the mercury in the bomb. Results with both bulbs were in complete agreement.

The ice-point of the resistance thermometer was redetermined and found to be unchanged. A recalculation of the previous calibration discovered a small error, which had the effect of giving values of $(\partial p/\partial T)_V$ too high, by about 0.5%. At the close of the investigation the thermometer was sent to the Bureau of Standards for recalibration; the results agreed with our recalculation.

The high pressure manometer having broken, it was not considered necessary to repair it, as the linear relationship between pressure and temperature had been sufficiently established by the previous work. This reduced

² W. Westwater, H. W. Frantz and J. H. Hildebrand, *Phys. Rev.*, **31**, 135 (1928); Hildebrand, *ibid.*, **34**, 649 (1929).

the pressure range from 20 to 15 atmospheres. The other two manometers were recalibrated, giving agreement with the earlier calibration.

Constant volume was maintained by use of a delicate relay and a dry cell. The relay was connected to the 110-volt lighting circuit in which a lamp was placed. In view of the extremely low current passed at the contact of the mercury and the platinum wire, it is not believed that any emulsification with the liquids took place. The ease with which contact could be broken and re-established at pressures hardly distinguishable supports this.

The runs were made in practically the same manner. At least seven observations were made in each temperature interval, usually with both increasing and decreasing temperatures. It was found easy to hold the temperature constant to within 0.001° for ten minutes, while taking an observation, and the pressure to within less than 0.02 atm., usually to 0.01 atm. Check readings were made at each point. Different points were never more than 0.02 atm. off a straight line.

The corrections for the thermal expansion and the compressibility of the Pyrex bulb were made in the same way as formerly. The values of the compressibility, usually unknown, were determined by successive approximations from the coefficient of expansion and the experimentally measured thermal pressure coefficient.

The values of T_1 , the temperature for $P = 1$ atm., and of $(\Delta P/\Delta T)_V$ were determined from the experimental points by a least square calculation based upon the linear relationship between P and T . Table II shows the agreement for one run between the observed and smoothed out pressures. This may be taken as a fair sample of the accuracy obtained throughout the investigation.

TABLE II

DEVIATION OF OBSERVED PRESSURES FROM LINEAR RELATIONSHIP			
Run 1 for CCl_4	P , atmospheres		Diff.
t	Obs.	Calcd.	
20.396		1.00	
20.416	1.24	1.23	+0.01
20.557	2.86	2.87	— .01
20.760	5.23	5.26	— .03
20.899	6.86	6.85	+ .01
21.078	8.95	8.93	+ .02
21.257	11.01	11.01	.00
21.363	12.24	12.24	.00
21.576	14.73	14.72	+ .01

The results for all the pure liquids investigated are summarized in Table III. The molal volumes have been calculated from the known densities as given in the "International Critical Tables." The values of the van der Waals a have been calculated from the thermodynamic equation for the change in energy with volume

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \quad (2)$$

together with the equation

$$a = v^2(\partial E/\partial V)_T \quad (3)$$

previously found to be applicable to these data. The values of a given are in atm. $\times \overline{cc.}^2$ and v is the molal volume. The constancy of a shown in both Tables III and IV again bears witness to the accuracy of Equation 3 for this range.

The corresponding data for mixtures are given in Table IV.

TABLE III
THERMAL PRESSURE COEFFICIENTS, $(\partial P/\partial T)_V$, ENERGY-VOLUME COEFFICIENTS,
 $(\partial E/\partial V)_T$, AND VAN DER WAALS "a" FOR PURE LIQUIDS

Substance	t , °C. at 1 atm.	$(\partial P/T\partial)_V$, atm. Obs.	per degree Correc.	Molal vol- ume, cc.	a , atm. \times liters ²
CCl ₄	20.40	11.63	11.40	96.54	31.18
	20.63	11.63	11.40	96.57	31.23
	25.84	11.23	11.02	97.19	31.18
	31.25	10.92	10.72	97.84	31.23
	37.09	10.55	10.36	98.56	31.22
					31.21
SiCl ₄	21.43	8.86	8.76	114.79	33.98
	27.51	8.55	8.46	115.76	34.06
	33.62	8.21	8.12	116.78	34.01
	35.82	8.10	8.01	117.17	33.96
					34.00
SiBr ₄	20.72	11.63	11.43	126.02	53.35
	24.97	11.37	11.18	126.51	53.31
	31.23	11.03	10.84	127.22	53.39
	36.48	10.75	10.57	127.69	53.38
					53.36
TiCl ₄	21.78	12.03	11.74	110.14	42.00
	25.04	11.77	11.49	110.53	41.86
	29.99	11.46	11.20	111.09	41.89
	36.21	11.06	10.82	111.83	41.87
					41.90
SnCl ₄	24.71	11.13	10.91	117.59	44.85
	27.35	10.92	10.71	118.02	44.80
	32.07	10.64	10.44	118.68	44.86
	37.12	10.33	10.14	119.38	44.84
					44.84
SnBr ₄	32.98	12.64	12.24	131.51	64.79
	35.03	12.50	12.11	131.72	64.76 ₅
	38.47	12.29	11.91	132.12	64.82
					64.79

