POLARIZABILITY AND COHESION ENERGY

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N.V. BOEK- EN STEENDRUKKERIJ EDUARD IJDO — LEIDEN

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CONTENTS.

CHAPTER III.

CHAPTER IV.

CHAPTER V.

CHAPTER VI.

INTRODUCTION.

All substances, when sufficiently cooled under suitable conditions, will pass into the liquid state and, ultimately, become solid. This shows that attractive forces exist between all molecules. We may give these forces the general name of cohesion forces.

In some cases they consist mainly in the attractive forces between the ions of which the substance is composed. In such cases they lead to greater complexes, which are called coordination lattices, in which the idea of molecules is completely lost. These cases will not be considered in this thesis.

The investigation will be confined to the compounds, in which these Coulomb forces, for whatever reason, are of very little importance compared to the cohesion forces indicated below.

While in compounds such as NaCl, CaO, etc. the particles of which they are composed have such a decidedly ionic character that it is, roughly speaking, permissible to describe the cohesion forces as mutual action of the charged particles, in other cases, either because of polarization or of covalent bond, the ionic character is so much enfeebled, that the remaining field of the ions can only be recognized as a relatively weak dipole or multipole field.

In these cases it is better — and at any rate more convenient for calculation — to describe the cohesion forces as the mutual action of dipoles (if necessary poles of higher order), as was first done by Keesom[1]), or as the mutual influence of the dipole of one molecule and the dipoles induced by polarization in the other molecules (Debye[2])).

In cases where there are no dipoles still attractive forces remain

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[1]) W. H. Keesom, Proc. Amsterdam **15**, 240, 256, 417, 643 (1913); **18**, 636, 868, 1568 (1916); **23**, 939 (1920); **24**, 162 (1922); Physik. Z. **22**, 129, 643 (1921); **23**, 225 (1922).

[2]) P. Debye, Physik. Z. **21**, 178 (1920); **22**, 302 (1921).

between the molecules. Attempts have been made to explain these forces as attraction of poles of a higher order. Since we have learned, however, that in the atoms of the rare gases poles of this kind cannot be accepted, another explanation must be found. In 1930 London [1]) demonstrated by a quantum mechanical treatment, that there is always an attraction between the particles even when these have no electric charge, dipoles or poles of higher order, which in first approximation is proportional to the square of the polarizability as long as we confine ourselves to the same particles, and to the product of the polarizibilities of the particles in cases where the particles are different. It seems unnecessary to point out, that this kind of attraction is of a completely different kind to that, which exists between two material particles and which is usually called Newton attraction. This effect is always very small compared to the London attraction.

Other formulas for the London attraction have been derived later [2]).

As London energy is found in all molecules we may expect to find the simplest cases if we confine ourselves for the present to molecules without an electric moment, as then the London energy is the only cohesion energy. As the polarizability plays an extremely important part in the cohesion phenomena, it may be expected that a closer study of this quantity will throw more light upon cohesion in general and upon the phenomena which are directly connected with it.

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[1]) London Z. Physik. 63, 245 (1930); Z. Physik. Chem. B 11, 222 (1931).

[2]) Cf. H. Margenau, Physic. Rev. 37, 1425 (1931); 38, 748, 1786 (1931).
J. C. Slater and J. G. Kirkwood, Physic. Rev. 37, 682 (1931).
J. G. Kirkwood, Physik. Z. 33, 57 (1932).
For a critical review of these formulas cf. H. Hellmann, Acta physicochimica U.S.S.R. 2, 273 (1935).

CHAPTER I.

POLARIZABILITY.

When a molecule is brought into a homogeneous electric field of strength $\vec{F}$ an electric dipole $\vec{m}$ will be induced in it proportional to this field. Even when the field is not homogeneous the moment may be presented by

$$\vec{m} = \alpha \vec{F}$$

in which $\vec{F}$ gives the strength of the field in the molecule and α is the polarizability of the molecule. This expression will only be valid if the changes in the field over the extent of a molecule are small. We wish to lay stress upon the fact, that in this way we have neglected the „anisotropy" of the polarizability i.e. the phenomenon, that the polarizability may be different in different directions.

If we bring a substance into an external electric field $\vec{E}$ per unit of volume a dipole will be induced, which is called the polarization $\vec{I}$. According to the phenomenologic theory of electricity the polarization is dependant on $\vec{E}$ and the electric displacement $\vec{D}$ according to the equation

$$\vec{D} = \vec{E} + 4\pi \vec{I}.$$

The derivation of this relation and the whole theory of dipoles and polarizability may be found in numerous monographs. In this chapter a brief sketch of the theory will be sufficient [1]).

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[1]) P. Debye, Polare Molekeln, Leipzig 1929.

P. Debye und H. Sack, Handbuch der Radiologie, Leipzig 1934, Bd. 6/2, p. 69.

J. v. Vleck, Theory of Electric and Magnetic Susceptibilities, Oxford 1932.

We will call the internal field $\vec{F}$.

The dependence of $\vec{E}$, $\vec{I}$ and $\vec{F}$ is as follows:

$$\vec{F} = \vec{E} + \frac{4\pi}{3}\vec{I}$$

From the equation

$$\vec{D} = \varepsilon\vec{E}$$

in which ε is the dielectric constant, we can find

$$\frac{\varepsilon - 1}{\varepsilon + 2}\frac{M}{d} = \frac{4\pi}{3}N\gamma = P.$$

Here P is the molecular polarization, M the molecular weight of the substance, d the density, and γ is a quantity depending upon the temperature, which is given by the equation

$$\gamma = \alpha + \frac{\mu^2}{3kT} \text{ }^{1)}$$

in which μ represents the dipole moment of the substance in question, k the constant of Boltzmann and T the absolute temperature.

The molecular polarization may be considered as the sum of the three polarization effects:

1st. the electronic polarization P_E, caused by the displacement of the electrons by the external field,

2nd. the atomic polarization P_A, caused by the relative displacement of the atoms or ions by the external field,

3rd. the orientation polarization P_0, caused by the permanent dipoles.

O. Fuchs and K. L. Wolf, Dielektrische Polarisation, Leipzig 1935.

H. Stuart, Molekülstruktur, Berlin 1934.

A. E. van Arkel and J. H. de Boer, La valence et l'Electrostatique, Paris 1936, Chapter IV.

J. Estermann, Erg. exact. Naturwiss. **8**, 258 (1929).

H. Sack, Erg. exact. Naturw. **8**, 307 (1929).

C. P. Smyth, Dielectric Constant and Molecular Structure, New-York, 1931.

J. Frenkel, Acta physicochimica U.S.S.R. **4**, 341 (1936).

1) P. Debye, Physik. Z. **13**, 97 (1912).

P_E and P_A are in first approximation independent of the temperature, but of course P_0 is not. We may write

$$\frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3\,kT} \right) = P_E + P_A + P_0 \,.$$

Recently serious criticism has been made on this formula by Onsager[1]). He shows that the term $\frac{\mu^2}{3\,kT}$ is not quite correct. As we are interested, however, in α only, this does not harm to our considerations. Our object is to learn something more concerning the binding forces in molecules, and therefore we are particularly interested in the electronic and atomic polarization $P_E + P_A$.

Now

$$\frac{4\pi}{3} N\alpha = P_E + P_A .$$

For non-polar substances P_0 is always equal to 0, for dipole containing ones we may determine $P_E + P_A$ in such a way, that we measure ε for electric vibrations of a very high frequency. In this case the dipoles cannot follow the rapidly changing external field quickly enough so that there is no orientation and the term

$$P_0 = \frac{\mu^2}{3\,kT}$$

vanishes. For frequencies of visible light, for instance, the orientation effect completely disappears and we may write then

$$\frac{\varepsilon - 1}{\varepsilon + 2} \; \frac{M}{d} = \frac{4\pi}{3} N\alpha = P_E + P_A .$$

For the cases where non-polar substances are considered and also apparently non-polar substances, that are substances containing dipoles in a rapidly changing field, the equation first given by Maxwell

$$\varepsilon = n^2$$

holds, in which n represents the refractive index.

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[1]) L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).

Our formula becomes

$$\frac{n^2-1}{n^2+2}\,\frac{M}{d}=\frac{4\pi}{3}\,N\alpha=P_E+P_A.$$

This equation is known as the equation of Lorentz and Lorenz[1]). The calculation by Lorentz showed, that this formula holds only strictly in the limit, when $\lambda \rightarrow \sim$, taking the ultra-red absorption area into consideration. The value of

$$\frac{n^2-1}{n^2+2}\,\frac{M}{d}$$

can of course also be calculated for other wave-lengths. This value is called the specific molecular refraction, which we shall abbreviate to „refraction" in the following. The term refraction is often used for n but for this quantity we shall use the more rational term refractive index.

Refractive indices are often measured for the three hydrogen lines H_α ($\lambda = 656\ \mu\mu$), H_β ($\lambda = 486\ \mu\mu$), H_γ ($\lambda = 434\ \mu\mu$) and the Na-line D ($\lambda = 589\ \mu\mu$).

We shall indicate these refractive indices by n_α, n_β, n_γ and n_D, the corresponding refractions by R_α, R_β, R_γ and R_D.

The refractive index which we find by extrapolating to infinity the values for the wave-lengths of the visible light, ignoring the ultrared absorption area, we call $n_\sim$ and the corresponding refraction $R_\sim$.

According to the dispersion theory the refraction depends on the specific frequencies of the electrons and atoms as given by the following equation

$$R(\nu)=\sum_i \frac{C_i}{\nu_i^2-\nu^2}$$

in which ν_i represents the frequency of the i-th transition, and ν the frequency of the incident light.

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[1]) H. A. Lorentz, Ann. Physik [3] **9**, 641 (1880).

L. Lorentz, Ann. Physik [3] **11**, 70 (1881); Videns. Selsk. Skrifter **8**, 205 (1869); **10**, 485 (1875).

Classically C_i may be presented by

$$\frac{f_i N e^2}{2 \pi m},$$

in which N represents the number of Avogadro, e and m the charge and the mass of the particle, and f_i the number of times that the particle in question occurs. The electrons and atoms in question are considered to be bound in a quasi-elastic way. According to quantum mechanics the C_i's are to be considered as intimately connected with the transition probability of the i-th absorption transition. A more exact formula for the refraction is

$$R(\nu) = \frac{4 \pi}{3} \sum_k N_k \alpha_k$$

in which N_k is the number of molecules in the k-th state per gram-molecule and α_k the polarizability of this state, while

$$\alpha_k = \frac{1}{2 \pi^2 h} \sum_j \frac{(p_{kj})^2 \nu_{kj}}{\nu_{kj}^2 - \nu^2}$$

in which ν_{kj} is the frequency corresponding to the transition $k \rightarrow j$ and p_{kj} is the corresponding electric moment [1]).

p_{kj} and ν_{kj} are independent of the temperature, but at higher temperature the number of molecules N_k will change in favour of the higher energy levels k according to Boltzmann's e-formula.

We see that with the increase of ν (λ decreases) R increases too. As the vibration of the electrons lie in the ultraviolet area these only can follow the vibrations of the visible light.

The refraction of the visible light, thus, gives principally the contribution of the displacement of the electrons. If we pass to the longer wave-lengths the heavy atoms and groups of atoms, if they carry an electric charge, will be able to follow the frequencies of the incident light, and atomic polarisation begins to occur. The first to point this out was Ebert [2]). We may thus write

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[1]) H. A. Kramers, Nature **113**, 673 (1924; **114**, 310 (1925).
H. A. Kramers and W. Heisenberg, Z. Physik. **31**, 681 (1925).

[2]) L. Ebert, Z. physik. Chem. **113**, 124 (1925); **114**, 430 (1925).

$$R = P_E + P_A = \sum_i \frac{C_{E_i}}{\nu_{E_i} - \nu^2} + \sum_j \frac{C_{A_j}}{\nu_{A_j}^2 - \nu^2}$$

in which ν_{E_i} represents the specific frequencies of the electrons and ν_{A_j} of the atoms.

We will now extrapolate to a wave-length $\lambda \rightarrow \sim$. For this we can use the values measured in the visible spectrum and extrapolate them (according to the Helmholtz-Kettner method [1])). This means, that we ignore the ultra-red absorption area ($C_{A_j} = 0$) and find thus merely the electronic polarisation

$$R_\sim = P_E = \frac{n^2_\sim - 1}{n^2_\sim + 2} \frac{M}{d}$$

P_E is not entirely independent of the temperature, the value increases about 1 ‰ per 10 degrees. Fuchs and Wolf [2]) give an extensive list of literature on the subject.

In this thesis we shall study the cohesion forces between particles. In the cases considered, the cohesion is mainly due to London attractions. These are only the consequence of the polarization due to the electrons. Our aim is, therefore, to determine the P_E values, or, as we only compare substances one with another, to determine values, which are proportional to P_E. As we shall see later, R_D is proportional to P_E, at least for the substances, considered in this thesis (p. 37 and 117). We may thus take as the fundamental formula for our theory

$$\alpha \sim \frac{n_D^2 - 1}{n_D^2 + 2} \frac{M}{d}$$

It appears that the second member is not entirely independent on the temperature. The expression

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{d}$$

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[1]) P. Debye and H. Sack, Handbuch der Radiologie, Leipzig 1934, Bd. 6/2, p. 113.

[2]) O. Fuchs and K. L. Wolf, Dielectrische Polarisation, Leipzig 1935, p. 248.

increases slightly with a rise of temperature for all liquid compounds in about the same ratio, namely 1 ‰ per 10 degrees 1).

The circumstance that P_E and R_D have the same dependence upon temperature is an essential condition for our method of taking R_D as measure for the electronic polarizability.

How the dependence upon temperature may be understood physically will be explained later (p. 126).

Another important point to be considered is whether in the formula

$$\frac{n^2-1}{n^2+2}\ \frac{M}{d}=\frac{4\,\pi}{3}\ N\,\alpha$$

the factor $\frac{4\,\pi}{3}$ is correct for all substances. This factor is only of strict application to the fully disordered state (gas) or in a cubic crystal, in other cases we have no certainty as to whether we can apply the factor $\frac{4\,\pi}{3}$. For a long time it was thought that various irregularities must be attributed to the fact that the factor $\frac{4\,\pi}{3}$ was not justified 2).

Further reseach has shown, however, that it is justifiable to apply this factor in liquids 3).

For our purposes it is sufficient if the factor remains constant in various substances, and in connection with the above and with

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1) O. Fuchs and K. L. Wolf, Dielektrische Polarisation, Leipzig 1935, p. 252. Here various other quotations of literature can be found.

A. F. Holleman, Recherches Refractiométriques de feu J. F. Eykman, Haarlem 1919, p. 13.

E. Hückel, Theoretische Grundlagen der Organischen Chemie, Leipzig 1935, p. 84.

H. Stuart, Molekülstruktur, Berlin 1934, p. 113.

W. A. Roth and F. Eisenlohr, Refraktometrisches Hilfsbuch, Leipzig 1911, p. 78.

F. Eisenlohr, Spektrochemie Organischer Verbindungen, Stuttgart 1912, p. 19.

L. Meyer, Z. physik. Chem. B **8**, 45 (1930).

2) K. Lichtenecker, Physik. Z. **27**, 115 (1926).

3) H. Sack, Ergebn. d. exakt. Naturw. **8**, 387 (1929).

L. Meyer, Z. physik. Chem. B **8**, 44 (1930).

the fact that we are considering compounds which are very similarly composed, we need not be anxious to this point.

It is perhaps useful to point out here, that formerly innumerable „refraction formulas" were suggested (for the development of this kind of refractometry see the accounts by Schoorl and Eisenlohr[1])). An attempt was made to construct a quantity that was practically independent on temperature. The most succesful of these is the Eykman formula[2])

$$R = \frac{n^2 - 1}{n + 0.4} \quad \frac{M}{d}$$

This formula, however, has no theoretical foundation. For our purpose the Lorentz-Lorenz formula is the best as it is theoretically sound. The constancy of α is by no means essential to the theory, in fact we shall see, that α is bound to increase with the temperature. If a „refraction constant" independent on temperature is desired Eykman's formula is certainly most to be recommended.

