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Forces between Tetrahalide Molecules*

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A review of the evidence furnished by melting and boiling points, entropy of fusion and evaporation, crystal structure, ionic-bond character, radii, Raman frequencies, energy of evaporation and differential energy of expansion, polarizability, and solubility relations has led to the following conclusions: (1) Hindrance to rotation is small in liquid CCl_4 and CBr_4 but increases with increasing radius ratio of central atom to halide atom. This indicates that the van der Waals radii of the halide atoms in these liquids are considerably smaller than those assigned by Pauling. (2) In spite of the hindrance to rotation, the solubility relations can be calculated with considerable accuracy by means of equations derived for spherical molecules with radial force fields. (3) Attraction between molecules of different species is not appreciably influenced by the kind of bonding orbitals of the central atom, but is strongly influenced by the ionic character of the bond. (4) The apparent anomaly of the low boiling point and internal pressure of $SiCl_4$ is due to the large increase in molal volume between CCl_4 and $SiCl_4$; the attraction constant increases uniformly with M-X distance in the series of chlorides of C, Si, Ge, Ti, Sn. (5) The attraction constant is closely related to the square of the polarizability, in accordance with the London theory. (6) The two isotropic Raman frequencies for the chlorides of C, Si, Ge, Ti, Sn, Pb decrease uniformly with increasing M-X distance. (7) None of the properties of $SiCl_4$ requires for its explanation the assumption of "double bond resonance."

THE PROBLEM

THE study of the liquid state should obviously begin with liquids composed of simple spherical molecules, of which the inert gases furnish the best and practically only examples, but the cost of most of them and the inconvenient and short temperature range of their liquid forms offer practical obstacles to the gathering of the desirable variety of experimental data. An even stronger reason for turning to polyatomic molecules is the fact that nearly all the solutions in which we are practically interested are composed of polyatomic molecules, so that the elucidation of the behavior of monatomic liquids takes us but a short way towards desired goals. The substances that have appealed to me as the most attractive substitutes for the group 0 elements have been the tetrahalides, and my coworkers and I have for many years been gathering information regarding both the pure substances and their solutions. They possess the next best thing to spherical symmetry, they are obtainable in quantity, and they offer a wide range of intermolecular forces, so different, in the case of $SiCl_4$ and SnI_4, for example, as to give two liquid phases.[1]

Among the more obvious questions that present themselves are the following:

1. To what extent are we justified in treating these tetrahedral molecules as if they had spherical symmetry, due to rotation in the liquid state? Formulas for solubility relationships derived for spherical molecules have proven applicable to a remarkable degree to solutions of polyatomic molecules[2] nevertheless, the evidence shows, as has been pointed out by Halford,[3] that free rotation in tetrahalides is more and more restricted as larger central atoms are chosen.

2. Instead of considering the molecular fields of the tetrahalides as radial from their central atoms, would it be better, in view of the short range of the London forces, to consider the halogen atoms as the main centers of attraction, as I once suggested?[4] The fact that these forces become so weak at a distance of two molecular diameters as to contribute but little to the energy of vaporization has long been evident.[5] It is particularly well illustrated by the fact that such substances as OsO_4, OsF_8, and UF_6 are very volatile despite the many electrons in their central atoms and the extreme non-volatility of the metals themselves.

3. What influence does bond character have upon intermolecular forces?

4. Why do boiling points, internal pressures and solvent powers show $SiCl_4$ apparently out of line, as shown in Table I?

In attempting to answer these questions, it seems best to exclude the halides of the sixth group elements because of instability or lack of

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* Presented at the symposium on liquids at Atlantic City, April 17, 1947, under the auspices of the Division of Physical and Inorganic Chemistry.

[1] J. H. Hildebrand and G. R. Negishi, J. Am. Chem. Soc. **59**, 339 (1937).

[2] Cf. R. D. Vold, J. Am. Chem. Soc. **59**, 1515 (1937).

[3] R. S. Halford, J. Chem. Phys. **8**, 496 (1940).

[4] J. H. Hildebrand, Trans. Faraday Soc. **33**, 144 (1937).

[5] Cf. J. H. Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York), second edition, p. 71.

TABLE I.

	CCl₄	SiCl₄	GeCl₄	SnCl₄
Boiling point, °K	350	332	360	386
Internal pressure, energy of vap. per cc	73.7	56.8	65.5	86.4
Solubility of I_2, mole percent at 25°C	1.15	0.50	—	—

tetrahedral symmetry. Stevenson and Shoemaker[6] have found, for example, that TeCl₄ has a bipyramidal structure and Vogt and Biltz[7] found that it is a good conductor of electricity in the liquid state. It has, furthermore, a higher entropy of vaporization than a normal liquid and a low solvent power for iodine.[8]

Any answers given to the questions stated above must be consistent with all of the pertinent physico-chemical properties of these substances, therefore, these properties are reviewed in the paragraphs immediately following.