TABLE IV
THERMAL PRESSURE COEFFICIENTS AND VAN DER WAALS a FOR SOLUTIONS.
COMPOSITION IS 50 MOLE PER CENT. EXCEPT AS STATED

Substance	t , °C., at 1 atm.	$(\partial P/\partial T)_V$, atm. Obs.	per degree Correc.	Molal vol- ume, cc.	a , atm. \times liters ²
CCl ₄ -SiCl ₄	21.03	10.13	9.98	105.68	32.79
	25.10	9.90	9.74	106.25	32.82
	29.68	9.57	9.44	106.90	32.68
	35.87	9.26	9.13	107.81	32.81
			Av.		32.78
CCl ₄ -TiCl ₄	20.69	11.85	11.59	103.40	36.42
	25.43	11.55	11.30	103.95	36.47
	31.10	11.23	11.00	104.63	36.66
	36.68	10.77	10.65	105.28	36.58
					36.53
CCl ₄ -SnCl ₄ 75 25	23.13	11.54	11.22	102.33	34.82
	29.38	11.00	10.80	103.11	34.74
	35.51	10.64	10.46	103.89	34.85
					38.41
CCl ₄ -SnCl ₄ 50 50	21.71	11.38	11.26	107.42	38.31
	25.32	11.26	11.05	107.89	38.40
	30.41	10.94	10.74	108.54	38.41
	35.65	10.59	10.40	109.22	38.27
					38.35
CCl ₄ -SnCl ₄ 25 75	22.76	11.33	11.11	112.59	41.68
	28.43	10.96	10.75	113.36	41.67
	34.36	10.61	10.42	114.16	41.77
					41.71
CCl ₄ -SiBr ₄	20.36	11.77	11.44	111.47	41.58
	27.09	11.31	11.04	112.24	41.76
	30.67	11.07	10.81	112.66	41.69
	34.92	10.80	10.56	113.16	41.67
					41.68
CCl ₄ -SnBr ₄	22.16	12.61	12.27	113.77	46.89
	26.14	12.31	11.98	114.24	46.79
	32.43	11.89	11.61	114.97	46.84
	35.23	11.66	11.44	115.30	46.90
					46.85 ₅
SiCl ₄ -SiBr ₄	23.87	10.26	9.98	120.80	43.26
	27.43	9.90	9.74	121.29	43.07
	31.96	9.71	9.55	121.93	43.32
	35.73	9.53	9.38	122.47	43.45
					43.27 ₅

TABLE IV (Concluded)

Substance	$t, ^\circ\text{C.}, \text{ at } 1 \text{ atm.}$	$(\partial P/\partial T)_V, \text{ atm. per degree Obs.}$	$\text{per degree Correc.}$	Molal volume, cc.	$a, \text{ atm.} \times \text{liters}^2$
SiCl ₄ -SnBr ₄	20.53	11.26	11.03	122.53	48.64
	26.18	10.90	10.69	123.28	48.64
	30.34	10.67	10.47	123.86	48.77
	35.78	10.34	10.15	124.64	48.72
					48.69
SiBr ₄ -SnBr ₄	23.10	12.51	12.13	128.46	59.29
	27.62	12.19	11.83	128.97	59.20
	31.89	11.90	11.56	129.44	59.10
	37.03	11.58	11.26	130.02	59.05
					59.16

Table V gives data for the pure liquids at 25° recalculated from the mean values of a found in Table III. Values for other temperatures are here omitted because they can readily be calculated.