For many years is was thought that the refraction could be composed purely additively from so-called „atomic refractions". These numerical values were repeatedly recalculated[3]) until the last and most critical calculation by Eisenlohr[4]) produced the „atomic refractions" which are now found in all tables.

It can be seen, however, that a difference must be made for different kinds of oxygen, nitrogen, etc. while „increments" must be introduced for „double" and „threefold" links.

This means of course that we must descriminate between different kinds of carbon. If we add, that for „conjugated" systems ($C = C - C = C$ or $O = C - C = O$) extra exaltations must be introduced, which are not even constant, it is clear that we cannot

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[1]) N. Schoorl, Chem. Weekblad **23**, 282 (1926).

F. Eisenlohr, Spektrochemie Organischer Verbindungen, Stuttgart 1912, p. 19.

[2]) J. F. Eykman, Rec. trav. chim. **14**, 185 (1895).

A. F. Holleman, Recherches Refractométriques de feu J. F. Eykman, Haarlem 1919, p. 13, 185.

[3]) For a survey see F. Eisenlohr, Speektrochemie Org. Verbindungen, Stuttgart, 1912, p. 37.

[4]) F. Eisenlohr, Z. physik. Chem. **75**, 585 (1910); **79**, 129 (1912).

expect this ,,calculating refractometry" 1) to throw much light upon the structure of matter. The most that can be said is, that an increment or exaltation indicates an increased refraction, and therefore the presence of electrons with a lower specific frequency, i.e. weakly bound electrons. The ,,release" of the electrons may go so far that the specific frequencies (i.e. the absorption of light) come into the visible spectrum. What has been called the ,,chromophore" groups are often those with double links or conjugated systems. The grouping called ,,chinoid" is a typical example.

It has, thus, no use at all in determining ,,atomic refractions" with great accuracy (3 decimals! as at most 2 can be determined correctly) and it is strange that up to very recent times attempts have been made to determine these ,,atomic refractions" 2).

Henne and co-workers 3) calculated the atomic refraction of *F* in ethene and ethane derivatives containing both fluorine and chlorine by subtracting from the refraction values found constant ,,atomic refractions" for C, H, Cl etc. In this way they found values for *F* which naturally varied within very wide limits.

Swientoslawski quite rightly pointed out, that there is no sense in determining these values so exactly 4).

In spite of everything, however, it may be said that in organic chemistry the laws of additivity according to Eisenlohr are satisfied to a certain extent. This is not surprising, when we consider, that in applying it we are working with very large molecules, so that the ,,atomic refractions" only have the significance of mean

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1) S. van Woerden, Thesis, Leiden 1924.

2) F. Swarts, J. Chim. Phys. **20**, 30 (1923)..

G. Schumann, Z. physik. Chem. A **106**, 397 (1931).

P. Bruylants, J. Verhulst and R. Mercks, Bull. Soc. Chim. Belg. **42**, 177 (1933).

P. Ceuterick, Bull. Soc. Chim. Belg. **45**, 545 (1936).

Ch. de Hoffmann and E. Barbier, Bull. Soc. Chim. Belg. **45**, 565 (1936).

3) E. G. Locke, W. R. Brode and A. L. Henne, J. Am. Chem. Soc. **56**, 1726 (1934).

A. L. Henne and E. C. Ladd, J. Am. Chem. Soc. **58**, 402 (1936).

A. L. Henne and D. M. Hubbard, J. Am. Chem. Soc. **58**, 404 (1936).

A. L. Henne and M. W. Renoll, J. Am. Chem. Soc. **58**, 890 (1936).

4) W. Swientoslawski, J. Am. Chem. Soc. **42**, 1945 (1920).

values. The true contribution to the refraction of a particular atom dependent upon its surroundings and the state of its links, we shall never learn in this way.

We must therefore have recourse to the simple molecules. Here, indeed, we must expect great deviations from the additivity, and considering the small number of atoms per molecule we have to deal with, it will be fairly easy to determine the true individual atomic refractions.

We shall now first consider the theoretical significance of the refraction. Fajans and Joos[1]) assume and we shall apply it in the following, that the refraction of a particular system may be considered as the sum of the refractions of the composing parts, that, however, the latter are not necessarily constant, but depend on a great variety of influences. Every deviation of the additivity is therefore understood as a change in the refraction of at least one of the composing parts. We adhere thus, to the localizability of the refraction.

We can still attribute to a particular atom (ion) a particular refraction. In general this is not necessarily the case with a particular physical quantity, for example, the energy of a NaCl lattice. Here the total energy cannot be split up into parts of which one belongs to the Na^+-ion and the other to the Cl^--ion.

It is of some importance to remark here, that P_A cannot be considered to be localizable but it is a typical a quantity of the kind of the energy of a NaCl lattice.

According to Fajans and Joos the refraction is a measure for the „deformation". An atom (ion) will be the less polarized by an external electric field, the more it was already polarized itself in its state of chemical binding. The lower, therefore, the „polarizability" and thus the refraction of particular atom (ion) the more it is polarized. An ion will be the less polarized when it is situated in a weaker electric field. Thus it can be said that the larger the electric field in which a particular atom (ion) lies, the smaller will be the refraction of that atom (ion). Fajans and Joos[2]) have observed, accordingly, that in all kind of com-

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[1]) K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

[2]) K. Fajans and G. Joos, loc. cit.

pounds the refraction of the halogen atoms (ions) increases when the cations have a smaller charge or a larger radius, that is, when they produce a smaller field. To give an example: in the LiCl → CCl_4 series the refraction of the chlorine ion decreases, in the LiCl → RbCl series the refraction of the chlorine ion increases.

Fajans and Joos confirm this with extensive numerical data, both for halogen and for oxygen ions, in both simple compounds and complexes [1]).

According to Fajans the cations in compounds will have a higher refraction due to the presence of the field of the anions, and this effect should be the stronger, the smaller the anions and the larger the charge they carry. As the refraction of the cations is small the changes of this kind will be very small. This effect, however, never has been proved in an experimental way. We do not agree with Fajans on this point. If there is a change of the refraction of the cations, it will be a decrease, as follows from a theory which we shall develop later (p. 87).

Generally speaking, therefore, at the formation of a compound from free ions, there is a decrease of the refractions of both the cation, and the anion.

By comparing several atoms and ions of rare gas structure with eachother Fajans and Joos attempted to give with considerable accuracy how great the refraction of a hypothetical ion is in a free state (for the *Na-D*-line). This is the case if the atom (ion) in question is not submitted to an electric field and this will be the extreme values for the refraction of the anions and of the cations. The first values that were calculated by Fajans and Joos were later recalculated with new data [2]). The differences from the values previously found were very slight. The last values will be used in the following as our standard values.

The polarizability of free ions can be calculated from the corrections in the Rydberg terms for ions with rare gas structure, as well as by the method mentioned above. This method was first given by Born and Heisenberg [3]). The calculations

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[1]) Cf. K. Fajans, Z. Krist. 61, 18 (1925).
J. H. de Boer, Kon. Ac. Wet. Amsterdam 36, 161 (1927).

[2]) K. Fajans, Z. physik. Chem. B 24, 103 (1934).

[3]) M. Born and P. Heisenberg, Z. Physik 23, 388 (1924).

were recently repeated by Meyer and Meyer[1]) on the basis of quantum mechanics. They were obliged of course to confine themselves to the positive ions.

The polarizability may also be determined from the quadratic Stark effect. The energy levels of an ion of rare gas structure in an electric field may be represented [2]) by

$$W = W_0 + A_1 F_1 + A_2 F^2 + \ldots\ldots$$

in which $A_2 = \frac{-\alpha}{2}$. Pauling[3]) made use of this to calculate the polarizabilities of the free gaseous ions. The values obtained from these three different methods are in good mutual agreement [4]).

Schoppe[5]) calculated the refractions of the cations of the alkali halides following the method of Wolf and Herzfeld, to be discussed below. His results are in very good agreement with those of Meyer and Meyer and to some extent with those of Fajans and Joos. In the following we shall use Fajans' latest values as our norm. They are borrowed from the refraction value for the *Na-D*-line, as our values are in the following.

Fajans[6]) has given a formula for the change of the refraction of a halogen ion at the transition from free ion to the crystalline form as alkali salt which is acceptable and approximately correct

$$\Delta R_a = - C_a \frac{R_a^2}{r^4}.$$

C_a is a constant value for all halogens, R_a is the refraction of the anion, ΔR_a is the decrease of the refraction R_a and r the lattice constant. This formula has been derived theoretically by Neugebauer[7]) later. From his theory it also follows that

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[1]) J. E. Meyer and M. G. Meyer, Phys. Rev. 43, 605 (1933).

[2]) J. H. Jones, Proc. Roy. Soc. London **A 105**, 650 (1924).

[3]) L. Pauling, Proc. Roy Soc. London **A 114**, 198 (1927).

J. H. Vleck, The theory of Electric and Magnetic Susceptibilities, Oxford 1932, p. 203—225.

[4]) Cf. G. Kortüm, Das optische Verhaltnis gelöster Elektrolyten, Stuttgart 1936, p. 49.

[5]) R. Schoppe, Z. physik. Chem. B **24**, 259 (1934).

[6]) K. Fajans, Z. physik. Chem. **130**, 724 (1927).

[7]) Th. Neugebauer, Z. Physik **94**, 655 (1935).

not the ordinary electrostatic forces cause the ,,stiffening" of the anions. According to him the effect is caused by the overlapping of the electronic clouds; in this case, parts of such a cloud come under the influence of a polarizing forces of the nuclei, which are thus no longer screened. These forces are supposed to cause the ΔR's. The van der Waals forces have practically no influence upon the change of the refraction.

The deformation theory, which is here only very cursorily sketched, is of great importance because various facts can now be brought under one point of view, to mention only the regularities, which occur in the determination of the (apparent) refraction of ions dissolved in water and the course of the values $R_{solution} - R_{solid}$ and $R_{gas} - R_{solid}$ of the alkali halides.

Herzfeld and Wolf[1]) have shown, that the refraction is closely connected with the lattice energy. The larger the lattice energy, the more difficult it is to remove an electron, and thus the electric polarizability decreases as the lattice energy increases. The greater the last value is, the more the absorption will move towards the short wave lengths of the spectrum. The specific frequencies become larger and therefore the refraction smaller. These results correspond to those of Fajans of Joos. The refraction of anions is decreased by the presence of cations and this effect is larger when the field of the cations is larger (small ionic radius and/or greater charge), which again includes a larger lattice energy.

The two conceptions of Fajans and Joos and of Wolf and Herzfeld lead to the same qualitative result. This can easily be understood in the following way. The theory of the first two authors is that the electrostatic field determines the polarizability. In total the ion in question is subjected to a force equal to 0, otherwise it would not be at rest. The electrostatic force is counteracted by the Born repulsion and it is the question now, how it can be explained, that the energy of the bond runs parallel to a particular part of the forces, viz. the electrostatic ones. Essentially this is due to the fact that in a state of equilibrium the Born repulsion force is equal to the electrostatic forces, but

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[1]) K. F. Herzfeld and K. L. Wolf, Ann. Physik. **78**, 35 (1925).

the potential that belongs to the first is small in comparison to the potential of the electric forces.

Figure 1 shows the course of the potential energy with the

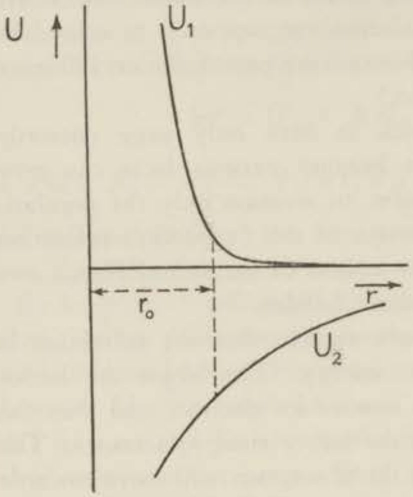

Fig. 1.

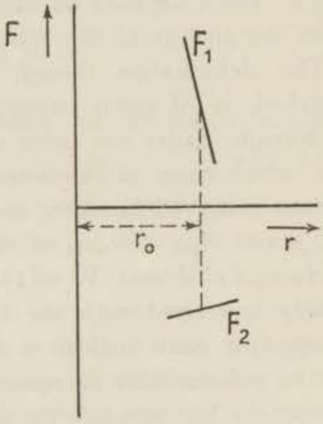

Fig. 2.

distance. U_1 is the energy of the Born repulsion, U_2 the energy of the electrostatic forces.

$$U_1 = A\, e^{-ar}.$$

Now

$$F_1 = -\left(\frac{\partial U_1}{\partial r}\right) \text{ and } F_2 = -\left(\frac{\partial U_2}{\partial r}\right)$$

F_1 and F_2 represent the Born repulsion force and the electrostatic attraction. The course is given in figure 2.

The state of equilibrium is given by r_0. Now it is known, generally speaking, that

$$\left| U_1 \right|_{r=r_0} \ll \left| U_2 \right|_{r=r_0}$$

and

$$U_2 = -\Sigma \frac{a_n}{r^n}$$

Therefore

$$(F_2)_{r=r_0} = -\Sigma \frac{n a_n}{r_0^{n+1}}$$

The principle term in U_2 is $-\frac{a_1}{r}$ so that approximately

$$(U_2)_{r=r_0} = r_0\,(F_2)_{r=r_0} + \Sigma\,\frac{(n-1)\,a_n}{r_0^{\,n}}$$

If therefore $(U_1)_{r=r_0}$ is of the order of magnitude of

$$\Sigma\,\frac{(n-1)\,a_n}{r_0^{\,n}}$$

it is comprehensible that the total energy and the electrostatic forces (without Born repulsion) run parallel, especially when we confine ourselves to consideration of the sequence of the energies or electrostatic fields, as r_0 is always of the some order of magnitude.

Van Arkel and de Boer[1]) have applied the theory of Fajans and Joos to the few data that were known concerning the halogenated methane and ethane derivatives. For the refraction per H atom in the methane derivatives they found in the groups

CH_4	1.63
CH_3	—
CH_2	1.56
CH	1.51

and in ethane derivatives in the groups

CH_3	1.71
CH_2	1.59
CH	1.48

in the supposition that the refractions of F, Cl, Br and I would be constant.

If we regard a molecule merely as a number of charged spheres, that act only on each other with Coulomb forces, the H atoms that lie in the strongest field (those of the CH group) have the smallest refraction. But this is not correct. It will be shown that the H atom of the CH group has on the contrary, the largest

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[1]) A. E. van Arkel and J. H. de Boer, Z. Physik. Chem. 122, 101 (1926).

refraction. This *H* atom lies in the weakest field. This is due to the large induced dipoles in the halogen atoms present.

This conception, which deviates from the one formerly accepted is confirmed in numerous ways. We shall return to this more in detail later (Chapter V).

We have seen that Br and I are extremely sensitive in the refraction ($\Delta R_a \sim R_a^2!$) and it is natural to suppose, that in methane derivatives the refractions of F, Cl, Br and I will not be constant.

In connection with the remarks made above, it seemed of some interest to examine the most simple organic compounds with regards to their refraction.

We have examined systematically as far as possible all the methane derivatives to see whether the refraction of F, Cl, Br and I are really constant or follow the rules of Fajans and Joos.

This series of compounds has some advantages over any arbitrarily chosen series:

1. The carbon is tetravalent, so that there are a great number of compounds, while we can compare compounds with the most minute changes with one another.
2. For the preparation of most substances in this series there are suitable methods to be found in literature.
3. These compounds can be obtained with a sharp boiling point and other well defined physical constants (refractive index, density) in contrast for exemple to Sn derivatives of which it is still uncertain whether the compound $SnCl_2Br_2$, for instance, described in literature, is not a mixture of $SnCl_4$ + $SnBr_4$ or at any rate does not pass into it in the course of time.