MELTING POINTS

Melting points in °K, from a resumé kindly furnished by Professor Leo Brewer, are given in Table II and plotted against molal weight in Fig. 1. We see that the points for the halides of silicon, germanium, tin and lead increase with molecular weight about as one might expect from the behavior of the inert gases. Indeed, if the slope of the curve for the rare gases is taken to indicate the effect of increasing molecular weight upon melting and boiling points of symmetrical, non-polar molecules, then the increase in melting point and boiling point for the tetrahalides is largely determined by molecular weight, with the weights of the central atom and the halide atoms counting equally. It is evident, however, that the points for the halides of carbon, vanadium and titanium are distinctly higher than for the others, suggesting that the processes involved in these cases are somewhat different. Divergent melting points for CCl₄ and CBr₄ may be attributed to a different solid lattice, for, unlike the others, they have transition points 24.8° and 43.2°, respectively, below their melting points. The melting

process is evidently much the same with the case of the others, as indicated by practically identical entropies of fusion of four chlorides given in Table III reproduced from a paper by Frederick and Hildebrand.[9] In the cases of CCl₄ and CBr₄, sums of the entropies of transition, Δs_t, and of fusion, Δs_f, are less than the entropy of fusion for the other four. Mark[10] found that the lower temperature form of CBr₄ is monoclinic, the higher form tetragonal, and Dickinson[11] reported that SnI₄ has a cubic unit cell of 8 molecules with pyritohedral symmetry. According to Hassell and Kringstad,[12] TiBr₄ and TiI₄ have the same crystal structure as SnI₄. Raeder[13] found that the following form mix-crystals in all proportions, indicating indentical crystal structure: SnCl₄ and SnBr₄; SnBr₄ and SnI₄; TiCl₄ and TiBr₄.

Turkevich, Conner and Smyth[13a] have given definite evidence that the CCl₄ molecules are

TABLE II. Meltings and boiling points, and ratios, °K.

	Chlorides			Bromides			Iodides		
	T_m	T_b	T_b/T_m	T_m	T_b	T_b/T_m	T_m	T_b	T_b/T_m
C	250	350	1.40	363	463	1.28	444	dec.	—
Si	206	330	1.60	278	426	1.57	394	561	1.42
Ge	224	357	1.59	299	462	1.54	419	dec.	—
Sn	240	386	1.61	303	480	1.58	418	621	1.48
Pb	258	dec.	—	—	—	—	—	—	—
V	247	427	1.73	—	—	—	—	—	—
Ti	250	409	1.63	311	503	1.62	423	630	1.49
Zr	710	604	0.85	723	630	0.87	772	704	0.91
Hf	705	590	0.84	693	595	0.86	—	—	—
Th	1038	1195	1.14	952	1130	1.19	839	1110	1.32

rotating between the transition point and the melting point, which is in harmony with the fact that they acquire more entropy in the transition than in fusion. CBr₄ must be doing the same thing, although the higher C_p found by Frederick and Hildebrand for the higher solid form, 42.9 cal. compared with 35.0 cal. for the monoclinic form and 36.7 cal. for the liquid, indicates that rotational energy is still being acquired above the transition point. We shall return later to the question of rotation.

The higher values for TiCl₄ and VCl₄ and the still higher values for ZrCl₄, HfCl₄ and ThCl₄,

[6] D. P. Stevenson and V. S. Shoemaker, J. Am. Chem. Soc. 62, 1267 (1940).
[7] A. Vogt and W. Biltz, Zeits. f. anorg. allgen, Chemie 133, 277, 312 (1924); see also J. H. Simons, J. Am. Chem. Soc. 52, 3483 (1930).
[8] J. H. Hildebrand, J. Phys. Chem. 43, 109 (1939).

[9] K. J. Frederick and J. H. Hildebrand, J. Am. Chem. Soc. 61, 1555 (1939).
[10] H. Mark, Ber. d. d. chem. Ges. 57B, 1820 (1924).
[11] R. G. Dickinson, J. Am. Chem. Soc. 45, 958 (1923).
[12] O. Hassell and H. Kringstad, Zeits. f. physik. Chemie B15, 274 (1932).
[13] M. G. Raeder, Thesis (Trondhjem, 1929).
[13a] A. Turkevich and C. P. Smyth, J. Am. Chem. Soc. 62, 2468 (1940); W. P. Conner and C. P. Smyth, ibid., 63, 3424 (1941).

raise the question whether the type of bonding electrons is responsible, d and s instead of s and p for the tin group. It seems sufficient, however, to attribute these differences to greater ionic character of their bonds, with greater tendency for higher coordination about the central atom. The ionization potential of Zr is 6.92 electron-volts while that of Sn is much higher, 7.30 electron-volts.[14] The difference in ionic character between ZrI_4 and SnI_4, with melting points of 772°K and 418°K respectively, is strikingly indicated by the absence of color in the former and the orange color in the latter.[15]

BOILING POINTS

Boiling points, also plotted in Fig. 1, are strikingly parallel to melting points for the silicon, germanium, tin and titanium halides, but not so for the others. This is brought out in Table III, which gives the ratios, T_b/T_m. The smaller ratios for CCl_4 and CBr_4, are in the direction to be expected for more nearly symmetrical molecules; this ratio is only 1.04 for argon. The same reason explains the decrease of the ratio in going from the chlorides of Si, Sn and Ti to their iodides.

The sublimation of the solid halides of Zn and Hf must be regarded as further evidence of their salt character.

MOLECULAR DIMENSIONS

The distance between the centers of the central atoms and the halogen atoms, as determined by electron diffraction, are given in Table IV, along with molal volumes at 25°. Let us re-examine the evidence of these figures on the question of restricted rotation. The "Hildebrand rule"[16] ap-
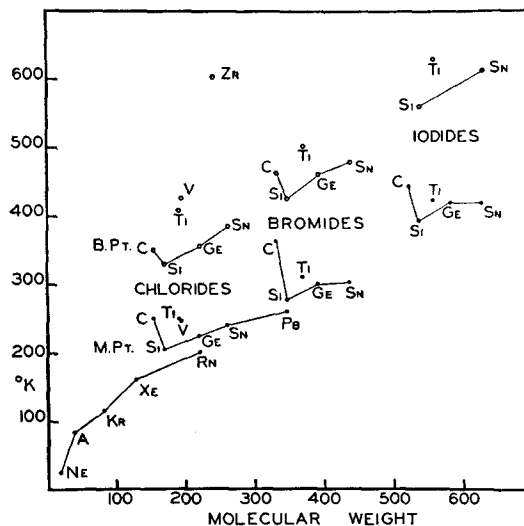

FIG. 1. Melting and boiling points of tetrahalides.