TABLE V
DATA FOR PURE LIQUIDS AT 25°

Subs.	Molal volume, cc.	$(\partial P/\partial T)_V, \text{ atm./deg.}$	$(\partial E/\partial V)_T, \text{ atm.}$	$v(\partial E/\partial V)_T, \text{ liter-atm.}$	$v^2(\partial E/\partial V)_T = a, \text{ atm.} \times \text{liters}^2$
CCl ₄	97.09	11.11	3311	321.4	31.21
SiCl ₄	115.36	8.57	2554	294.7	34.00
TiCl ₄	110.50	11.51	3430	379.2	41.90
SnCl ₄	117.64	10.86	3236	381.2	44.84
SiBr ₄	126.52	11.18	3332	421.8	53.36
SnBr ₄	130.62	12.74	3799	496.3	64.79

Table VI gives experimental values of three different functions for the solutions at 25°, $(\partial E/\partial V)_T$, $v(\partial E/\partial V)_T$ and $v^2(\partial E/\partial V)_T = a$, in comparison with values calculated from the corresponding functions of the pure liquids. The first two are calculated on additive basis, the a on the basis of the oft used assumption³ that a for the mixture is given by

$$a = N_1^2 a_1 + 2N_1 N_2 a_{12} + N_2^2 a_2 \quad (4)$$

and that a_{12} , referring to the constant of attraction for unlike molecules, is given by

$$a_{12} = \sqrt{a_1 a_2} \quad (5)$$

Substituting 5 in 4 gives

$$a = (N_1 \sqrt{a_1} + N_2 \sqrt{a_2})^2 \quad (6)$$

It will be observed that the best arrangement between observed and calculated values is for additivity of $v(\partial E/\partial V)_T$. Except for the mixtures of carbon tetrachloride with stannic chloride, the agreement is probably within the limit of error. The fact that this particular system shows the largest deviation is very striking, for if these tetrahalides are arranged in series according to molal volumes, boiling points, or any of the three

³ Cf. J. J. van Laar and R. Lorenz, *Z. anorg. allgem. Chem.*, 171, 41 (1928).

For the substances studied this is probably very nearly but not quite true; hence a for volumes so different as liquid and gas might be expected to show a small difference. The only evidence on this point has already been given in the case of carbon tetrachloride. For the other substances the necessary data of sufficient accuracy are not yet at hand but are being obtained through measurements of vapor pressure.

Second, if we dismiss any departure of $\partial E/\partial V$ from being a pure volume function as a negligible effect of higher order, the simple form of the function, a/v^2 , calls for some comment. For a dilute gas this form results, as is well known, from the kinetic theory. The law of force between the molecules determines the magnitude of a but not the exponent of V , all laws of intermolecular attraction yielding V^2 . The intermolecular forces are operative chiefly during binary collisions whose frequency varies as the square of the concentration. The closeness of approach during a collision, however, is not affected by the volume. In dealing with solids, on the other hand, it has always been assumed that a change in volume is accompanied by a corresponding change in mean molecular distance. If this is true, an intermolecular potential proportional to $1/r^m$ would correspond to $\partial E/\partial V$ proportional to $1/V^{(m/3) + 1}$. The quantum mechanical analysis of van der Waals forces by London⁶ has led to $m = 6$, which corresponds to $\partial E/\partial V$ proportional to $1/V^3$. The fact that the liquids yield $1/V^2$ instead of $1/V^3$ may be interpreted as indicating that they are much nearer to gases in their nature than to solids. This is in harmony with the existence of more degrees of freedom in the liquid than in the solid. The correspondence might be expected to be less for polar molecules and we have cited elsewhere^{5a} the strong departure of liquid methyl alcohol from the $1/V^2$ relation.

We may also recall the deviation from the $1/V^2$ relation when the liquid is so highly compressed, or strongly cooled, that repulsive forces begin to play an important role.^{5a} An accurate study of $\partial E/\partial V$ under pressures between 1 atm. and 1000 atm. would probably reveal the necessity of substituting some more complicated function of volume, even in the range studied in this investigation.

Third, it is of interest to ask how closely the attraction constant depends upon the size for molecules surrounded by the same halogen. Table VII gives again the values of a for the tetrachlorides under investigation together with the interhalogen distance, in Ångströms, as determined by Wierl⁴ for the gaseous molecules by electron diffraction. The last column gives the ratio of the former quantity to the latter. If the one were a function of the other this ratio should change in some regular way. It is evident that this is approximately but not accurately the case. We may hazard the guess that the bonds between central atom and the chlorine atoms are not

⁶ F. London, *Z. Physik*, **63**, 245 (1930).

completely buried within the molecules, but influence the external field, as already suggested in connection with stannic chloride.

TABLE VII
RELATION BETWEEN VAN DER WAALS a AND INTERHALOGEN DISTANCE, l

Subs.	atm. \times liters ²	l , Å.	Ratio
CCl ₄	31.21	2.98	10.5
SiCl ₄	34.00	3.29	10.3
TiCl ₄	41.90	3.61	11.6
SnCl ₄	44.84	3.81	11.8

Finally, it is possible to calculate the compressibility from our figures for $\partial P/\partial T$ together with the coefficients of expansion to be got from the density-temperature functions. The compressibility at 25° is given in Table VIII for the five substances which are liquid at this temperature.