The series of the halogenated methane derivatives is, therefore, the most convenient in which to see if we can learn more about the mutual influence of the halogen atoms.

Our research had also another purpose. In 1924 van Arkel and de Boer¹) gave some simple rules for the calculation of

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¹) A. E. van Arkel and J. H. de Boer, Physica 4, 382, 392 (1924).

the boiling points of the halogenated methane derivatives, for the present without any theoretical basis. By extending his theory van Arkel found various rules for the boiling points of ethane derivatives, alipathic hydrocarbons (saturated and unsaturated), the halogen derivatives of these and numerous aromatic compounds.

In 1932 van Arkel and de Groot[1]) showed, that the rules for the boiling points of the methane derivatives can easily be found by applying the ,,dispersion forces'', the existance of which was first demonstrated by means of quantum mechanics[2]). The London forces between two particles (atoms, ions) prove to be closely connected with the electric polarizability of the particles. The process applied by van Arkel and de Groot, comes to this, that they treat the electric polarizability of the halogen atoms as a constant, but where this is apparently not the case, it may be regarded as a refinement of the theory, if we do not treat them in that way. A precise knowledge of the refraction of each individual ion was therefore essential, and it now appears that we are actually able to predict where deviations of the boiling point, calculated according to van Arkel and de Boer must occur and of what order of magnitude these deviations will be.

Van Arkel and de Boer's research on the carbon derivatives does not apply in every detail to the analogous Si, Ge and other inorganic compounds. But by constantly comparing van Arkel and de Boer's results with the known refractions of these compounds we were finally able to trace various secundary effects which somewhat obscured the theory of the boiling point hitherto.

The aim of this thesis is therefore, to trace the connection between the polarizability (which is closely connected with the refraction) and the cohesion energy (expressed in the boiling point) of various compounds which lie both in the inorganic and the organic field. We will try to throw a bridge from the deformation theory of Fajans and Joos on the one hand to the theory of cohesion forces as developed by van Arkel on the other hand.

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[1]) A. E. van Arkel and W. de Groot, Physica **12**, 211 (1932).

[2]) F. London, Z. Physik **63**, 245 (1930); Z. physik. Chem. B **11**, 222 (1931).

In the first part of this thesis the above problems in various inorganic compounds are carefully examined (Chapter II). Here we treat the connection between boiling point and refraction entirely on the basis of data in literature. In this part of the research we are obliged to be satisfied with a boiling point accuracy of 1 %; there are no discussions that go into detail at all in this part.

The second part is of a different kind. Here, on the basis of our measurements, combined with published data, the refraction is traced of simple organic compounds, especially the methane derivatives. Their connection with the boiling point, the dipole moment, the restoring force constant and the reactivity is discussed in detail. In this part we discuss in Chapter III the method of measurement and the errors involved. In Chapter IV the preparation of the compounds to be examined, their purification and the measuring of them, that is, the whole of the experimental work is treated.

In Chapter V the interpretation of the results is given. Here a short discussion of several physical and chemical properties of these compounds can be found.

Finally in Chapter VI we discuss in how far deviations may be expected from the mixture law for refraction in mixtures.

Chapter III to VI will show how succesfully we may apply purely electrostatic and other considerations of models to organic compounds and how many physical and chemical properties of this catagory of compounds we may understand satisfactorily by this somewhat simplified and rough representation and, thus, bring them under one point of view.

CHAPTER II.

THE RELATION BETWEEN COHESION ENERGY AND POLARIZABILITY OF INORGANIC HALIDES.

A. General theory. The relation between cohesion energy and polarizability of Carbon and Silicon derivatives.

It will require a certain energy to bring a molecule from a system (gaseous, liquid, solid) into a hypothetical state, in which it is entirely free from the influence of other molecules of the system. The energy needed to bring a grammolecule of the substance in question out of the system into this free state we shall call cohesion energy [1]).

This quantity is in many cases difficult to calculate, we shall therefore follow a process given by van Arkel [2]) and coworkers. The greater the cohesion energy of a considered compound, the higher will be its boiling point. Van Arkel makes a certain part of the boiling point T_S [3]) responsible for the London cohesion energy (T_L) and a part for cohesion energy due to the induction effect (T_D). In the following we shall always regard the boiling point as a measure for the total cohesion energy.

The boiling point T_S of the compounds acquired by replacing all hydrogen atoms in CH_4 by halogen atoms can simply additively be calculated according to van Arkel and de Boer [4]). Thus we may take for fluorine 36°, for chlorine 87.5°, for bromine 115.5° and for iodine 156°. If this method of calculation

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[1]) Cf. A. E. van Arkel, Chem. Weekblad **31**, 470 (1934).

[2]) A. E. van Arkel and W. de Groot, Physica **12**, 211 (1932).
A. E. van Arkel and J. L. Snoek, Rec. trav. chim. **52**, 719 (1933).

[3]) In order to join with the notation in literature we write T_S for the boiling point.

[4]) A. E. van Arkel and J. H. de Boer, Physica **4**, 382, 392 (1924).

is also applied to compounds in which not all the hydrogen atoms are replaced by halogen atoms (in which we must take 27° per hydrogen), these authors find a constant difference with the actual boiling point, a difference, which, as van Arkel and Snoek [1]) have shown later is due to the cohesion energy caused by the dipole which these compounds carry. These T_D values according to the most recent calculations [2]) are for the type CH_3X 81°, for the type CH_2XY 85° and for the type CHXYZ 45°, in which X, Y and Z are equal or different halogen atoms.

It must be emphasized here, that we consider the hydrogen as equivalent to the halogens, according to van Arkel and de Boer [3]). The hydrogen, thus, is regarded to be a negative ion.

Further van Arkel and de Groot [4]) have demonstrated, how the contribution of the London energy to the boiling point T_L in non-polar (= hydrogen free) methane derivatives can be represented by the formula

$$T_S = T_L = k\,\frac{(V - V_C)^2}{V}$$

which had been earlier deduced by van Arkel and de Boer [5]) empirically.

In the case under consideration $T_S = T_L$. k is a constant, V the molecular volume of the compound at boiling point, while V_c is the atomic volume of carbon according to Kopp ($V_C = 11$). The molecular volume V can be calculated additively from Kopp's atomic volumes $V_F = 11$, $V_{Cl} = 22.8$, $V_{Br} = 29.1$, $V_I = 39$. The constant k proves to be 4.30 ± 0.05 [6]).

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[1]) A. E. van Arkel and J. L. Snoek, Rec. trav. chim. **52**, 719 (1933).

[2]) A. E. van Arkel, Rec. trav. chim. **51**, 1081 (1932).

[3]) A. E. van Arkel and J. H. de Boer, La Valence et l'Electrostatique, Paris 1936, p. 119.

Cf. H. G. Trieschmann, Z. physik. Chem. B **24**, 22 (1936).

[4]) A. E. van Arkel and W. de Groot, Physica **12**, 211 (1932).

A. E. van Arkel, Rec. trav. chim. **51**, 1081 (1932).

[5]) A. E. van Arkel and J. H. de Boer, Rec. trav. chim. **44**, 657 (1925).

[6]) A. E. van Arkel and J. H. de Boer, Z. physik. Chem. 122, 101 (1926).

This formula does not give a rigid additivity as a quadratic member enters:

$$T_s = k\,(V - 2\,V_c) + k\,\frac{V_c^2}{V}$$

The deviations of the addivity are, however, at most a few percent, as a simple calculation shows. The values calculated by this formula and the purely additative ones show almost the same deviations[1]. The two methods, thus, may be regarded as of exactly the same value. Essential for the pure additivity is:

$$\frac{\sqrt{a}}{V} = \text{constant}\ ^{2)}.$$

This relation can of course not be satisfied for each halogen atom in various compounds. If we write for

$$V = V_c + \sum_1^4 V_x\ ^{3)}$$

in which V_x represents Kopp's volume of a halogen or hydrogen atom and if we suppose

$$V_c \ll \sum_1^4 V_x$$

the condition becomes

$$\frac{\sqrt{a}}{b} = \text{constant}\ ^{4)}$$

for every halogen atom in various compounds. This relation can be satisfied of course. This formula is the basis of the not purely additive formula

$$T_s = k_1\,\frac{(V - V_c)^2}{V}.$$

The consequence of the additivity is that the boiling points of CX_4, CX_3Y, CX_2Y_2, CXY_3 and CY_4 always increase by a very

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[1] A. E. van Arkel, Rec. trav. chim. **51**, 1081 (1932).

[2] a is the atomic constant according to van Laar.

[3] A. E. van Arkel and J. H. de Boer, Physica **5**, 134 (1925).

[4] a and b are the „atomic constants'' according to van Laar.

definite amount. The same applies to the series CHX_3, CHX_2Y, $CHXY_2$, CHY_3 and the series of compounds with more hydrogen atoms. Subsequent to this research several other methane derivatives have become known and the boiling points found agree with those calculated theoretically.

We here give a table of the newly found values of methane derivates, to an accuracy of 1°, about which so far nothing has been published as to whether they comply to additivity.

	exper.	calc.
CF_3Cl	193 [1])	195
CHF_2Cl	233 [2])	231
CH_2FI	326 [3])	331
CHF_3	189 [4])	180
CHF_2I	295 [4])	300

The boiling point of $CHFI_2$ and CHI_3 [4]) show considerable deviations. We shall return to it later (p. 147).

The application of the formula

$$T_S = k_1 \frac{(V - V_c)^2}{V}$$

for halogenated methane derivatives, which also contain hydrogen, in which for V_H the Kopp volume 5.5 is taken does not yield a constant T_D value and not even a value which shows a definite course. This must be imputed to the fact, that in the case of hydrogen we may not expect the same relation between polarizability and ionic radius as in the case of the halogens.

The boiling points of these compounds, however, can be calculated in very good agreement with the experiment, when we make

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[1]) O. Ruff and R. Keim, Z. anorg. allgem. Chem. **201**, 245 (1931).

[2]) H. S. Booth and E. M. Bixby, Ind. Eng. Chem. **24**, 637 (1932).

[3]) A. E. van Arkel and E. Janetzky, Rec. trav. chim. **56**, 167 (1937).

[4]) O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschatzky, Ber. **69**, 299 (1936).

use of additivity. But we must not forget that the T_D values found in this way are perhaps not quite exact the contribution to the boiling point of the dipole action.

We use for the contribution of a hydrogen ion to the boiling point ¼ of the boiling point of CH_4. But it is possible, that CH_4 is no sufficiently „screened" and that therefore a part of the boiling point must be attributed to cohesion which is not due to the influence of the halogen ions upon one another, a case of which we shall give examples later (p. 33 and 61).

When there is no total screening, additivity does not hold, as we shall see later. We have, thus, here an indication, that all the hydrogen containing methane derivatives are completely screened.

Van Arkel and de Boer[1]) have also examined the silicon derivatives. At that time only the boiling point of SiF_4 and the completely halogenated Silicon derivatives were known, which contain only chlorine, bromine and iodine.

The last proved to be completely additative. Further a few derivatives containing hydrogen were known, of which van Arkel and de Boer calculated the T_D values. In one special type these values proved to be inconstant. The contribution of the various atoms to the boiling point, as regards the London energy only, these authors deduced from the boiling points of SiH_4, SiF_4, $SiCl_4$, $SiBr_4$ and SiI_4, for H 40.5°, for F 46°, for Cl 82.5°, for Br 106.5° and for I 141° respectively.

Recently the boiling points have become known of $SiHFCl_2$, $SiHF_2Cl$, SiF_3Br, SiF_2Br_2, $SiFBr_3$, SiF_3Cl, SiF_2Cl_2 and $SiFCl_3$ from a research by Booth, Schumb and co-workers[2]).

We here give a table of the boiling points found in degrees Kelvin supplimented by a few others for comparison.

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[1]) A. E. van Arkel and J. H. de Boer, Physica 4, 382, 392 (1924).

[2]) H. S. Booth and W. D. Stillwell, J. Am. Chem. Soc. **56**, 1533 (1934).

W. C. Schumb and H. A. Anderson, J. Am. Chem. Soc. **58**, 994 (1936).

W. C. Schumb and E. L. Gamble, J. Am. Chem. Soc. **54**, 3943 (1932).

H. S. Booth and C. F. Swinehart, J. Am. Chem. Soc. **54**, 4751 (1932); **57**, 1333 (1935).

$SiHF_3$	193	SiF_4	178 [1]	SiF_4	178 [1]
$SiHF_2Cl$	223	SiF_3Cl	203	SiF_3Br	231
$SiHFCl_2$	255	SiF_2Cl_2	241	SiF_2Br_2	287
$SiHCl_3$	306	$SiFCl_3$	285	$SiFBr_3$	357
		$SiCl_4$	330	$SiBr_4$	426

We see, that the values of any particular vertical column do not form an arithmetical series at all, as demanded by additivity.

We shall see, that these deviations can be very elegantly explained by accepting a few simple hypotheses, and that at the same time they give us some new points of view [2].

Our hypothesis is, that a compound of the AXYZW type shows no interaction 1°. between the central atoms mutually and 2°. between the central atoms and the anions of other molecules, when the central atom can really be completely enclosed in the anions in a geometric model.

In this case there is no extra contribution to the boiling point and thus the compound satisfies the additivity. We shall see later, why this is the case (p. 45). We shall not detail, which of the two kinds of interactions is the main effect (for this cf. p. 77).

The question arises what special properties we must asign to the atoms which build up the molecule, in other words, what radii the atoms (ions) have. We shall take up a completely electrostatic point of view and we shall therefore consider all the compounds for the present as being composed of rigid ions, which are spherical. We are aware, that this is a supposition that certainly does not correspond exactly to reality, but as other and perhaps better methods of description entirely exclude quantitative calculations in the sense in which we carry them out, we shall use our model, which, seeing the results to which it leads, cannot be very far removed from truth.

Let us take, for instance, a compound of the type AX_4. We will imagine the molecule as the well known tetrahedron with the central ion at its centre of gravity.

We may now distinguish two cases:

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[1] This value is the latest in the literature, and given by O. Ruff and E. Ascher, Z. anorg. allgem. Chem. **196**, 415 (1931).

[2] J. M. Stevels, Chem. Weekblad **34**, 334 (1937).

In the first case the halogen atoms are so large, that they lie against eachother while the central ion „fits" in the cavity, which has been formed between the halogen ions.

In the second case the central ion is so large, that the four attached halogen ions do not touch eachother.

In the first case we have therefore anion-cation contact, and in the second case anion-anion contact.

It is obvious, that there will be a certain critical relation in which case 1 will become case 2. This is

$$r_A = 0.225\, r_X$$

as can be shown by a simple calculation. r_A is the radius of the central ion, while r_X represents the radius of the halogen ion.

For these ionic radii we will take the average values given by Pauling[1]) for the free ions, which agree with the values of Goldschmidt[2]), thus for

C	0.15 Å	F	1.36 Å
Si	0.40 Å	Cl	1.81 Å
		Br	1.96 Å
		I	2.18 Å

We know, however, that these values, at any rate in the compounds we shall consider here, by no means correspond to the reality. The ionic radii given here for the halogens are only approximately correct if an univalent cation is present and a coordination number 6. It might be asked, whether we could not calculate the ionic radii better by the method developed by Zachariasen[3]) who makes use of „univalent" ionic radii from which the correct ionic distance can be calculated by a coordination and a valency correction.

This method, however, may not be applied here, as it is only valid in a case of anion-cation contact, and we shall see that in our cases we are almost exclusively concerned with anion-anion contact.

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[1]) L. Pauling, J. Am. Chem. Soc. 49, 765 (1927).