TABLE III. Entropies of transition and fusion.

Substance	T_{tr}	Δs_t	T_m	Δs_f	$\Delta s_t + \Delta s_f$
CBr_4	320.0	4.44	363.2	2.61	7.05
CCl_4	225.44	4.79	250.23	2.31	7.10
$TiCl_4$	—	—	250.0	9.00	9.00
$TeCl_4$	—	—	497.2	9.07	9.07
$SiCl_4$	—	—	205.5	9.08	9.08
$SnCl_4$	—	—	239.9	9.11	9.11
SnI_4	—	—	417.6	11.01	11.01

[14] Cf. G. Herzberg, *Atomic Spectra and Atomic Structure* (Prentice-Hall, Inc., New York, 1937).

[15] For a discussion of color as an index of bond character, see K. S. Pitzer and J. H. Hildebrand, J. Am. Chem. Soc. **63**, 2472 (1941).

[16] J. H. Hildebrand, J. Chem. Phys. **7**, 233 (1938).

plied to the tetrachlorides of C, Si, and Sn shows the following entropies of vaporization at temperatures where the vapor volume is 49.5 liters, neopentane, "spherical," 20.1 e.u., CCl_4 20.7 e.u., $SiCl_4$ 21.2 e.u., and $SnCl_4$ 21.8 e.u. If the comparison is made at equal ratios of vapor to liquid volume, to correspond with the indications of the theory of corresponding states, as shown by Pitzer,[17] the results would hardly be altered, since these three liquids have nearly identical liquid volumes, indeed the spread between CCl_4 and the other two would be greater. It was concluded, therefore, that as the size of the central atom increases a certain amount of order is forced, which Halford[3] called "restricted rotation." That this must be the case follows from the relation of molecular dimensions to molal volumes. If the molecules are rotating, the volume swept by one is $4/3\pi R^3$, where R is the M-X distance plus the van der Waals radius, and the volume of 6×10^{23} molecules, close packed, divided by 0.74, gives the minimum volume the substance could occupy if its molecules were freely rotating. The maximum value of R that would permit free rotation in liquid CCl_4, calculated in this way, is 3.08A. This corresponds to an intermolecular distance between carbon atoms of 6.16A and between chlorine atoms of 2.64A. The actual $C-C$ distance found by Bray and Gingrich in liquid CCl_4 from x-ray diffraction

[17] K. S. Pitzer, J. Chem. Phys. **7**, 583 (1939).

TABLE IV.

	C	Si	Ge	Sn	Pb	V	Ti	Zr	Th
Chlorides									
Mol. vol., cc. 25°C	97.1	115.4	114.5	117.6	—	105.8	110.5	—	—
$M\text{-}X$ dist., A*	1.76[b]	2.00[b]	2.08[b]	2.30[b]	2.43[a]	2.03[c]	2.18[a]	2.33[a]	2.61[a]
Bromides									
Mol. vol., cc. 25°C		126.5	126.0	130.6			2.31[a]		
$M\text{-}X$ dist., A	1.94[a]	2.14[a]	2.29[a]	2.44[a]			2.31[a]		
Iodides									
$M\text{-}X$ dist., A	2.15[a]	2.43[a]	2.50[a]	2.64[a]					

* $M\text{-}X$ distances from (a) M. W. Lister and L. E. Sutton, Trans. Faraday Soc. **37**, 393 (1941); (b) L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936); (c) N. Lipscomb and A. G. Whittaker, J. Am. Chem. Soc. **67**, 2019 (1945).

is 6.4A,[18] so that there is room in the liquid for free-rotation, confirming the evidence found by Turkevich, Conner, and Smyth.[13a] Such rotation would not be possible, however, if the van der Waals radius of Cl were as large as 1.80A, the value assigned by Pauling,[19] which would require a C−C distance of 7.12A. That value for the chlorine radius is evidently too large for liquid CCl_4, which, it should be remembered, is under an internal pressure of 3000 atmospheres. The shortest intermolecular Cl−Cl distance in solid Cl_2[20] is 2.77A, near enough to the distance given above for a close-packed but rotating structure, 2.64A, to permit the rotation for which we have independent evidence. If, now, 1.32A is assumed as the van der Waals radius of Cl, from the inter-molecular distance in solid Cl_2, and added to the $M\text{-}X$ distance in $SnCl_4$, 2.30A, we obtain 3.62A for R, much larger than the value, 3.33A, which would be required for free rotation in liquid $SnCl_4$ at 83°C. This is in accord with the evidence furnished by its excess entropy of vaporization.

The molal volume of SnI_4 is 165 cc at 145°C, from which its maximum radius permitting free rotation would be 3.65A. Subtracting the $M\text{-}X$ distance, 2.64A, leaves only 1.01 for the van der Waals radius of iodine, much too small compared with the value derived from solid iodine,[20a] which is 1.77A. We see why SnI_4 crystallizes to a non-rotating structure. The intermolecular I−I distance in solid SnI_4, according to Dickinson, is

4.21A. All of this is in accord with the evidence from entropy of vaporization given in the preceding section and is to be taken into account in the formulation of intermolecular forces.