TABLE VIII
COMPRESSIBILITIES AT 25°, IN RECIPROCAL ATMOSPHERES

	$\left(\frac{\partial P}{\partial T}\right)_V$ atm./deg.	$\frac{1}{V_{25}} \left(\frac{\partial V}{\partial T}\right)_P \times 10^6$	$\frac{1}{V_{25}} \left(\frac{\partial V}{\partial p}\right)_T \times 10^6$
CCl ₄	11.11	1228	1105
SiCl ₄	8.57	1416	1652
TiCl ₄	11.51	1033	898
SnCl ₄	10.86	1173	1080
SiBr ₄	11.18	968	866

Summary

Certain properties of six liquid tetrahalides and seven of their binary solutions have been investigated as part of a systematic study of forces between like and unlike molecules of a high degree of symmetry.

The expansion on mixing was measured for seven liquid pairs, and is expressed by the value of $10^5 k$ in the equation, $\Delta V/V = k N_1 N_2$, (N_1 and N_2 are the respective mole fractions) with the following results: CCl₄-SiCl₄, 56; CCl₄-TiCl₄, 340; CCl₄-SnCl₄, 1632; CCl₄-SiBr₄, 732; CCl₄-SnBr₄, 884; SiCl₄-SnBr, 444; SiBr-SnBr₄, 372.

The thermal pressure coefficient, $(\partial p/\partial T)_V$, was measured with precision for the six pure liquids and for the liquid pairs mentioned above. The volume coefficient of energy was calculated by the equation, $(\partial E/\partial V)_T = T(\partial p/\partial T)_V - P$. It is a pure volume function, a/v^2 , within a few tenths of a per cent. for the range studied. The values of a for the pure liquids, in liters² \times atmospheres, for a mole of liquid, are, CCl₄, 31.21; SiCl₄, 34.00; TiCl₄, 41.90; SnCl₄, 44.84; SiBr₄, 53.36; SnBr, 64.79. The values of a for seven mixtures are given in the text, and their calculation from the values for the pure substances is shown and discussed.

The validity of the calculation of $(\partial E/\partial V)_T$ as a pure volume function is examined.

The exponent 2 in a/v^2 indicates that the liquids are like gases, from a kinetic standpoint, for if the molecules were uniformly spaced, the inverse sixth power of intermolecular potential, deduced by London for van der Waals forces, would lead to a/V^3 .

The magnitude of a is approximately but not exactly a function of the interhalogen distance for the tetrachlorides.

The following values of compressibility at 25° were calculated: CCl₄, 1105; SiCl₄, 1652; TiCl₄, 898; SnCl₄, 1080; SiBr₄, 866; each in reciprocal atmospheres $\times 10^7$.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

NITROGEN COMPOUNDS OF GERMANIUM. II. EQUILIBRIUM IN THE SYSTEM Ge-NH₃-Ge₃N₄-H₂. THE DISSOCIATION OF GERMANIC NITRIDE¹

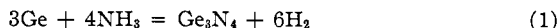
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Introduction

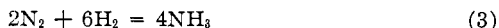
Finely-divided germanium has been shown to react with ammonia gas at temperatures ranging from 600–750° to produce germanic nitride according to the equation²



This reaction was found to be readily reversible in the same temperature interval. Since germanium and germanic nitride exist as solid phases at these temperatures, the equilibrium constant for the reaction may be expressed as³

$$K_1 = (f_{\text{H}_2})^6 / (f_{\text{NH}_3})^4 \quad (2)$$

From the ammonia equilibrium



an expression for the constant may be written as

$$K_2 = (f_{\text{NH}_3})^4 / (f_{\text{N}_2})^2 (f_{\text{H}_2})^6 \quad (4)$$

It then follows that

$$K_1 \times K_2 = K_3 = 1 / (f_{\text{N}_2})^2 \quad (5)$$

Germanic nitride is known to dissociate at high temperatures to yield nitrogen and metallic germanium^{2,4,5}



¹ Presented at the meeting of the American Chemical Society in Indianapolis, Indiana, April, 1931.

² Johnson, *THIS JOURNAL*, **52**, 5160 (1930).

³ The fugacity is used in this paper in place of the pressure since the magnitude of the latter assumes relatively high values. At low pressures the two terms are identical.

⁴ Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

⁵ Hart. Master of Science Thesis, University of Chicago, August, 1930.