[2]) V. M. Goldschmidt, Ber. 60, 1263 (1927).

[3]) W. H. Zachariasen, Z. Krist. 80, 137 (1931).

The anion-anion contact in this kind of compounds — at any rate those which contain Br of I — is shown by the crystal structure. Hassel and Kringstad[1]) find that the lattices of SiI_4, TiI_4 and GeI_4 might be composed of a face-centered cubic lattice of iodine ions, in which the small central ions are found in the cavities. The lattice constants are equal to one another completely. This suggests a similar structure for the molecule in the liquid state, namely a „screened" configuration of the AI_4-molecule.

These structure determinations also strengthen our opinion that we are here concerned with compounds which we may consider heteropolar. If they were homopolar, we should need to use Pauling's atomic radii of „covalent" bound atoms[2]) to describe the molecule; then, however, the atomic radii of the central atoms are so large and the halogen atoms so small that a constant lattice constant could never have been found.

According to Pauling[3]) it is not possible to calculate for complicated molecules such as these, whether the heteropolar or the homopolar conception produces a minimum of energy. In Pauling's opinion a number of structures of SiF_4 (the purely heteropolar and those with one, two, three or four covalent bound atoms) have their minimum of energy close beside each other. Neither the extreme heteropolar SiF_4 nor the extreme homopolar SiF_4 represents the true normal condition, which lies in between.

Neither can we estimate which of the two extremes comes nearest to this. In SiF_4 that is composed of small ions it cannot be strictly defined. We know, at any rate, that when the positive ion is larger, generally speaking, the compound will behave in a more heteropolar manner.

In the following we shall use entirely heteropolar methods of description and we shall see, that this yields good results. We have seen already, that the method of calculation of Zachariassen is not applicable, as we are concerned with anion-anion contact. Moreover, this method gives us the ionic

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[1]) Hassel and Kringstad, Z. physik. Chem. B **13**, 1 (1931; B **15**, 274 (1932).

[2]) L. Pauling, Proc. Nat. Acad. Sci. U.S.A. **18**, 293 (1932).

[3]) L. Pauling, J. Am. Chem. Soc. **54**, 999 (1932).

distances and we want the ionic radii, in any case the proportion of these values.

To obtain this, we suppose, that this proportion in the molecules is the same as in the free state of the ions. This representation is, of course, by no means exact, but as we shall see from the following, these ionic radii are only used for orientation. They do not form an essential point in the further theory.

For the radius of the hydrogen ion various disagreeing values are given in literature. We may perhaps conclude from the well-known fact that the atomic volume for hydrogen in our kind of compounds is so much smaller than that for the halogen ions (for instance in the methane derivatives $V_H = 5.5$, $V_F = 11$, $V_{Cl} = 22.8$ etc.) that in this kind of compounds at any rate the hydrogen takes up less space than the fluorine.

We now see at once that in carbon derivatives the relation

$$r_A < 0.225\, r_X \qquad (X = H,\ F,\ Cl,\ Br \text{ or } I)$$

is always satisfied, if we use the radii here accepted. Here, therefore the action of the central ion outside the molecule is very small; the small central ion is completely „screened" (r_H is certainly larger than 0.66 so that for CH_4 also the screening is complete). The additivity is here quite comprehensible [1]).

In the silicon derivatives, however, the case is somewhat different. For $SiCl_4$, $SiBr_4$ and SiI_4

$$r_A < 0.225\, r_X$$

(for $SiCl_4$ $r_A = 0.225\, r_X$, so that here complete screening occurs). For SiF_4 and thus for SiH_4 this condition is no longer fulfilled. Here we must ascribe the cohesion energy in part to the interaction of the central ions on eachother and of the central ion on the anions of surrounding other molecules.

In the following we shall abbreviate this to „interaction". The contribution to the boiling point of the hydrogen and fluorine ions as understood in the sense of van Arkel and de Boer, we must not calculate, therefore, by simply dividing the boiling point of SiF_4 and SiH_4 by four, as is permissible in the other cases

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[1]) Cf. A. E. van Arkel and W. de Groot, Physica 12, 211 (1932).

(Cl, Br, I in Si derivatives, H, F, Cl, Br and I in C derivatives).

This purely geometric conception agrees with several chemical facts. As we know, the methane derivatives never give rise to complex formation, while of the Si derivatives it is only the SiF_4 that can form complexes (K_2SiF_6!).

We ought to formulate this matter in a different way. Complex formation is an indication that interaction will take place. On the other hand, the absence of complex formation is not a complete proof of the absence of interaction.

Two instances may be given

1st. The complex formation may be absent, because the central ion is so small that no other ions can group themselves around it. This is the case with the carbon derivatives for instance.

2nd. There is no complex formation, because it would cause too great a waste of energy. This is the case, for instance, when the positive metal ion in question is too small.

Of the iodostannates only the Rb_2SnI_6 and Cs_2SnI_6 are known. The compounds of smaller metal ions (Li, Na, K) are not known. Although, therefore, according to the above it may be possible to form a complex $SiH_6^=$, it is probably impossible for energetic reasons to prepare substances such as Cs_2SiH_6, K_2SiH_6 and Li_2SiH_6.

If we now examine the boiling points of the series

SiF_2Cl_2	241	SiF_2Br_2	287
$SiFCl_3$	285	$SiFBr_3$	357
$SiCl_4$	330	$SiBr_4$	426

we see that they are completely additive. We assume that in these compounds the central ions are entirely screened off and we see that two „large" halogen atoms (Cl, Br, I) are sufficient to ensure complete screening and thus complete additivity. Roughly speaking in the SiF_2Cl_2 we may take the mean radius of the anions as 1.58 Å. 0.225 r_X becomes equal to 0.36 Å, which is, although somewhat smaller, yet of the order of magnitude of the Si^{++++} ion. We see, thus, that our hypothesis of the rigid spheres is not quite exact, which was to be expected.

It should therefore again be emphasized that the purely geometric representation is only of use as an orientation.

The fact of complete screening, however, can be demonstrated by another method with complete satisfaction, as we shall see later. From the above table we can calculate the values for the true contribution to the cohesion of the fluorine ion. We find [1]) from

SiF_2Cl_2	F = 38°	(Cl = 82.5°)
$SiFCl_3$	F = 37.5°	(Cl = 82.5°)
SiF_2Br_2	F = 37°	(Br = 106.5°)
$SiFBr_3$	F = 37.5°	(Br = 106.5°)

The fact that these four values, calculated from entirely independent series, agree so well seems to indicate that this mehod is correct. With these values we were able to predict the boiling points of $SiFClBr_2$ and $SiFCl_2Br$ [2]) which were quite recently prepared by Schumb and Anderson [3]).
We find:

	exp.	calc.
$SiFClBr_2$	333	333
$SiFCl_2Br$	309	309

We assume for F 37.5°, that is 7° per fluorine ion lower than ¼ of the boiling point of SiF_4. We can calculate in reversal from this how many degrees in the compounds SiF_3Cl, SiF_3Br and SiF_4 must be attribued to interaction. This value will be represented in the following by T_M, as it gives the result of a mutual action of the central ions and the halogen ions of other molecules.

	T_S	ΣT_X	T_M
SiF_3Cl	203	195	8
SiF_3Br	231	219	12
SiF_4	178	150	28

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[1]) A calculation more in detail is to be found in the article by J. M. Stevels, Handelingen van het 26ste Natuur en Geneesk. Congres, 164 (1937).

[2]) J. M. Stevels, Chem. Weekblad 34, 440 (1937).

[3]) W. C. Schumb and H. A. Anderson, J. Am. Chem. Soc. **59**, 653 (1937).

We see, thus, in the case of one large halogen ion an interaction of about 10°, in the case of SiF_4 28°.

We find incomplete screening also in the mixed silicon derivatives containing hydrogen (of which unfortunately only one series is known viz. $SiHX_3$).

We now assume, that the screening is complete with two „large" halogen ions. The contribution to the boiling point due to London cohesion of the hydrogen ions we call T_H.

The boiling point of SiH_4 is 161°. We thus find for the interaction in SiH_4: $4\,(40 - T_H)$ and in SiH_2X_2: 0.

We shall indicate the interaction of $SiHF_3$, $SiHF_2Cl$ and SiH_3Cl by $T_{M\,(SiHF_3)}$, $T_{M\,(SiHF_2Cl)}$ and $T_{M\,(SiH_3Cl)}$ respectively. Then we have the following equations:

$$T_{M(SiHF_3)} = \tfrac{1}{4}\,T_{M(SiH_4)} + \tfrac{3}{4}\,T_{M(SiF_4)} = 61 - T_H \tag{I}$$

$$T_{M(SiHF_2Cl)} = {}^1/_3\,T_{M(SiH_3Cl)} + {}^2/_3\,T_{M(SiF_3Cl)} \tag{II}$$

Now it is known, that the T_D values in the silicon derivatives are not constant, but increase, when passing to larger halogen ions. As the difference in the T_D values are small, we assume that they form an arithmetical series in the series $SiHF_3 \rightarrow SiHCl_3$. Therefore,

$$T_{S(SiHF_3)} = 193 = 3\,T_F + T_H + T_{M(SiHF_3)} + T_{D(SiHF_3)} \tag{III}$$

$$T_{S(SiHF_2Cl)} = 223 = 2\,T_F + T_{Cl} + T_H + T_{M(SiHF_2Cl)} + T_{D(SiHF_3)} + \delta \tag{IV}$$

$$T_{S(SiHFCl_2)} = 255 = T_F + 2\,T_{Cl} + T_H + T_{D(SiHF_3)} + 2\,\delta \tag{V}$$

$$T_{S(SiHCl_3)} = 306 = 3\,T_{Cl} + T_H + T_{D(SiHF_3)} + 3\,\delta \tag{VI}$$

We have, thus, six equations with six unknows. By resolving them, we find:

$$\begin{aligned}
T_H &= 21\\
T_{M(SiHF_3)} &= 40\\
T_{M(SiHF_2Cl)} &= 19\\
T_{M(SiH_3Cl)} &= 33\\
T_{D(SiHF_3)} &= 19.5\\
\delta &= 6
\end{aligned}$$

We give here a table of the silicon derivatives, as far as known, which show T_D and T_M values:

	T_S	T_L	T_D	T_M
SiH_4	161	84	—	77
SiH_3Cl	243	145.5	64.5	33
SiH_3Br	275	169.5	72.5	33
SiH_2Cl_2	281	207	74	—
SiH_2Br_2	339	255	84	—
$SiHF_3$	193	133.5	19.5	40
$SiHF_2Cl$	223	178.5	25.5	19
$SiHFCl_2$	255	223.5	31.5	—
$SiHCl_3$	306	268.5	37.5	—
$SiHBr_3$	383	340.5	42.5	—
$SiHI_3$	478	444	34	—
SiF_4	178	150	—	28
SiF_3Cl	203	195	—	8
SiF_3Br	231	219	—	12

$T_{M(\mathrm{SiH_3Br})}$ is supposed to be equal to $T_{M(\mathrm{SiH_3Cl})}$. The T_M values are large in the cases of four „small" anions, and much lower in the cases of three „small" anions. For the T_D values there is always a small increase, when heavier halogen ions are introduced. (To the exception $SiHI_3$ we shall return later (p. 148)).

The rise of T_D from $SiHF_3$ to $SiHCl_3$ is 18°, from $SiHCl_3$ to $SiHBr_3$ 5°, but we must not forget that the change from F to Cl is much greater than from Cl to Br. Here thus the difference between „large" and „small" halogen ions is again conspicuous. The ratio of the differences of the ionic radii

$$\frac{r_{Cl} - r_F}{r_{Br} - r_{Cl}}$$

is also of about the order of magnitude of 3.5.

We thus come to the conclusion that the central ion in SiF_4 and SiH_4 is not completely screened. For the London contribution to the boiling point we must introduce for *F* and *H* in silicon derivatives 37.5° and 21° respectively and not as formerly 46° and 40.5°. Should the above seem to be rather arbitrary, the following will show that our hypothesis may really be considered as correct.

Let us take the various completely halogenated silicon derivatives and examine their T_L values, that is, only that portion of the boiling point that corresponds to the cohesion of the enclosing ions. We can then calculate the constant k, from the formula for the boiling point according to van Arkel and de Boer

$$T_S = k_1 \frac{(V - V_{Si})^2}{V}$$

This k_1 value, in the *Si* series is, however, not constant. We find:

SiF_4	5.81	SiF_4	5.81	$SiCl_4$	4.85
SiF_3Cl	5.48	SiF_3Br	5.29	$SiCl_3Br$	4.77
SiF_2Cl_2	5.20	SiF_2Br_2	4.98	$SiCl_2Br_2$	4.70
$SiFCl_3$	4.99	$SiFBr_3$	4.80	$SiClBr_3$	4.65
$SiCl_4$	4.85	$SiBr_4$	4.63	$SiBr_4$	4.63
$SiCl_4$	4.85	$SiBr_4$	4.63	$SiFCl_3$	4.99
$SiCl_3I$	4.61	$SiCr_3I$	4.53	$SiFCl_2Br$	4.91
$SiCl_2I_3$	4.45	$SiBr_2I_2$	4.49	$SiFClBr_2$	4.84
$SiClI_3$	4.37	$SiBrI_3$	4.41	$SiFBr_3$	4.80
SiI_4	4.35	SiI_4	4.35		

If we had not introduced our correction for SiF_4, SiF_3Cl and SiF_3Br, we should have found values, that were much higher. The Si series yields, thus, no constant in contrast to the methane series, in which van Arkel and de Boer found the value 4.30 with an irregularity of 1 %, which may be attributable to experimental errors.

We can now ask ourselves, what is the real significance of this constant? To answer this question we must briefly follow its derivation according to van Arkel and de Groot[1]). In the formula

$$T_S = k \frac{[\Sigma \sqrt{a_n}]^2}{b}$$

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[1]) A. E. van Arkel and W. de Groot, Physica **12**, 211 (1932).

which is directly based upon London's cohesion formula ¹) the authors show that

$$\sqrt{a_n} = \frac{\sqrt{\varphi_n \alpha_n}}{\sqrt{r^3_n}}$$

r_n is the radius of the n-th ion, α_n its polarizability and φ_n its mean excitation potential.

As we shall see later, there is, generally speaking, no direct relation between these r_n's and the distances from the centre of the cation to the centre of the anion. As can easily be seen the r_n's are, approximately, proportional to the ionic radii in the sense, we used them before. Now φ_n is approximately proportional to r_n^{-1} while α_n is proportional r_n^5. This relation holds for the free halogen ions and the rare gases. According to van Arkel and de Groot this relation is the condition for the equation

$$\frac{\sqrt{a_n}}{V_n} = \text{constant},$$

which is again essential for the additivity of the boiling points of these compounds.

According to the deformation theory of Fajans and Joos ²) the polarizability is a function of the electric field E ³). We may thus write

$$\alpha_n = A' (E)\, r^5_n.$$

A' is here still a function of the field. We shall continue to derive $A' (E)$, in other compounds as well, from the values we assumed for the ionic radii. This is permissible, because we are considering analogous compounds all the time. The coordination and valancy correction thus always remain the same; the ionic radii in all compounds are contracted to the same degree, apart from the influence of the Born repulsive forces, which might cause very small deviations. As, however, according to our representation we are concerned almos exclusively with anion-anion contact in cases of com-

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¹) J. London, Z. Physik. 63, 256 (1930); Z. Physik. chem. B 11, 222 (1931).

²) K. Fajans and G. Joos, Z. Physik 231 (1924).

³) E has here and in the following the same significance as F_2 on p. 16 and 17.

plete „screening" even the Born repulsion coefficient is the same. There is a possibility and even a probability — that in the silicon series the polarizability is not proportional to the fifth power of the ionic radius, but as long as we ascribe a purely numerical significance to $A'(E)$, it is always permissible to use the equation

$$\alpha_n = A'(E)\, r_n^5.$$

In the cases we examine the theories of Fajans and Joos and Herzfeld and Wolf run entirely parallel[1]). We can read for $A'(E)$ also a function A' of the energy. We shall regard $A'(E)$ as a purely arithmetical quantity.