RAMAN FREQUENCIES

There are four principal Raman frequencies for regular tetrahedral molecules, one, denoted by ν_1, is attributed to the "breathing" or vibration along the $M\text{-}X$ bond, a second, ν_2, is for the bending of the bonds, and is influenced by their stiffness and also by interhalogen repulsions, and the third and fourth are anisotropic vibrations, in which the central atom is displaced, along with the halogen atoms, from its rest position. The first two, in which the central atom remains at rest, are not dependent on its mass and therefore offer a clearer means of comparing the different compounds of the same halogen.

Several investigators have analyzed these frequencies on the basis of various bond models, but let us begin by a simple, inductive approach. Haun and Harkins,[21] who determined the Raman frequencies for $GeCl_4$, plotted them with the frequencies for the chlorides of C, Si, and Sn against the period of the several central atoms in the Periodic System, obtaining a decreasing, broken line. Delwaulle and Francois[22] have plotted these frequencies against the atomic weight of the central atom, getting curves with $TiCl_4$ and $TiBr_4$ falling out of line. These irregularities largely disappear if the $M\text{-}X$ distance is used as the abscissa, as can be seen in Fig. 2, for in the cases of simple vibrations, ν_1 and ν_2, which are

[18] E. E. Bray and N. S. Gingrich, J. Chem. Phys. **61**, 351 (1943).
[19] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1944), p. 189.
[20] W. H. Keesom and K. W. Tactonis, Proc. Acad. Sci., Amsterdam, **39**, 314 (1936).
[20a] P. M. Harris, E. Mack, Jr., and F. C. Blake, J. Am. Chem. Soc. **50**, 1583 (1928).

[21] R. R. Haun and Wm. D. Harkins, J. Am. Chem. Soc. **54**, 3917 (1932).
[22] L. Delwaulle and F. Francois, J. phys. radium, **7**, 15, 53 (1946).

independent of the mass of the central atom. It should be remembered that the M-X values are mostly subject to an error of about ± 0.02A. The frequencies are from the compilation by Hertzberg,[23] except for $PbCl_4$, the values for which, $\nu_1 = 327$ cm^{-1} and $\nu_2 = 90$ cm^{-1}, have just been obtained by my colleagues, Professor W. Gwinn and Mr. J. T. Neu at my suggestion, to see whether they would conform to this plot. They will publish the details. The frequency along the bond, ν_1, varies linearly with both chlorides and bromides. The bond bending frequency, ν_2, is concave upward, as might be expected from the increased crowding of the halide atoms as the central atom becomes smaller. Table V compares the interhalogen distances and shows where the strain is greatest.

The regularity shown in Fig. 2 gives but scant basis for assuming that any one of these molecules has an exceptional character. It is noteworthy that Urey and Bradley found that only $TiCl_4$ deviated even to a minor extent from the model they used. A similar result was found by Gordy,[24] using a different model. It would be a little greater using Lister and Sutton's value of M-X, 2.18A instead of the older value he used, 2.21A.

Departures of measured M-X distances from the sum of assigned values of covalent radii have been explained by assuming double bond resonance[25] in the cases of $SiCl_4$, $TiCl_4$, and VCl_4. More recently, however, bond shortening has been more generally explained by an empirical correction taking into account differences in electronegativity.[24] If resonance exists in $SiCl_4$ and $TiCl_4$ it seems to have remarkably little effect on
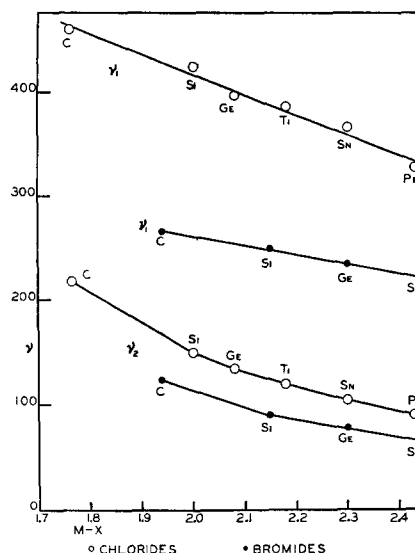

FIG. 2. Isotropic Raman frequencies. Bond stretching, ν_1; bond bending, ν_2.

frequency as correlated in Fig. 2. It has been invoked by Lipscomb and Whittaker to explain the discrepancy between their value for the $V-Cl$ distance, 2.03A, and the value 2.12A reported by Palmer[26] for the same distance in vanadium oxytrichloride. There is, however, another serious discrepancy, that between 2.03A for VCl_4 and 2.18A for $TiCl_4$, a difference too great to accord with the rather close agreement in other properties of VCl_4 and $TiCl_4$ shown in Table VI.

It seems unlikely that the M-X distances in VCl_4, and $TiCl_4$ are seriously affected by different ratios of covalent to ionic binding, since the ionization potentials of V and Ti are nearly identical. Nor is there reason to suppose that the color and paramagnetism of VCl_4 have an appreciable relation to its external field of force.

TABLE V. Interhalogen distances.

| | v. d. Waals elements | Tetrahalides | | | | | | |
		C	Si	Ge	Ti	Sn	Zr	Th
Chlorides	2.77[20]	2.89	3.27	3.40	3.57	3.76	3.81	4.27
Bromides	3.30*	3.18	3.53	3.74	3.78	3.99	—	—
Iodides	3.54[20a]	—	3.98	4.09	—	4.32	—	—

* B. Vonnegut and B. E. Warren, J. Am. Chem. Soc. **58**, 2459 (1936).

[23] G. Hertzberg, *Infra-Red and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945). See also, Kohlrausch, *Ramanspektren* (Becker and Erler, Leipzig, 1943); H. C. Urey and C. A. Bradley, Phys. Rev. **38**, 1969 (1931); J. E. Rosenthall, *ibid* **45**, 538 and 730 (1934), and **49**, 535 (1936).

[24] W. Gordy, J. Chem. Phys. **14**, 305 (1946).

[25] See reference 19, p. 228ff, and reference *c to Table IV.

TABLE VI.

	T_m	T_b	T_b/T_m	Vol., cc., 25°C	M-X, A
VCl_4	251	425	1.69	105.8	2.03
$TiCl_4$	243	410	1.69	110.5	2.18

The apparent association of VCl_4 dissolved in CCl_4, inferred by Simons and Powell[27] from freezing point depression, may be due, instead, to some degree of mutual solubility in the solid

[26] K. J. Palmer, J. Am. Chem. Soc. **60**, 2360 (1938).

[27] J. H. Simons and M. G. Powell, J. Am. Chem. Soc. **67**, 75 (1945).

TABLE VII. Intermolecular attraction.

	CCl₄	SiCl₄	GeCl₄	SnCl₄	TiCl₄	CBr₄	SiBr₄	SnBr₄	SnI₄
ΔH_{vap} kcal., 298°K	7.83	7.19	8.09	9.55	9.62	—	10.38	—	13.70*
$V\Delta E$ kcal.×liters	7.04	7.62	8.60	10.55	9.98	—	12.40	—	21.65
$V^2(\partial E/\partial V)$ kcal.×liters	7.56	8.23	—	10.95	10.15	—	12.90	15.67	—
aR^3 from $V\Delta E$, relative	221	297	360	532	454	—	676	—	1860
aR^3 from $V^2(\partial E/\partial V)$	237	321	—	552	462	—	703	1073	—
$\alpha\times10^{24}$	10.23	11.10	12.12	13.45	14.07	14.06	15.9	18.3	27.8
k/α^2	2.2	2.5	2.5	3.0	2.3		2.7	3.2	2.4

* $T=450°K$.

phase. The situation is evidently one calling for a determination of the electron-diffraction patterns of both substances by the same investigator.

THE STRENGTH OF INTERMOLECULAR ATTRACTION

Hildebrand and Wood[28] derived the formula

$$E_g - E_l = \Delta E_{vap} = \frac{-2\pi N^2}{V} \int W\epsilon r^2 dr \qquad (1)$$

for the energy of vaporization of a monatomic liquid of molal volume, V, whose structure is expressed by the radial distribution function, W. N is the Avogadro number, r is the distance from a central molecule and ϵ is the potential energy of a pair of molecules, which is ordinarily expressed by the difference between a repulsive term, oversimplified to j/r^n, where $n \approx 9$, and an attractive term, k/r^6, according to the dispersion theory of London, i.e.,

$$\epsilon = j/r^n - k/r^6. \qquad (2)$$

Substituting 2 in 1 gives,

$E_g - E_l = \Delta E_{vap}$

$$\frac{-2\pi N^2}{V}\left(j\int \frac{Wdr}{r^{n-2}} - k\int \frac{Wdr}{r^4} \right) \qquad (3)$$

W, and hence the integrals, are not sensitive to small changes in V, so that $V\Delta E_{vap}$ is nearly constant, and we may write

$$V\Delta E_{vap} \approx a \approx V^2(\partial E/\partial V)_T. \qquad (4)$$

The "constant," a, is the familiar van der Waals constant, although it does not necessarily have the same numerical value as the one calculated in the usual way from critical data.

The above formulas are derived for spherical molecules with radial fields of force so that to apply them to the tetrahedral molecules here considered involves a simplification not to be overlooked, but one which is nevertheless enlightening, so we proceed to do it. Westwater, Frantz and Hildebrand[29] and Hildebrand and Carter[30] measured $(\partial p/\partial T)_v$ accurately for a number of tetrahalides, calculated $(\partial E/\partial V)_T$ and showed that $V^2(\partial E/\partial V)_T$ is constant to a high degree over the range studied. Hildebrand[31] compared the two methods of obtaining values of a given in Eq. 4 and found that $V\Delta E_{vap}$ is several percent larger than $V^2(\partial E/\partial V)$, as shown here in Table III. The values of ΔE are based upon the heats of vaporization in the summary by Kelley.[32] This accords with the fact that W is not strictly constant, but is a function of volume. We have no analytical expression for this variation and must be content with a consideration of the qualitative effect. Representing the repulsive and attractive integrals of Eq. 3 by I_r and I_a, respectively, we can write,

$$V^2\left(\frac{\partial E}{\partial V}\right) - V\Delta E_{vap} = 2\pi N^2\left[j\frac{\partial I_r}{\partial \ln V} - k\frac{\partial I_a}{\partial \ln V}\right]. \qquad (5)$$

When the liquid is moderately expanded, the attraction is balanced in large part by thermal agitation rather than by repulsion, hence the k-term is larger than the j-term, but $(\partial I_a/\partial \ln V)$ is negative, hence the left hand member of Eq. 5 is positive, in accord with the data in Table VII.

Let us make, next, an approximate evaluation of the attraction constant, k, for certain of these

[28] J. H. Hildebrand and S. E. Wood, J. Chem. Phys. **1**, 12 (1933).

[29] W. Westwater, A. W. Frantz, and J. H. Hildebrand, Phys. Rev. **31**, 135 (1928).

[30] J. H. Hildebrand and J. M. Carter, J. Am. Chem. Soc. **54**, 3592 (1932).