If we fill in the last named formula we have

$$T_S = k_2' \frac{\left[\sum \frac{\sqrt{\varphi_n}\, A'(E)\, r^5_n}{\sqrt{r^3_n}}\right]^2}{V}$$

For the present we confine ourselves to compounds in which the anions are all alike. Then the formula becomes

$$T_S = k_2' \{A'(E)\}^2 \frac{(V - V_c)^2}{V}$$

in which $k_1 = k_2' \{A'(E)\}^2$; k'_2 is here a universal constant, which holds in all compounds of the AX_4 type.

We can now calculate $A'(E)$ by the formula

$$A'(E) = k_3' \frac{\sqrt{T_S V}}{V - V_c}$$

k_3' is also a universal constant and $k_2' = \frac{1}{k_3'^2}$

On the other hand $A'(E)$ may be calculated from the refraction. We represent by $R_\sim(X)$ the refraction of the halogen ion X extrapolated to a wave-length $\lambda \rightarrow \sim$, by $R_D(X)$ the refraction of ion X for the wave-length of the Na-D-line.

As mentioned above, for our α we only need to know the electronic polarizability and thus $P_E = R_\sim$. The atomic polarization

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[1]) K. F. Herzfeld and K. L. Wolf, Ann. Physik. 78, 35 (1925); cf. also A. E. van Arkel and J. H. de Boer, La valence et l'electrostatique, Paris 1936, p. 101 and 161, and Chapter I of this thesis.

does not play a part in the polarizability, when we apply this quantity in the London formula.

We can assume $R_D = (1 + m) P_E$. In analogously composed compounds m will not vary very much, either in the gaseous or liquid state. This is shown by the extensive material collected by Fajans and co-workers regarding the R_D and $R_\sim$ values, from which we calculate the m values.

		R_D	$R_\sim$	$m \cdot 10^2$
BCl_3	(liquid) [1])	20.97	20.2	3.8
BBr_3	(,,) [1])	29.95	28.8	4.0
CCl_4	(,,) [4])	26.45	25.77	2.6
$SiCl_4$	(,,) [1])[4])	28.67	27.97	2.5
$SiBr_4$	(,,) [1])	40.78	39.4	3.5
$SnCl_4$	(,,) [4])	35.11	33.83	3.8
$SnBr_4$	(,,) [4])	48.73	46.18	5.5
$AlCl_3$	(gaseous at 230°) [2])	23.22	22.57	2.9
$AlBr_3$	(,, ,, 300°) [2])	32.65	31.41	3.9
AlI_3	(,, ,, 380°) [2])	52.68	50.24	4.8
CCl_4	(,, ,, 180°) [3])	26.60	25.88	2.8
$SiCl_4$	(,, ,, 180°) [3])	29.01	28.20	2.9
$SnCl_4$	(,, ,, 200°) [3])	35.94	34.59	3.9
$SnBr_4$	(,, ,, 360°) [3])	50.19	47.71	5.2

We see, that for this kind of compounds $(1 + m) = 1.025$ to 1.055. The equation

$$R_D = 1.04\, R_\sim$$

shows an error of about 1.5 % which is quite permissible within the scope of our calculations.

This equation is also confirmed by all the methane derivatives we examined (p. 117). It appears to hold not only for the symmetrical compounds AX_4 but for the asymmetrical ones and even

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[1]) K. Fajans, Z. physik. Chem. **B** 24, 147 (1934).

[2]) F. K. V. Koch and H. Kohner, Z. physik. Chem. **B** 24, 198 (1934).

[3]) P. Hölemann and H. Goldschmidt, Z. physik. Chem. **B** 24, 207 (1934).

[4]) P. Hölemann, Z. physik. Chem. **B** 32, 358 (1936).

for those with contain hydrogen. Obviously m increases in a particular series from Cl to I, a fact which has been long known, dispersion increases from Cl to I. If we use the R_D values as a measure for polarizability, therefore, they are for the I derivatives somewhat too high. The error, however, is only of the order of magnitude of 1 %, which does not damage our calculations.

If compounds of the AX_2 type are further compared[1]) it will be seen, that m is much larger and the constancy is not a satisfactory. These compounds, however, will not be considered. It is a most fortunate accident, that in all compounds of the AX_4 type the $(1 + m)$ value is constant up to about 1 %.

In the table SnI_4 is not included; here we find a value for m of 11.6, but this substance shows a strong absorption in the green and blue[2]). Let it be emphasized again, as Fajans and Joos have also pointed out, that R_D may only be regarded as measure for the polarizability when the refraction for the *Na-D*-line is not disturbed by adjacent absorption. Mathematically this is expressed in this way, that the various lines of absorption lie so far away, that we can describe the dispersion of the visible light properly and sufficiently by a „double" dispersion formula

$$\frac{n^2 - 1}{n^2 + 2} = \frac{C_1}{\nu^2_{E0} - \nu^2} + \frac{C_2}{\nu^2_{A0} - \nu^2}.$$

The lines of absorption lie so far from the *Na-D*-line that they seem to form a mean value. In some cases mentioned above it is even possible to represent the dispersion by one term

$$\frac{n^2 - 1}{n^2 + 2} = \frac{C}{\nu^2_{E0} - \nu^2}.$$

This means that the influence of the ultra-red absorption upon the refraction is only of a diminishing nature[3]).

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[1]) M. A. Bredig, Th. v. Hirsch and J. Wüst, Z. physik. Chem. B 24, 182 (1934).

H. Goldschmidt and P. Hölemann, Z. physik. Chem. B 24, 212 (1934).

[2]) P. Hölemann and H. Goldschmidt, loc. cit.

[3]) K. Fajans and G. Joos, Z. Physik 23, 5 (1924).

From

$$\alpha = A'(E)\, r^5_X$$

follows

$$A'(E) = \frac{3\, R_{\sim}(X)\, 10^{24}}{4\, \pi N r^5_X}$$

or

$$A\,(E) = \frac{3\, R_D(X)\, 10^{24}}{4\, \pi N r^5_X}$$

in which

$$A\,(E) = (1 + m)\, A'(E).$$

$A\,(E)$ thus, gets the significance of the ratio of the atomic refraction for the *Na-D*-line and the fifth power of the ionic radius, with a suitable factor. It is a quantity without any physical meaning, but is so far useful, that it links up the boiling point with the refraction.

It is obvious that we must know the values of the refraction at the boiling point R_D^B [1]).

Only the refractions at 20° are known, so that we must introduce a correction. For a molecule AX_4 we take

$$R_D^B = 4\, R_D^B\,(X) + R_D\,(A).$$

In the cases we examine $R_D\,(A)$ is very small: $R_D\,(C) = 0.03$ and $R_D\,(Si) = 0.1$ [2]).

The refraction shows a positive temperature coëfficient in general of about $1^{\circ}/_{00}$ per 10°. We may represent the refraction at the boiling point by

$$R_D^B = R_D^{20} + (T_s - 293)\, 10^{-4}\, R_D^{20}$$

or also

$$R_D^B = R_D^{20}\, \{1 + (T_s - 293)\, 10^{-4}\}$$

and as $R_D\,(A) \ll R_D^B$

$$R_D^B\,(X) \doteq R_D^{20}\,(X)\, \{1 + (T_s - 293)\, 10^{-4}\}$$

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[1]) Cf. A. E. van Arkel and J. H. de Boer, Z. physik. Chem. **122**, 101 (1926).

[2]) K. Fajans and G. Joos, Z. Physik **23**, 1 (1924).

On the basis of the following data:

	$T_L = T_S$	V	$V - V_c$	$R_D^{20}(X)$ 1)	$R_D^B\ (X)$	r_X
CF_4	150	55	44	1.70	1.67	1.36
CCl_4	349	102.2	91.2	6.60	6.64	1.81
CBr_4	462	127.4	116.4	9.74	9.90	1.96
CI_4	624	167	156	16.28	16.83	2.18

We can now calculate the $A'(E)$ values from the boiling points and the boiling volumes (I) and the $A(E)$ values from the refractions (II).

We find:

	$A'(E)$ (I)	$A(E)$ (II)
CF_4	$2.064\ k_3'$	0.141
CCl_4	$2.071\ k_3'$	0.135
CBr_4	$2.084\ k_3'$	0.135
CI_4	$2.069\ k_3'$	0.135

Also

$$A(E) = (1 + m)\, A'(E).$$

W therefore have the equation

$$2.075\ k'_3 = \frac{0.135}{1 + m}$$

Let us call

$$k_3 = (1 + m)\, k_3'$$

then k_3 can be calculated. We find then

$$k_3 = 0.0651 \quad \text{and} \quad k_2 = \frac{1}{k_3^2} = 236.3.$$

By means of k_3 we can thus calculate from the boiling temperatures and boiling point volumes the $A(E)$ values which correspond to those which we calculated from the refraction for the *Na-D*-line. k_2 and k_3 are constants, which are chosen is that way, that at any rate in the carbon derivatives there is agreement.

The constants according to their origin are universal and should therefore hold for all posible compounds.

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1) Cf. Chapter V.

According to Van Arkel and de Boer we know that in the carbon derivatives at any rate $A\,(E)$ is constant to about 1 %. This is shown here by two independent methods. The value of CF_4 only, calculated from the refraction (method II) shows a slight deviation, we shall see later to what this might be ascribed.

With the aid of the constants k_2 and k_3 the $A\,(E)$ values can be calculated from the boiling temeprature and the boiling point volumes and from the refractions.

We will now apply this to the compounds SiX_4 and we assume

$$A\,(E) = 0.0651\ \frac{\sqrt{T_S V}}{V - V_{Si}}$$

It is here of course better to write

$$A\,(E) = 0.0651\ \frac{\sqrt{T_L V}}{V - V_{Si}}$$

as in some *Si* derivatives T_S it not equal to T_L.

From the data:

	T_L	V	$V - V_c$	$R_D\,(X)$	$R_D^B\,(X)$	r_x
SiF_4	150!	71	40	2.07 (0° C)	2.04	1.36
$SiCl_4$	330	119.4	88.4	7.23 (180° C)	7.14	1.81
$SiBr_4$	426	146.2	115.2	10.18 (20° C)	10.32	1.96
SiI_4	564	187	156	—	—	—

we can again calculate $A\,(E)$ in two ways.

Here we reckon for V_F: 10, for V_{Cl}: 22.1, for V_{Br}: 28.8, for V_I: 39 and for V_{Si}: 31.

The first three values are slightly different to Kopp's volumes as used by van Arkel and de Boer. How we arrived at these values will be detailed later ¹). R_D (F), R_D (Cl) and R_D (Br) are taken from the most recent research: R_D (F) from Klemm and Henckel ²), R_D (Cl) from Hölemann and Goldschmidt ³), R_D (Br) from Fajans and Joos ⁴) who have

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¹) See Chapter II B.

²) W. Klemm and P. Henckel, Z. anorg. allgem. Chem. 213, 115 (1933).

³) P. Hölemann and H. Goldschmidt, Z. physik. Chem. B 24, 199 (1934).

⁴) K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

determined the refractions of SiF_4, $SiCl_4$, $SiBr_4$, from which, after correction for the refraction of the Si^{++++} ion (0.1)[1]) the R's can be calculated. The temperature correction is calculated in a analogous way to that used for the methane derivatives. By both methods we find for A (E) in the SiX_4 series:

	I	II
SiF_4	0.168	0.173
$SiCl_4$	0.146	0.145
$SiBr_4$	0.141	0.141
SiI_4	0.135	—

The agreement may be considered good. Again we see that the A (E) values for fluorine, calculated by II are greater than those by I. This may perhaps be accounted for by the refraction values for the C^{++++} ion and the Si^{++++} ion which are slightly incorrect, being only estimated, and this of course gives relatively the greatest error in the F value.

We will take the values of column I as the basis for our further reasoning, as these seem to be the most reliable.

In the case of carbon derivatives column I is pretty constant, as should be the case, while on the whole method II gives more uncertainty, as explained above.

Moreover, we should here remark the values found for A (E) in SiF_4 is a confirmation of our hypothesis that there is an important interaction. The value of 150° for the London energy only yields an A (E) value entirely in agreement with the theoretical expectations. If we had taken 183° for the London energy (i.e. the entire boiling point) we should have found, according to method I for A (E) 0.186, which is much higher than the value according to method II. This is, as we have seen, not in agreement with the methane series. We must expect that the A (E) value, calculated by method (I) will prove to be lower than that calculated by method (II).

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[1]) K. Fajans and G. Joos, Z. Physik. 23, 1 (1924).

Now

$$T_S = k_2 \frac{\left[\sum_n \frac{\sqrt{\varphi_n}\, A_n\,(E)\, r_n^5}{\sqrt{r_n^3}}\right]^2}{V}$$

or also

$$T_S = k_2 \frac{\left[\sum_n A_n\,(E)\, V_n\right]^2}{V}$$

These $A_n\,(E)\,V_n$ values are for F: 1.68, for Cl: 3.23, for Br: 4.06 and for I: 5.27. By means of these we find:

	T_L	V	$\Sigma A_n\,(E)\,V_n$	k_2
SiF_4	150!	71	6.72	236
SiF_3Cl	195!	83.1	8.27	237
SiF_2Cl_2	241	95.2	9.82	238
$SiFCl_3$	285	107.3	11.37	237
$SiCl_4$	330	119.4	12.92	236
SiF_3Br	219!	89.8	9.10	238
SiF_2Br_2	287	108.6	11.48	237
$SiFBr_3$	357	127.4	13.86	237
$SiBr_4$	426	146.2	16.24	236
$SiCl_3Br$	353	126.1	13.75	235
$SiCl_2Br_2$	376	132.8	14.58	235
$SiClBr_3$	400	139.5	15.41	235
$SiCl_3I$	387	136.3	14.96	236
$SiCl_2I_2$	445	153.2	17.00	236
$SiClI_3$	508	170.1	19.04	238
SiI_4	563	187	21.08	237
$SiBr_3I$	465	156.4	17.45	239
$SiBr_2I_2$	503	166.6	18.66	241
$SiBrI_3$	528	176.8	19.87	236
$SiFCl_2Br_2$	309	114	12.20	237
$SiFClBr_2$	333	120.7	13.03	237

For the constant k_2 we find thus 236.5 with a deviation of at most 1.5 (= 0.7 %). The only abnormalities are in $SiBr_3I$ and $SiBr_2I_2$: here the boiling points are probably erroneous. It is here very doubtful, if these compounds really have been prepared, and not mixtures of $SiBr_4$ and SiI_4 or even more substances [1].

In the additive calculation according to van Arkel and de Boer these are the only compounds which show a deviation.

In the above calculations we cannot expect a greater accuracy than 1 %. This accuracy is even very surprising, when we remember, how many uncertainties are introduced, which can give rise to errors: the dispersion, the temperature correction, the uncertainty of the ionic radii and the hypothesis of their contraction to the same extent, when molecules are formed.

It is indeed no wonder that we find a constant in the silicon series as the A (E) values according to this method are so chosen that k becomes constant. The fact, however, that these values of A (E) agree well with those calculated from the refraction, proves that an actual significance must be attached to this method of calculation. The table also shows that the values for T_s in the cases of SiF_4, SiF_3Cl and SiF_3Br have been found correctly and that in these compounds there actually is an extra interaction contribution to the boiling point.

It may not appear to be justifiable to use the A (E) values of X in SiX_3Y, SiX_2Y_2 etc., as we have done above. As we shall see later [2]) this is not quite correct. The deviations, however, are slight, so that for the calculation of the boiling point with an accuracy of 1 % this method is permissible. We can easily imagine in the following way, why the F ion in $SiFCl_3$, for instance, is found in about the same field as in SiF_4. It is true that in $SiFCl_3$ the field of the central ion present in the F ion is less counteracted by the larger Cl ions than in SiF_4, but the Cl ions are more polarizable, so that larger induced dipoles are formed, which again counteract the field of the central ion. Thus the different forces compensate one another approximately. It is obvious, that these considerations are of general application, so that there is no ob-

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[1]) Cf. J. W. Zwartsenberg, Thesis to be published later, Leiden.

[2]) See Chapter V.

jection to applying the $A\,(E)$ values obtained from the unmixed Si derivatives to the mixed Si derivatives, at any rate in our approximation of 1 %.

It is important to observe here, that the Si derivatives show additivity of the boiling point (at any rate in those containing heavier halogen atoms) while they do not satisfy the formula of van Arkel and de Boer in the old sense.

For all the substances, which we shall discuss in the following (Chapter IIC — IIF), we shall consider a complete addivity as a criterion for complete screening, seeing that a theory as developed above, may be applied in the same way. Deviations of additivity, thus, are explained by a particular interaction.

B. The relation between polarizability, volume and cohesion.

In this part we shall discuss the relation between polarizability, cohesion forces and volume. Generally speaking, the volume occupied by a substance consists of two parts: one part is filled up by the molecules (or ions), the other part by the remaining nonpolarizable space between the molecules.

When we consider screened molecules no forces of significance (except the London ones) will act outside of them and the intermolecular volume will be large: substances, that crystallize in molecule lattices have relatively a large molvolume [1]).

When the molecules considered, however, give rise to a more important external field, a contraction will occur and the intermolecular volume will decrease. This effect is demonstrated especially by the dipole containing methane derivatives.

Biltz and Sapper [2]) have investigated the zero volume V_0 of this substances and they find:

X	Cl	Br	I
CH_3X	35.4	39.6	46.6
CH_2X_2	47.3	54.1	66.0
CHX_3	59.7	70.2	86.7
CX_4	74.6	88.4	112

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[1]) W. Biltz, Raumchemie der festen Stoffe, Leipzig 1934, p. 131.

[2]) W. Biltz and A. Sapper, Z. anorg. allgem. Chem. **203**, 304 (1932).

For CH_4 Biltz gives 30.6 and we can, thus, now calculate how great the contraction is in respect to the additivity. The values run parallel in the dipole moments of the compounds.

	contr. in %	μ
CH_3Cl	12.5	1.86
CH_2Cl_2	10.0	1.57
$CHCl_3$	6.1	1.15
CH_3Br	10.7	1.79
CH_2Br_2	9.1	1.39
$CHBr_3$	5.1	1.09
CH_3I	8.6	1.60
CH_2I_2	7.4	1.10
CHI_3	5.4	0.91

The gas kinetic volume of this kind of methane derivatives is additive and the boiling point volume apparently also. At these higher temperatures the molecules seem to be so far removed from eachother that the electric field of the dipole which decreases rapidly (with the third power of the distance) has no effect upon them.

We shall see later, however, that contraction due to „interaction" in symmetrical molecules, can be found up to the boiling point. This is shown by the fact that the relation $V_S = 1.41\ V_0$ seems to hold for all this kind of compounds and those of the type AX_3 [1]) although V_0 shows in some cases a contraction. It would seem therefore, that the „interaction" decreases with a power lower than the 3rd and we shall actually see later that the interaction must probably taken as a Coulomb action (Chapter II*F*).

To summarise, we may say, that a Coulomb interaction is observable both at the absolute zero and at the boiling point, dipole interactions are no longer perceptable at boiling point and in the gaseous state, but they are at the absolute zero. These arguments cannot, of course, be applied in their full extent, considering the inadequate way in which they have been deduced.

When in our type of molecules the cations become larger, the

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[1]) W. Fischer, Z. anorg. allgem. Chem. **211**, 321 (1933).

interaction will increase more and more, the type of crystallization passes from a molecule lattice to a coordination lattice, and the volume is contracted to a great extent. The tables on page 57 and 67 confirm this for the tetrahedral molecules. The same is observed by Biltz for many other substances. A characteristic exemple borrowed from him [1]) follows in the next table, in which we give the zero volume V_0 of a grammolecule of some substances.

BCl_3	61.0	$SbCl_3$	68.5
$AlCl_3$	53.3	$BiCl_3$	64.2

Although the central atoms in the bottom row are larger than those in the upper one the molecular volumes are highest in the upper row, because it is composed of substances that crystallize in molecular lattices only, while the substance in the bottom row crystallize in plate or coordination lattices. The last are, therefore, relatively closely packed. To summarise, we see thus, that a large interaction gives rise to a large contraction in the volume. This effect is mainly due to the decrease of the intermolecular volume.

Now we will discuss an other effect, which is moreover of a much smaller order of magnitude. We have to return to the formula derived in Chapter II A, which gives us the London contribution to the boiling point

$$T_L = k_2 \frac{\left[\sum_n \frac{\sqrt{\varphi_n \alpha_n}}{\sqrt{r_n^3}}\right]^2}{V}$$

For compounds of the AX_4 type

$$\alpha_n^2 \sim \frac{r_n^3}{\varphi_n}(T_L V)_n.$$

We know now that

$$\varphi_n \sim \frac{1}{r_n}$$

If we call the polarizability of the ion X in the molecule AX_4 $\alpha_{X(A)}$ we have

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[1]) W. Biltz, Raumchemie der festen Stoffe, Leipzig 1934, p. 131.

$$\alpha_{X(A)} \sim r_n^2 (\sqrt{T_L V})_{AX_4}$$

$$\alpha_{X(A)} \sim (\sqrt{T_L V})_{AX_4} V_{X(A)}^{2/3}$$

We write $V_{X(A)}$ because we cannot tell beforehand whether V_X is constant.

For the C and the *Si* series we have, thus.

$$\alpha_{X(Si)} = (\sqrt{T_L V})_{SiX_4} V_{X(Si)}^{2/3} = \sqrt{T_{L(SiX_4)} (4 V_{X(Si)} + V_{Si})} \, V_{X(Si)}^{2/3}$$

$$\alpha_{X(C)} = (\sqrt{T_L V})_{CX_4} V_{X(C)}^{2/3} = \sqrt{T_{L(CX_4)} (4 V_{X(C)} + V_C)} \, V_{X(C)}^{2/3}$$

We now write

$$V_{X(Si)} = V_{X(C)} + \Delta_X.$$

In this and the following discussions we assume the volume of the central ions to be constant values and we attribue all changes to changes in the halogen ions. Generally speaking, of course, this is not true, but we know that the deformability of the halogen ions greatly exceeds that of the tetravalent positive ions, so that the variations in volume of the latter are negligible compared to the former.

By developing in a series we find

$$V_{X(Si)}^{2/3} = V_{X(C)}^{2/3} + {}^2/_3 \, \Delta \, V_{X(C)}^{-1/3} - {}^1/_9 \, \Delta^2 \, V_{X(C)}^{-11/3} \ldots\ldots$$

It appears that the third term is so small that it may be neglected in comparison with the second.

We find now

$$\frac{\alpha^2_{X(Si)}}{\alpha^2_{X(C)}} = \frac{T_{L(SiX_4)} (4 V_{X(C)} + 4 \Delta_X + V_{Si}) \{ V_{X(C)}^{2/3} + {}^2/_3 \, \Delta_X V_{X(C)}^{-1/3} \}^2}{T_{L(CX_4)} (4 V_{X(C)} + V_C) \, V_{X(C)}^{4/3}}$$

$$\frac{\alpha^2_{X(Si)}}{\alpha^2_{X(C)}} = \frac{T_{L(SiX_4)} (4 V_{X(C)} + 4 \Delta_X + V_{Si}) (1 + {}^4/_3 \, \Delta_X V_{X(C)}^{-1})}{T_{L(CX_4)} (4 V_{X(C)} + V_C)}$$

$$\frac{\alpha^2_{X(Si)}}{\alpha^2_{X(C)}} = \frac{T_{L(SiX_4)}}{T_{L(CX_4)}} \frac{\left(4 V_{X(C)} + {}^{16}/_3 \, \Delta_X + 4 \Delta_X + V_{Si} + \dfrac{{}^4/_3 \, V_{Si} \, \Delta_X}{V_{X(C)}} \right)}{(4 V_{X(C)} + V_C)}$$

Instead of the α values we may, of course take the *R* values.

We will not use here the R_D^B values that we have earlier deduced. These were calculated with the aid of an estimated temperature coefficient. Here, however, it is better to compare two directly measured values with eachother. As the boiling temperature of the compounds in the *C* series vary little from those in the *Si* series (at most 36°, which gives a deviation of the order of magnitude of $4\,^0/_{00}$) and we are only concerned with the ratios of the α's we can take these values for any temperature, provided we use the same temperature for both substances. We choose for CF_4 and SiF_4 0° and borrow the values from Klemm and Henkel[1]. For CCl_4 and CBr_4 we take the values of our measurements at 20°. The values used for $SiCl_4$ and $SiBr_4$ are taken from Fajans and Joos[2]. The F values are found in the gaseous state (we use them in absence of better data). The Cl and Br values are compared in the liquid state, as is rational, as we try to determine the corrections to the Kopp volumes, which hold for the liquid state.

The quotient $\frac{\alpha_{I(Si)}}{\alpha_{I(C)}}$ unfortunately never can be determined because both CI_4 and SiI_4 are solid at 20° and very unstable above their melting point.

The expression $\frac{\alpha_{I(Si)}}{\alpha_{I(C)}}$ is chosen here equal to 1.025 found by extrapolation of the expressions $\frac{\alpha_{Cl(Si)}}{\alpha_{Cl(C)}}$ and $\frac{\alpha_{Br(Si)}}{\alpha_{Br(C)}}$. The last are 1.06 and 1.045 respectively. On the basis of the ionic radii of Cl, Br and I 1.81, 196 and 2.18 Å respectively, we can estimate $\frac{\alpha_{I(Si)}}{\alpha_{I(C)}}$ about 1.025 by graphic extrapolation (fig. 3).

We see, thus, that $\frac{\alpha_{X(Si)}}{\alpha_{X(C)}}$ increases regularly from *I* to *F*.

We now find:

	$\alpha_{X(C)}$	$\alpha_{X(Si)}$	$T_{L(CX_4)}$	$T_{L(SiX_4)}$	$V_{X(C)}$	$C = 9.33 + \frac{4\,V_{Si}}{3\,V_{X(C)}}$
F	1.81	2.07	146	150	11	13.09
Cl	6.60	7.01	349	330	22.8	11.15
Br	9.74	10.2	462	426	29.1	10.75
I	$\frac{\alpha_{X(Si)}}{\alpha_{X(C)}} = 1.025$		624	564	39	10.39

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[1] W. Klemm and P. Henkel, Z. anorg. allgem. Chem. **213**, 115 (1933).

[2] K. Fajans and G. Joos, Z. Physik **23**, 1 (1924).

From this we can now calculate Δ_X and find

$$\begin{aligned}\Delta_F &= -\ 0.3_2\\ \Delta_{Cl} &= -\ 0.0_3\\ \Delta_{Br} &= +\ 0.3_3\\ \Delta_I &= +\ 0.6_8\end{aligned}$$

We must not attach to much value to these Δ's as there are various sources of error. In the first place $\alpha_{Br(C)}$ is determined in solutions of CBr_4, while applying the mixture law (see Chapter VI) and $\alpha_{I(C)}$ is not obtained from direct measurement but by a process of extrapolation (see p. 128). Another cause of error is that we have here worked with the refraction values of the *Na-D*-line, which, however, probably does not make much difference in the ratio considered. In the third place we may doubt the correctness of the refraction value for C^{++++} and Si^{++++}, as given by Fajans and Joos. We have already commented upon this

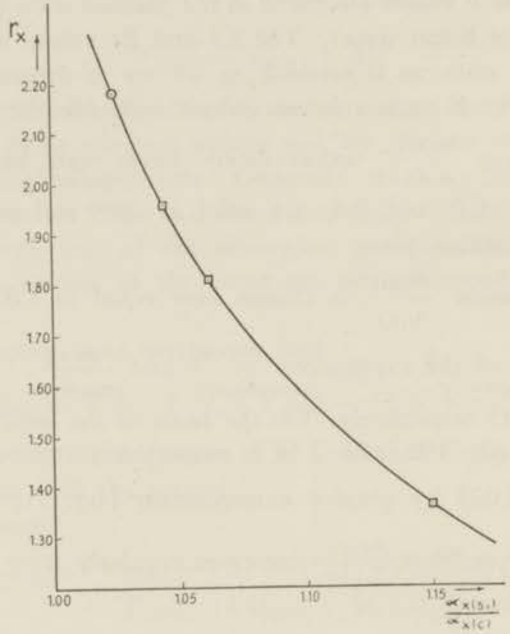

Fig 3.

(p. 42). Finally, a very small error arises from the breaking of the development in a series. Of all these sources of error the first is probably the most serious, but in spite of everything it is very remarkable how these refraction values, derived from very different authors, all lead to the same course in the Δ_X values. The absolute value of Δ_X cannot be determined in this way, as the Kopp values of C and Si are not known exactly. An error in these Kopp values gives rise to about the same error in the absolute values of Δ_X. We can, however, obtain these wanted absolute values by the following reasoning:

If we calculate the values of $\frac{\alpha_{X(Si)}}{\alpha_{X(C)}}$ we see, that these diminish from F towards I. This is quite natural, as the refraction of an halogen ion, when the field becomes larger (transition to a smaller central ion) will become smaller, and relatively less, the larger the refraction was already. (An ion that is strongly polarized will not easily be polarized further.) Our hypothesis is this: the specific volume of a halogen ion will be greater the stronger the field in which it lies and the relative change in volume will be greater as the relative change of the field is greater. Now $\frac{\alpha_{X(Si)}}{\alpha_{X(C)}}$ is a measure of the relative change of the field.

In SiI_4 and CI_4, the I ions are found in practically the same field. The volume of I will thus be the same in both compounds so that we can say $\Delta_I = 0$. From this follows:

$$\begin{aligned} \Delta_I &= 0 \\ \Delta_{Br} &= -0.3 \\ \Delta_{Cl} &= -0.7 \\ \Delta_F &= -1 \end{aligned}$$

From this we can calculate the volume of the halogen ions in Si derivatives

$$\begin{aligned} V_I &= 39 \\ V_{Br} &= 28.8 \\ V_{Cl} &= 22.1 \\ V_F &= 10 \end{aligned}$$

and according to the above $\frac{\alpha_{X(Si)}}{\alpha_{X(C)}}$ and $\frac{V_{X(C)}}{V_{X(Si)}}$ must follow the same course, as is indeed found to be the case

	$\frac{\alpha_{X(si)}}{\alpha_{X(c)}}$	$\frac{V_{X(c)}}{V_{X(si)}}$
F	1.15_0	1.10
Cl	1.06_2	1.03
Br	1.04_5	1.01
I	1.02_5	1.00

As we see, the changes from Cl to Br and from Br to I are small, and of the same order of magnitude, while the change from F to Cl is larger and also of the same order.

In general the dispersion in $\frac{\alpha_{X(si)}}{\alpha_{X(c)}}$ is larger than in $\frac{V_{X(si)}}{V_{X(c)}}$, thus polarizability is more „sensitive" to changes of the field than the volume. Finally, it is possible that $\frac{V_{I(c)}}{V_{I(si)}}$ is actually greater than 1, for instance 1.02 which could make the agreement of the tables even better.

According to Biltz the most polarizable ion will undergo the greatest deformation, and thus the relative change of volume in the I ions will be greater than in the F ions for instance. The order in which the polarizability decreases is

I Br Cl H[1]) F[1])

and according to Biltz, the volume of the hydrogen should be then only slightly variable, which is certainly contrary to the facts. We give, however, the following series in preference to Biltz:

H F Cl Br I

This is the order of increasing size of the ions. The internal forces decrease in passing from H to I.