[31] J. H. Hildebrand, Phys. Rev. **34**, 984 (1929).

[32] K. K. Kelley, Bull. U. S. Bur. Mines **383**, (1934).

substances. Let us apply the evidence found by Campbell and Hildebrand[33] that the form of the distribution function, W, depends only on the degree of expansion of the liquid, and should therefore be the same for different liquids if expressed as a function not of r but of $\rho = r/R$, where R is some fixed parameter such as the van der Waals' radius in the case of a spherical molecule. Substituting ρR for r in Eq. 3 and taking $n = 9$, a reasonable value, and combining with Eq. 4 gives

$$a = \frac{2\pi N^2 k}{R^3} \int \frac{Wd\rho}{\rho^4} - \frac{2\pi N^2 j}{R^6} \int \frac{Wd\rho}{\rho^7}. \quad (6)$$

The integral is assumed to be nearly the same for any pair of liquids and exactly the same under the same degree of expansion, when, accordingly, $k \propto aR^3$, if we neglect the comparatively small repulsive term. For comparable values of R we may use the M-X distances plus the van der Waals halogen radii, given previously from the solid halogens. These values of R are included in Table VII, also aR^3, in arbitrary units, since we are able to obtain only relative values. These values, which are roughly proportional to the attraction constant, k, are plotted against M-X in Fig. 3. The smooth increase justifies the conclusion that the attraction constant for like pairs increases regularly. This would not be the case if the chloride atoms were at the same time the main centers of attraction and in the same electronic state from the standpoint of the London forces. Indeed, if these molecules were freely rotating and their chlorine atoms were equal as centers of attraction, then k should decrease with increasing size due to decreasing average density of chlorine atoms on the surface of the sphere. That the attraction constant increases indicates that the character of each particular bond with the central atom strongly affects the magnitude of the intermolecular force, due either to the bond being more exposed, more ionic, or both.

According to London,[34] the attractive potential between a pair of molecules is

$$\epsilon = -3h\nu_0\alpha^2/4r^6, \quad (7)$$

where α is the polarizability and $h\nu_0$ the internal zero-point energy, which is approximately given by the ionization potential. We do not know this last for the molecules under consideration, but it is worth noting that our approximate k is roughly proportional to α^2, as shown by the ratios in the last row of Table VII, and by the positions of the crosses in Fig. 3. The connection between polarizability, molecular field strength and bond type was set forth many years ago by Fajans and Joos,[35] who showed that the refraction of Cl^-, and therefore its state, differs in different compounds. In general, the stronger the field of the central atom the tighter the electronic shell of the halide atom. And Fajans,[36] in discussing the difference between AlF_3 and SiF_4, stated that it is due in part to the greater screening of the Si^{+4} but in part, also, to its larger deforming effect upon the F^-, by reason of its small size and greater charge. This deformation is to be regarded as equivalent to the introduction of partially covalent character into the bond.

Figure 3 shows $SiCl_4$ falling in line with the higher chlorides, a fact which, like the Raman frequencies previously cited, argues against the assumption of a double bond resonance peculiar to this molecule. The only members of these series which call for special explanation are CCl_4 and CBr_4. They differ from the others in having less ionic bond character and in the compression of their halide atoms indicated in Table V, but it
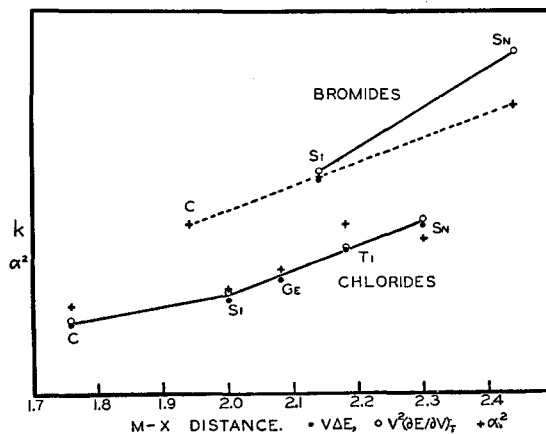

FIG. 3. Variation of intermolecular-attraction constant, k, and polarizability, α (relative scales), with M-X distance.

[33] J. A. Campbell and J. H. Hildebrand, J. Chem. Phys. 11, 334 (1943).
[34] F. London, Trans. Faraday Soc. 338, (1937).
[35] K. Fajans and G. Joos, Zeits. f. Physik 23, 27 (1924).
[36] K. Fajans, Zeits. f. Elektrochemie 34, 443 (1928).

TABLE VIII. Expansion on mixing; percent at 50 mole percent ($t = 35°$ for $SnBr_4$ solutions, 25° for all others).

	CCl_4	$SiCl_4$	$TiCl_4$	$SnCl_4$	$SiBr_4$	$SnBr_4$
M-X dist. ÷halide radius	0.97	1.11	1.21	1.28	1.10	1.36
CCl_4	—	0.014	0.083	.408	0.184	0.221
$SnBr_4$		0.111			0.093	

is not clear why either of these factors should increase polarizability and intermolecular potential.

TETRAHALIDE SOLUTIONS

One of the most carefully investigated solutions of a pair of tetrahalides is CCl_4 with $SiCl_4$, whose vapor pressures were measured by Wood[37] and heats of mixing by Vold,[38] both in this laboratory.