The hydrogen ion is the most variable ion which is a well known fact (cf. the volume of CH_4, LiH and CsH with those of the resp. fluorides), while in F to I according to the theory developed above the relative change of volume decreases. We may say in general, that the smallest ion undergoes relatively the greatest change of volume.

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[1]) The polarizabilities of F and H in methane derivatures are about the same. For F the deviations from the standardvalue are very small, for H these deviations are much larger (cf. Chapter V). Generally the polarizability of H is larger than the standard value of F (for example CHI_3), in some cases, however, it is smaller (for example CH_4).

The theory of this effect developed below, moreover, demands this.

The change of volume and polarizability, run in opposite directions. It must, therefore, be considered as accidental that in methane derivatives the polarizability is proportional to the $^5/_3$th power of the volume of the halogen ions. If we turn to the Si, Ge and the remaining tetrahedral derivatives we know that α increases for all halogen ions, and for F relatively to the greatest extent.

According to the above V_X decreases and also relatively to the greatest extent for F. It is obvious that $A\,(E)$ values given by the equation

$$\alpha = A\,(E)\, V^{5/3}$$

will slowly increase in iodides and rapidly in the fluorides in a transition from light to heavier central ions.

We always calculate, however, $A\,(E)$ as $\frac{\alpha}{r^5{}_X}$, by which the course of $A\,(E)$ remains the same, though not as striking as in the case, that we had taken $V_X^{5/3}$ in the denominator, considering that r_X^5 is a constant quantity.

Our postulate is, that in a smaller field the volumes of the halogen ions are smaller too. This can easily be seen in the following way and the theory teaches, that it is just the relation between volume and polarizability which is essential.

When the polarizability is greater, the London attraction between two ions, will be greater too and the state of equilibrium with the repulsive forces will be reached, at a smaller distance between the two ions. The specific volumes of the ions, thus, seem to be smaller. It is clear, that the effect will be the greater, the more α is increased relatively. For this reason, we may expect, that the changes in the volume will be the greatest for F ions.

When passing from the C to the Si series, the distance from the central ion to the centre of the anions increases. The field, therefore, decreases, and as a consequence of this the polarizability increases and the specific volume of the ion decreases. It is obvious, that according to this theory, the contraction in the case of a strong external field ,is not only due to the decrease of the volume of the intermolecular space. In fact, the external field counteracts the field of the central ion which causes the effect, described above, and in this way it can be seen ,that in the case of a strong external field the contraction is due mainly to the decrease of the volume of the intermolecular space, but also to a decrease of the volumes of the ions.

How is it, that C has such a small Kopp volume compared to Si while they lie in practically the same cavity? The Kopp volume of C and Si is nothing but the non-polarizable portion of the material. In the first place we have to remember that in the case of the least polarized ions a much larger cavity remains than in the more polarised ones.

We give here a schematic drawing (fig. 4 and 5) (in one plane with 3 halogen ions, which has no essential consequence). From this the great difference between the cavity of Si and C is immediately seen. In the second place in consequence of the greater size of the silicon derivatives the intermolecular space will also be much greater. This is of course the main effect.

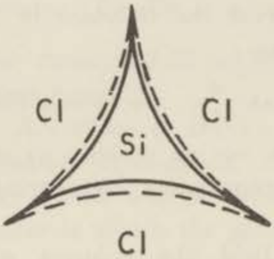

Fig. 4.

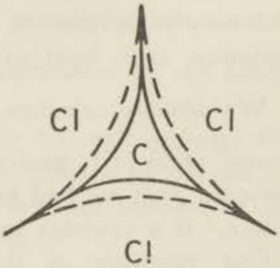

Fig. 5.

The course of the Δ_x is also found by Biltz[1]) and co-workers. They found the zero volumes of halides and chalcogenides respectively of a particular element to lie approximately on a straight line, when plotted against the volumes of the potassic halides and it is of general application, that with an increase of the atomic number of the positive ion in a particular vertical column of the Periodic system the molecular volume rises more rapidly from the fluorides to the iodides. All this only holds if we keep the same coordination of the positive ion.

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[1]) W. Biltz, Raumchemie der festen Stoffe, 1934.

We may now apply this to the C and Si derivatives. We first calculate the differences between the zero volumes of the carbon and silicon series Δ and multiply them by 1.41, to make them comparible to the boiling point volumes.

We obtain in this way $4\,\Delta_X$ added to a certain constant, which is due to the difference of the Kopp volumes of silicon and carbon.

We find:

	$V_{0(CX_4)}$	$V_{0(SiX_4)}$	Δ	$\underbrace{1.41\,\Delta = 4\,\Delta_X + C}$	$4\,\Delta_X$	Δ_X	Δ_X'
AF_4	42.5	47.7	5.2	7.3	—7.8	—2.0	—1.0
ACl_4	74.6	83.1	8.5	12.0	—3.1	—0.8	—0.7
ABr_4	88.4	98.8	10.4	14.7	—0.4	—0.1	—0.3
AI_4	111	121.7	10.7	15.1	0	0	0

Δ_X' is the value earlier found from refraction data. The agreement is satisfactory, when we remember, the uncertainty of the V_0 values. Only Δ_X and Δ_X' calculated for the case of F do not agree. As we have already seen SiF_4 is the only molecule that is not completely screened. The central ions exercise an influence upon the anions of other molecules and the SiF_4 lattice will therefore not be a „pure" molecule lattice, but will be more tightly packed than CF_4, so that Δ_F calculated from the Biltz volumes comes out too small. These peculiarities again indicate the SiF_4 is not completely screened. The difference in volume for F calculated from the refraction data is therefore probably correct, as we have calculated it with the aid of the T_L value found for SiF_4 and not of the T_S value.

C. The relation between cohesion energy and polarizability of derivatives of Titanium, Zirconium, Hafnium and Thorium.

Refraction data of Titanium derivatives are restricted to $TiCl_4$. At 18° it shows a refraction for the *Na-D*-line of 37.29 [1]).

With $R_{Ti} = 0.6$, according to Fajans and Joos [2]) we calculate for R_D (Cl): 9.17 which is higher than the value for the

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[1]) A. Stiefelhagen, Thesis 1905, Berlin.

[2]) cf. K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

free ion 9.07. This may be due to the great dispersion of $TiCl_4$.

We now assume for a moment, that $TiCl_4$ has no interaction. With a value R_D (Cl) = 9 we can calculate about the A (E) value. We find $A(E) = 0.183$. By assuming a boiling point volume $V_S = 1.41\ V_0$ ($V_0 = 86.1$ according to Biltz) the specific volume of the Cl ions may be calculated from the boiling point (409°). We find from:

$$T_S = k_2 \{ A(E) \}^2 \frac{\{ \Sigma V_{Cl} \}^2}{V}$$

for $V_{Cl(Ti)}$ a value 19.8. This agrees admirably with our hypothesis, that with decreasing field the specific volume of the ions becomes less. We have therefore for the volume of the Cl ion in the C, Si and Ti series 22.8, 22.1 and 19.8 respectively. The refractions increase in this direction: 6.61, 7.14 and 9. We see that the last change is the largest.

In theory it is now possible to calculate from this the Kopp volume for Ti. We find $V_{TiCl_4} - 4\ V_{Cl(Ti)} = 42$. But too many uncertainties have gradually been introduced to consider the values for $V_{Cl(Ti)}$ and especially V_{Ti} as very accurate.

There are no refraction data known for TiF_4, $TiBr_4$ and TiI_4, as these substances are solid at 20° so that we cannot calculate A (E). Further V_X is not known and V_{Ti} only very inaccurately, so that we can draw no further conclusions here.

For the boiling points we find in literature:

TiF_4	557
$TiCl_4$	409
$TiBrCl_3$	427
$TiBr_2Cl_2$	449
$TiBr_4$	503
TiI_4	633

TiF_4 as might be expected shows a considerable interaction, the series $TiCl_4$, $TiBrCl_3$, $TiBr_2Cl_2$ have approximately additive boiling points which, however, do not agree with the boiling point of $TiBr_4$. There is some doubt whether Friedel and Guérin[1]) who

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[1]) C. Friedel and J. Guérin, Compt. Rend. **81**, 889 (1875), Ann. chim. phys. (5), **8**, 24 (1876).

prepared $TiBrCl_3$ and $TiBr_2Cl_2$ really had pure substances to deal with, and not a mixture of $TiCl_4$ and $TiBr_4$ [1]).

On the other hand, however, we must not forget, that $TiCl_4$ forms complexes, for instance $(NH_4)_2TiCl_6$ is known. This proves that $TiCl_4$ has an interaction. When we consider $TiBr_4$ and $TiBr_2Cl_2$ as completely screened and, moreover, the boiling point of $TiBr_2Cl_2$ as correct, we find for the London contribution to the boiling points of $TiBrCl_3$ and $TiCl_4$ 422° and 395° respectively. $TiCl_4$ should have an interaction, to which corresponds 14° in the boiling point.

This gives only a very small correction in the found $V_{cl(Ti)}$ value and it is of no use to recalculate it, as the value earlier found is very uncertain.

Not much can be said about the remaining elements in the principle series in the 4th column of the Periodic system. All halides of *Zr*, *Hf* and *Th* are solid at 20°. There is nothing known about the Kopp values either.

The following table is very instructive, giving the zero volumes according to Biltz [2]) of the compounds AX_4, in which A is an element of the principle series. The boiling points volumes are proportional to them.

A	C	Si	Ti	Zr	Th
AF_4	42.5	47.7	40	37	—
ACl_4	74.6 →	83.1	86.1	82.5	81
ABr_4	88.4 →	98.8 →	102	—	96.5
AI_4	111 →	121.7 →	126	—	—

The normal increase (from C to Si ± 10, from Si to Ti ± 4) is indicated by the arrows. For the chlorides these values are somewhat smaller for the iodides somewhat larger, owing to the specific volume effect described in Chapter II B.

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[1] cf. J. W. Zwartsenberg, thesis to be published, Leiden.

[2] W. Biltz, Raumchemie der festen Stoffe, Leipzig 1934, p. 32.

The difference between CCl_4 and $SiCl_4$, CBr_4 and $SiBr_4$, CI_4 and SiI_4 is mainly caused by the difference of the Kopp volumes of C and Si. In the case of CF_4 and SiF_4 we find only a difference of about 5 and this indicates a contraction effect.

At the dotted line the interaction begins to occur. If we go to the right V_0 finally becomes smaller, inspite of the fact that the central ion becomes larger. TiF_4 and all the halides of Zr, Hf and Th all boil very high. They have a strong electrostatic interaction. They can be well described as coordination lattices.

As we see, SiF_4 and perhaps $TiCl_4$ although not so conspicuously, belong to the kind of compounds too, of which the molecules are not completely screened.

D. The relation between cohesion energy and polarizability of Germanium derivatives.

Only three of the compounds of Germanium and halogens are properly known in regard to their refraction, namely GeF_4, $GeCl_4$ and $GeBr_4$. Klemm and Henkel[1]) found for the refraction of GeF_4: $R^{\circ}_D = 10.2$, or according to our temperature correction $R^{\beta}_D = 10.14$.

There are several measurements of $GeCl_4$. We shall reduce them to 30° as at this temperature there are reliable density determinations. The values by Roth and Schwartz[2]) for the refraction index n_D extrapolated to 30° yield 1.4605, by Laubengayer and Tabern 1.4590, while Miller gives for n_D^{30} 1.4573.

We take 1.4590 as the correct value. For the density d_4^{30} Sidgwick[3]) gives 1.8443 and Miller 1.8533. With d_4^{30} 1.849 we find for R_D^{30}: 31.70 and applying our temperature cor-

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[1]) W. Klemm and P. Henkel, Z. anorg. allgem. Chem. **213**, 115 (1933).

[2]) W. A. Roth and O. Schwartz, Landolt—Börnstein, Physikalisch-Chemische Tabellen, I Erg. Band, p. 526.

A. W. Laubengayer and D. L. Tabern, J. Phys. Chem. **30**, 1047 (1926).

J. G. Miller, J. Am. Chem. Soc. **56**, 2360 (1934).

[3]) N. V. Sidgwick and A. W. Laubengayer, J. Am. Chem. Soc. **54**, 948 (1932).

J. G. Miller, loc. cit.

rection $R_D^B = 31.88$. This value is very uncertain as neither n_D^{30} nor d_4^{30} are properly known.

By extrapolation of the values of Dennis and Hance[1]) we find for $GeBr_4$ for n_D^{30}: 1.6240. Sidgwick[2]) gives $d_4^{30} = 3.1002$. From this we calculate the molecular refraction of $GeBr_4$ $R_D^{30} = 44.68$ and $R_D^B = 45.37$.

The difficulty now is, that we do not know the amount of the refraction contribution of the central Ge ion. This ion has not a rare gas structure and it cannot therefore be directly calculated, according to Fajans and Joos[3]). We know, that it must be greater than the value of Ti for which Fajans and Joos give 0.6. Ti is namely the corresponding element in the Periodic system of the principle series. The Ge ion is almost of the same size as the Si ion; the ionic radii are 0.44 and 0.41 Å respectively. We shall assume for a moment that the volumes of the halogens in the Si and Ge series are the same; then we may write

$$\alpha_{X(Ge)} = \alpha_{X(Si)} \sqrt{\frac{T_{L_{GeX_4}} V_{GeX_4}}{T_{L_{SiX_4}} V_{SiX_4}}}.$$

The Kopp volume for Ge is not known, so that V_{GeX_4} cannot be calculated. By the relation $V_S = 1.41\,V_0$ we can write $\frac{V_{0GeX_4}}{V_{0SiX_4}}$ for $\frac{V_{GeX_4}}{V_{SiX_4}}$ and so use the Biltz volumes. We now calculate from the data

	$\alpha_{X(Si)}$	$T_{L_{GeX_4}}$	$T_{L_{SiX_4}}$	$V_{0_{GeX_4}}$	$V_{0_{SiX_4}}$
Cl	7.14	358	330	84.3	83.1
Br	10.32	458	426	102.9 [4])	98.8

$\alpha_{Cl(Ge)} = 7.49$ and $\alpha_{Br(Ge)} = 10.92$.

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[1]) L. M. Dennis and F. E. Hance, J. Am. Chem. Soc. **44**, 299 (1922).

[2]) N. V. Sidgwick and A. W. Laubengayer, J. Am. Chem. Soc. **54**, 948 (1932).

[3]) K. Fajans and G. Joos, Z. Physik **23**, 1 (1924).

[4]) Biltz gives for $V_{0_{GeBr_4}}$ about 100. We have calculated $V_{0_{GeBr_4}}$ from $V_{0_{GeCl_4}}$ by adding

$$4\,\frac{V_{Br(Ge)} - V_{Cl(Ge)}}{1.41} = \frac{4 \times 6.7}{1.41} = 18.6$$

From this we can calculate the contribution of the refraction of the Ge ion in $GeCl_4$ and $GeBr_4$. We find 1.92 and 1.69 respectively. These results may be considered to agree well, if we remember, that the refraction values of $GeCl_4$ and $GeBr_4$ are not known very accurately and, moreover, that the polarizability of the central ion is variable, especially those, which are themselves fairly well polarizable. We shall take as mean value about 1.8. We can calculate from this the contribution to the refraction of the F ion in GeF_4 as about 2.1. We thus find in compounds GeX_4 for the refraction of

F	2.1
Cl	7.49
Br	10.92

We can now calculate the $A\ (E)$ value by two methods.