The internal pressures of the two components, $\Delta E_{vap}/V$, computed by aid of the careful calculations of heats of vaporization from the vapor pressures, by Vold, are 73.7 cals./cc for CCl_4 and 56.8 cals./cc for $SiCl_4$. The equation derived by Hildebrand and Wood[27] for the partial molal energy of transfer of component 2 from pure liquid to a regular solution—one in which the thermal agitation is able to maintain random mixing—is

$$\bar{E}_2 - E_2{}^0 = \phi_1{}^2 V_2 D^2 \qquad (8)$$

where ϕ_1, is the volume fraction of component 1, V_2 the molal volume of component 2, and $D^2 = [(\Delta E_1/V_1)^{\frac{1}{2}} - (\Delta E_2/V_2)^{\frac{1}{2}}]^2$. The value of D from the figures given above is 1.05. Vold measured the heat of mixing the components in five mole fractions of $SiCl_4$ ranging from 0.18 to 0.86 and found a mean value of D of 1.12, a most gratifying agreement. The maximum heat of evolved per mole of mixture was 32.3 cals., while the value calculated from the equation and $D = 1.05$ is 28.0 cals.

The partial vapor pressures of these solutions, measured by Wood, show small deviations from Raoult's law in the same direction, with a maximum value of the free energy of mixing over that calculated for an ideal solution of 28.3 cals./mole. The measurements deviate among themselves as much as they do from the calculated values. They correspond to a mean value of $D = 0.84$, but the difference between this and 1.05 is hardly greater

than the experimental error. We may conclude that this system is regular according to the theory and indicates no marked departure in the attraction constant of the unlike molecules from the geometrical mean of the attraction constants of the like molecules; an assumption implicit in Eq. 8. It is gratifying that a treatment based upon spherical symmetry of the molecules applies as well as this to a solution of tetrahedral molecules. The agreement becomes less satisfactory when two species are chosen whose molecules have markedly different shapes.

Boiling point and freezing point curves for the binary solutions of $TiCl_4$ with CCl_4, $SiCl_4$ and $SnCl_4$ were obtained by Nasu.[39] The boiling point curves are hardly precise enough to permit calculating the rather small deviations from Raoult's law, but these are clearly greatest with $SiCl_4$ and least with $SnCl_4$, in accord with the order of internal pressures. The freezing point curve of $TiCl_4$ from $SnCl_4$ shows the separation of solid solutions, and is therefore useless for our purpose. The points for $TiCl_4$ from solutions in CCl_4 fall closely upon the Raoult's law line calculated from Latimer's[40] figure 2235 cal., for its molal heat of fusion, in harmony with the almost identical internal pressures of these components, $\Delta E/V$ is 81.7 cal./cc for $TiCl_4$ and 73.6 cal./cc for CCl_4 at 25°. These values, extrapolated to the low temperatures of the measurements would still be close together.

Nasu's freezing points of $TiCl_4$ from solutions with $SiCl_4$ deviate from the Raoult's law line approximately to the rather small extent demanded by the difference between their internal pressures, but the various uncertainties in the essential data at these low temperatures are sufficient to prevent any significant conclusion being drawn from the minor departures from the simple theory for regular solutions.

The solutions of $SiCl_4$ with SnI_4, investigated by Hildebrand and Negishi[41] accord with the great difference in their internal pressures in giving incompletely miscible liquids. The great difference between the liquid ranges of these two substances requires some extrapolation in order

[37] S. E. Wood, J. Am. Chem. Soc. 59, 1510 (1937).
[38] R. D. Vold, ibid. 59, 1515 (1937).

[39] N. Nasu, Sci. Rep. Tohoku Imp. Univ., 1st. Ser. 22, 972 (1933).
[40] W. M. Latimer, J. Am. Chem. Soc. 44, 90 (1922).
[41] J. H. Hildebrand and G. R. Negishi, J. Am. Chem. Soc. 59, 339 (1937).

to apply the formula for simple regular solutions based upon Eq. 8, which is

$$4.575T \log(x_2{}^i/x_2) = \phi_1{}^2 V_2 D^2, \qquad (9)$$

where x_2 is the mole fraction of component 2, here SnI_4, $x_2{}^i$ its mole fraction in an ideal solution. At the boiling point of $SiCl_4$, 59°C, its ΔE is 6180 cal. and its V is 122.0, giving $(\Delta E_1/V_1)^{\frac{1}{2}} = 7.12$. From the solubility data cited, $D = 3.68$ at this temperature, and therefore $(\Delta E_2/V_2)^{\frac{1}{2}} = 7.12 + 3.68 = 10.80$ for SnI_4. If the formula of Kelley[32] is used to compute the heat of vaporization of liquid SnI_4 at this temperature, one obtains $\Delta E = 18,360$ cal. and since $V_2 = 155.2$ cc, extrapolated for the liquid, $(\Delta E_2/V_2)^{\frac{1}{2}}$ would be 10.88. The close agreement with the above figure from solubility is doubtless fortuitous, in view of the assumptions involved, but it indicates, at least, that the internal pressures as calculated are adequate to account for the solubility relations found, without additional assumptions regarding the nature of the particular species.

Although the assumption of radial force fields involved in the formal treatment of the foregoing solutions appears to be about as adequate as one has any right to expect, it is my belief nevertheless that this is the fortunate result of the similar structures of these molecules, and that it would be theoretically preferable, although practically not worth the effort, to consider the atoms as the centers of the fields of force. The evidence for this comes from the entropy of vaporization of a pair of liquids whose molecules are very different in size but otherwise very similar specifically Cl_2 and CCl_4, and again, C_2H_6 and di-isopropyl.[42] The entropy depends more upon the separation of the peripheral atoms than of the molecular centers.

VOLUME CHANGES ON MIXING

Hildebrand and Carter[30] determined the changes in volume on mixing the tetrahalides shown in Table VIII. These were found, in all cases, to be remarkably small, the largest being only 0.4 percent. It can be seen, also, by aid of the ratios of M-X distance to van der Waals halide radius, that the expansions are roughly parallel to this ratio rather than to M-X distance

[42] J. H. Hildebrand, and T. S. Gilman, J. Chem. Phys. 15, 229 (1947).

alone. One may infer that the effect is due mainly to the geometry of the molecules, although influenced, probably, by difference in bond character, internal pressure, and degree of expansion.

CONCLUSIONS

The various lines of evidence surveyed in the foregoing pages seem to justify the following answers to the questions asked at the outset together with several additional inferences.

1. In the case of CCl_4 and CBr_4 the evidence is in favor of a degree of rotational energy sufficient to overcome the barrier of van der Waals repulsion between the halide atoms. This rotation becomes increasingly hindered, however, in passing to the compounds with larger central atoms and rotation must increasingly give way to oscillation. In spite of this restriction, however, the thermodynamic properties of tetrahalide solutions can be calculated with an accuracy sufficient for many purposes by means of equations derived for liquids composed of spherical molecules.

2. These equations, of course, assume that the field of force is central to the molecules, not to the peripheral atoms of polyatomic molecules. Although certain evidence favors the latter assumption, the far more complicated treatment that would be required does not seem ordinarily to be worth while. The halide atoms do not constitute centers of attraction at all uniform, but are greatly dependent upon the character of the central atom.

3. Intermolecular attraction between different species having the same halide atoms does not seem to depend noticeably upon the kind of bonding orbitals of the central atom, for $TiCl_4$ falls in line with $GeCl_4$ and $SnCl_4$ while $HfCl_4$ and $ZrCl_4$ do not. The attraction is strongly influenced by the degree of ionic character of the bond, increasing with the size and electropositive character of the central atom. A large radius ratio of central atom to halide atom permits coordination higher than four and greatly enhanced intermolecular force, as illustrated by comparing SnF_4 with $SnCl_4$. Attractive forces increase in the order chlorides, bromides, iodides, due to the increase in the number and polarizability of the halide electrons.

4. The apparent anomaly of the low boiling point and internal pressure of $SiCl_4$ is due only

to the considerable increase in molal volume be-
tween CCl_4 and $SiCl_4$; although the attraction is
less, the attraction constant is greater, increasing
almost linearly with molecular dimensions in the
order CCl_4, $SiCl_4$, $GeCl_4$, $TiCl_4$, $SnCl_4$. None of
the properties herein examined, including Raman
frequencies, indicates any exceptional character
for $SiCl_4$, such as the double-bond resonance that
others have assumed to account for the some-
what short M-X distance.

5. The only members of these series that ap-
pear to call for any unique explanation are CCl_4
and CBr_4, which have (a) high melting points
and low entropies of fusion, which seem to be
connected with crystal structure; (b) high boiling
points, which require a totally different explana-
tion; (c) slightly high Raman frequencies, which

may be ascribed to interhalogen repulsions and
covalent bonds; and (d) attraction constants and
polarizabilities slightly in excess of the linear
relationship to molecular dimensions exhibited
by the higher members of the series.

It seems appropriate, in conclusion, to call
attention to certain gaps in the experimental
data for these important substances which should
by all means be filled. They include crystal
structures of the solids, densities and expansivi-
ties of the solids, heat capacities and heats of
fusion, a redetermination of the M-X distance
for $TiCl_4$ and VCl_4 by the same investigator;
Raman spectrum of VCl_4; additional accurate
mutual solubility data; vapor pressures for $SnBr_4$
and nearly every thermodynamic property for
the fluorides.

Note on a Form of the Secular Equation for Molecular Vibrations

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By starting with the Hamiltonian form of the equations of motion, the problem of the small
vibrations of a polyatomic molecule can be solved with the aid of a secular equation twice
the usual size. This equation, however, is readily adapted to solution by electrical circuits and
has the important advantage of having as elements the force constants and inverse kinetic
energy coefficients ("G" matrix elements) directly. The force constant matrix elements occupy
one off-diagonal corner of the secular equation, the G matrix elements are in the other off-
diagonal corner, the circular frequencies ($2\pi\nu$) appear on the principal diagonal, and all other
elements are zero.

THE problem of small amplitude vibrations
of the atoms of a polyatomic molecule has
been extensively treated.[1] Its solution, as is well
known, involves some type of determinantal or
secular equation, which can assume many forms.
It is the purpose of this note to point out the
useful properties of one of the lesser known forms.

Consider that a set of "internal" coordinates
has been selected, such as $3N-6$ independent
interatomic distances and valence angles, where
N is the number of atoms. Let R_i be the deviation
of the ith coordinate from its equilibrium value.
Then the potential energy V of the molecule can

be expressed in the form

$$2V = \sum_{ij} F_{ij} R_i R_j, \qquad (1)$$

if the zero of energy is properly chosen and if
higher order terms (anharmonic terms) are neg-
lected. The constants F_{ij} are the force constants.

The kinetic energy can be expressed in terms
of the velocities $\dot{R}_i$ or in terms of the momenta P_i,
conjugate to the coordinates R_i. Let the kinetic
energy T be written as

$$2T = \sum_{ij} G_{ij} P_i P_j, \qquad (2)$$

where the G_{ij} are coefficients involving the masses
of the atoms and the geometry of the molecule
and are constants to the approximation ordi-

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[1] G. Herzberg, *Infrared and Raman Spectra of Polyatomic
Molecules* (D. Van Nostrand Company, New York, 1945).