I. By applying the formula

$$A\ (E) = 0.0651 \frac{\sqrt{T_L V}}{V - V_{Ge}}$$

II. By applying of the formula

$$A\ (E) = \frac{3 \times 10^{24} R^{B}_{D}\ (X)}{4\,\pi N r^{3}_{X}}$$

from the data

	T_L	V	$V - V_{Ge}$	$R^{B}_{D}\ (X)$	r_X
F	—	—	—	2.1	1.36
Cl	358	119.4	88.4	7.49	1.81
Br	458	146.2	115.2	10.92	1.96
I	633	187	156	—	—

we calculate

	$A\ (E)$ I	$A\ (E)$ II
F	—	0.178
Cl	0.152	0.152
Br	0.146	0.148
I	0.144	—

This indicates that $GeCl_4$, $GeBr_4$ and GeI_4 are completely screened, which is probable as no complexes of these compounds are known. There is no interaction. In GeF_4 we must expect that there will be interaction. We can now calculate the boiling point contribution purely due to the London energy of the F ions. We then find

$$T_L = k_2 \frac{\{A\,(E)\ (V - V_{Ge})\}^2}{V}$$

$$T_L = 236\ \frac{(0.178 \times 40)^2}{71} = \text{about } 168°.$$

As A (E) here is determined with little accuracy, it has no meaning to correct this value here for the difference between A (E) I and A (E) II for fluorides (cf. p. 42 and 71). GeF_4 has no boiling point but a sublimation point at + 238° K.

By extrapolating the line of the undercooled liquid to 1 atm. in the p-T diagram for GeF_4 constructed by Dennis[1]), a theoretical boiling point of about 210° is found.

The interaction in GeF_4 is thus 42° and greater than in the case of SiF_4. This was to be expected as, on one hand the Ge ion is larger so that it will be less screened and on the other hand the polarizability of the Ge ion is much greater than of the Si ion which may be the cause of a greater interaction too. Further, we can now calculate the refraction of the ion in GeI_4. This will be

$$R_D\ (\text{I}) = \frac{4\,\pi N\,A(E)\ r_I^5}{3 \times 10^{24}} = 18.00.$$

Quite recently the research by Booth and Morris[2]) has made known the boiling points of GeF_3Cl, GeF_2Cl_2 and $GeFCl_3$ so that we can give now the complete list

	T_S	T_L	T_M
GeF_4	(210)	168	42
GeF_3Cl	253	215.5	37
GeF_2Cl_2	270	263	7
$GeFCl_3$	311	310.5	0
$GeCl_4$	358	358	0

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[1]) L. M. Dennis and A. W. Laubengayer, Z. physik. Chem. 130, 520 (1927).

[2]) H. S. Booth and W. C. Morris, J. Am. Chem. Soc. **58**, 90 (1936).

By the aid of our calculated T_L value for GeF_4 we can calculate the T_L values for the mixed compounds containing Cl and F (3rd column). For this aim we must take $T_F = 42$. From this we see that in $GeFCl_3$ there is no interaction. GeF_2Cl_2 has a weak interaction (7°), perhaps this value is due to errors. GeF_3Cl causes an interaction which accounts for 37° of the boiling point. This value is smaller than in GeF_4 (42°) as was to be expected.

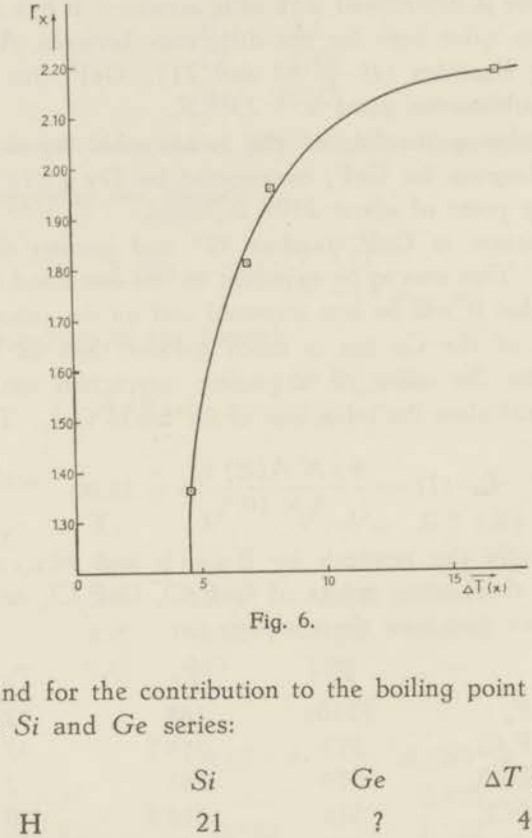

Fig. 6.

We found for the contribution to the boiling point of a halogen ion in the *Si* and *Ge* series:

	Si	*Ge*	$\Delta T\ (X)$
H	21	?	4.5
F	37.5	42	4.5
Cl	82.5	89.5	7
Br	106.5	114.5	8
I	141	168	17

The difference ΔT decreases from I to F and by taking $\Delta T(H) = 4.5$ (found by graphic extrapolation (fig. 6)) we can estimate the boiling point contribution of an H ion in the Ge series. We find thus 25.5°. The boiling point of various Ge derivatives containing hydrogen are known. They were determined by Dennis and co-workers[1]). The results are to be found in the following table. Here we give the calculated T_L values too.

	T_S	T_L (calc.)	$\Delta = T_D + T_M$	T_D	T_M
GeH_3Cl	301	166	135	75	60
GeH_2Cl_2	343	230	113	79	34
$GeHCl_3$	348	294	54	40	14
GeH_3Br	325	191	134	75	59
GeH_2Br_2	362	280	82	79	—

The Δ's (fourth column) are due both to dipole action and to interaction.

In the completely halogenated F containing Ge derivatives there is no dipole action. The differences calculated are therefore due entirely to interaction. We find for the interactions

A	AX_2F_2	AXF_3	AF_4
C	0	0	0
Si	0	10	28
Ge	0 X = Br) (X = Cl)7 ?	37	42

In the C series the dipole action is well known. We find for

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[1]) L. M. Dennis, W. R. Orndorff and D. L. Tabern, J. Phys. Chem. **30**, 1049 (1926).

L. M. Dennis and P. R. Judy, J. Am. Chem. Soc. **51**, 2321 (1929).

compounds with three H ions 81°, with two H ions 85° and with one H ion 45°.

For the Si derivatives we now find for Δ

	$\Delta = T_D + T_M$	
SiH_3Cl	97.5	101.5
SiH_3Br	105.5	
SiH_2Cl_2	74	79
SiH_2Br_2	84	
$SiHCl_3$	37.5	40
$SiHBr_3$	42.5	

(cf. Table on p. 33).

We see, that the dipole actions in SiH_2X_2 and $SiHX_3$, are of the same order of magnitude as in the corresponding C derivatives. We have already shown, that these compounds have no interaction. In SiH_3Cl and SiH_3Br we should expect interaction. We assume here also a dipole action, which is 6° lower than in the C derivatives, thus 75°. We find therefore, for the interaction in compounds of the SiH_3X type, if X is a „large" atom $101.5° - 75° = 26.5°$. In Chapter II A we found for this interaction by a quite different method 33°, which we may consider in agreement with this value, as both calculations have a very uncertain character. As mean value we take for $T_M = 30°$.

This agrees with the interaction that we found in SiF_3X which is of the order of magnitude of 10°.

We know nothing at all about the T_D values in hydrogen containing Ge compounds. Considering, that with the very great change from the carbon to the silicum derivates the dipole action hardly changes at all, we will take the dipole contribution of the Ge derivatives to be the same as in the Si derivatives, seeing that the transition from Si to Ge is only quite small (fifth column of the table on p. 63). By subtracting this from the Δ values we find the interaction T_M in the Ge derivatives (sixth column).

We can now draw up the following table for the interactions

A	AHX_3	AH_2X_2	AH_3	AH_4
C	0	0	0	0
Si	0	0	30	77
Ge	0 (X = Br)	(X = Cl) 34	60	81

The interaction in GeH_4 can be simply calculated from its boiling point (183°)[1] diminished by 4 × 25.5°.

We may consider the found interaction of $GeHCl_3$ (14°) as having no physical meaning, considering the many sources of error which influence these calculations and the fact, that the boiling point of $GeHCl_3$ is determined by extrapolating the vapour pressure temperature curve. We may conclude that 3 „large" ions are sufficient to screen the Ge ion completely.

The interaction in GeH_4 is slightly greater than SiH_4 and much larger than in GeF_4 and SiF_4, in the former of which it is slightly larger than in the latter. At the introduction of „large" halogen ions the interaction decreases, more rapidly in the Si than in the Ge series. This agrees with the fact, that Ge is greater than Si. Apparently in Si two „large" ions are sufficient to ensure complete screening. In the Ge series it is very remarkable, that 2 Cl ions do not provide complete protection, but 2 Br ions do. In GeF_2Cl_2 the interaction is so slight that in GeF_2Br_2 we can assume an interaction 0.

Remembering all this, it seems of some interest to investigate the complex formation of mixed Ge derivatives.

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[1] R. Schenk and A. Inker, Ber. **58**, 271 (1925).
R. B. Corey, A. W. Laubengayer and L. M. Dennis, J. Am. Chem. Soc. **47**, 112 (1925).

E. The relation between cohesion energy and polarizability of Tin derivatives.

The refraction of the Sn derivatives have been measured in the gaseous state by Hölemann and Goldschmidt[1]. We can calculate the values of the refraction at the boiling point with the usual temperature correction. SiI_4 gives an uncertain value as we find absorbtion lines in the blue and green areas of the spectrum.

	measurement temperature	T_s	R_D	R_D^B	$4R_D^B(X)$	$R_D^B(X)$
$SnCl_4$	473	386	35.94	35.6	32.9	8.2
$SnBr_4$	633	475	50.19	49.4	46.7	11.7
SnI_4	613	613	78.4	78.4	75.7	18.9

Here we assume for $R_{Sn} = 2.7$.

This value can be calculated as follows. According to Fajans and Joos' method[2] to determine the refraction for the *Na-D*-line we find for Zr the value 1.2.

Ge shows a refraction that is about 2.25 times as large as the refraction calculated for the free ion of the element in the same division of the Periodic System in the principle series viz: Ti.

The value for Sn will thus be about $2.25 \times 1.2 = 2.7$.

The specific volumes are difficult to estimate. Moreover SnI_4 certainly shows interaction as Rb_2Sn_6I and Cs_2SnI_6 are known. Li_2SnI_6, Na_2SnI_6 and K_2SnI_6 are not known, this is probably due to energetic causes[3].

Of $SnCl_4$ and $SnBr_4$ complexes are known so that here there is also interaction. It is therefore impossible to determine the Kopp volume for Sn as even SnI_4 must show an extra contraction due to interaction.

The effect of interaction is also clearly evident in the zero

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[1] P. Hölemann and H. Goldschmidt, Z. Physik. Chem. B 24, 199 (1934).

[2] K. Fajans and G. Joos, Z. Physik 23, 1 (1924).

[3] A. E. van Arkel and J. H. de Boer, La valence et l'Electrostatique, Paris 1936, p. 218.

volumes of the halides of the elements of the subordinate series of the Periodic System, as may be seen from the following table [1]:

A	C	Si	Ge	Sn	Pb
AF_4	42.5	47.7	46.4	40	—
ACl_4	74.6	83.1	84.3	89.7	92
ABr_4	88.4	98.8	100	105.6	—
AI_4	111	121.7	124	131.9	—

Only the F series shows a maximum, in the other series the increase of the contraction is less than the increase of the Kopp volume of the central ion. At the dotted line the interaction begins to occur.

In literature we find various mixed halogenated Si derivatives $SnClBr_3$ [2], $SnBr_2Cl_2$ [2], $SnBrCl_3$ [2], $SnCl_2I_2$ [2], $SnCl_3I$ [2], $SnBr_3I$ [3], $SnBr_2I_2$ [3] and $SnBrI_3$ [3].

The boiling points are not very definite. It is doubtful whether we have here really well defined compounds [4].

F. The relations between cohesion energy and polarizability of Boron derivatives.

Klemm and Henkel [5] give for the bond refraction of F, Cl and Br in BF_3, BCl_3 and BBr_3 2.00, 6.99 and 9.98 respectively. According to Fajans and Joos [6] the refraction of the B^{+++} ion is 0.05 so that we find for the refraction per halogen ion for F: 1.98, Cl: 6.97 and Br: 9.96. If we apply the temperature correction, these values become F: 1.96, Cl: 6.97 and Br: 10.03. They lie between the values for these halogens in compounds

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[1] W. Biltz, Raumchemie der festen Stoffe, Leipzig 1934, p. 82.

[2] A. Besson, Compt. rend. **124**, 683 (1897).

[3] C. Lenormand, J. Pharm. Chim. [6] **8**, 249 (1898), **10**, 114 (1899).

[4] cf. J. W. Zwartsenberg, Thesis to be published later, Leiden.
B. Trumpy, Z. Physik **66**, 790 (1930).
A. Kastler, Rev. Gen. Sci. pur. et appl. **47**, 522 (1936).

[5] W. Klemm and P. Henkel, Z. anorg. allgem. Chem. **213**, 133 (1933).

[6] K. Fajans and G. Joos, Z. Physik **23**, 1 (1904).

CX_4 and SiX_4 so that we can estimate the unknown value of BI_3 by extrapolation.

X	CX_4	BX_3	SIX_4
F	1.67	1.96	2.04
Cl	6.64	6.97	7.14
Br	9.90	10.03	10.32
I	16.83	(16.90)	17.25

The halogen ions in the B series lie in a smaller field than the C series but in a larger one than the Si series. We see also that the relative increase in the B series is less than in the C and Si series so that the value 16.90 will be about right. By means of the formula:

$$A\,(E) = \frac{3 \times 10^{24}\, R_D^B(X)}{4\,\pi\, N\, r_X^5}$$

we can now calculate $A\,(E)$ and find

	F	Cl	Br	I
$A\,(E)$	0.166	0.142	0.137	0.135

We will now see if we can calculate $A\,(E)$ also by

$$A\,(E) = k_3\, \frac{\sqrt{T_S V}}{V - V_B}.$$

But we do not know how great the Kopp volume for B is. This can be calculated from the Biltz volume for V_0 by the formula $V_S = 1.41\, V_0$. We know that there is a particularly lively interaction in BF_3 (complex formation) so that we may expect a contraction (as in SiF_4); this value therefore should not be taken into consideration. We now find:

	V_0	V_S	V_X	$\Sigma\, V_X$	V_B	
BCl_3	64.2	90.5	22.4	67.2	23.3	$V_B = 22.2.$
BBr_3	77.0	108.6	29.1	87.3	21.3	
BI_3	98.6	139	39	117.0	22.0	

For V_{Cl} here 22.4 is taken as the Cl ion in the BCl_3 is submitted to a field, that lies between that of CCl_4 and $SiCl_4$ as is shown by the refraction values. For V_{Br} 29.1 is taken as the Br ion lies in practically the same field as in CBr_4.

We see that for V_B a practically constant contribution remains. We now apply the formula

$$A\,(E) = k_3 \frac{\sqrt{T_s V}}{V - V_B}$$

and find

	T_s	V	$V - V_B$	$A\,(E)$ I	$A\,(E)$ II	k_3
BCl_3	286	90.5	67.2	$2.394\,k_3$	0.142	0.0590
BBr_3	363	108.6	87.3	$2.274\,k_3$	0.137	0.0601
BJ_3	483	139	117	$2.215\,k_3$	0.135	0.0611

This shows 1° that k_3 is not constant 0.0651 but smaller and 2° that k increases from BCl_3 to BI_3.

This can easily be seen. We must assume that the molecules BX_3 are flat. This is shown by the fact, that these compounds, in any case BF_3 [1]) and BCl_3 [2]) have a dipole moment = 0. A structure examination by means of electron rays points to a flat configuration [3]).

Moreover these compounds satisfy the equality

$$Z_V = 3\,Z_0,$$

in which Z_V = the number of valency electrons $3 + 3 \times 7$ and Z_0 = the number of electrons of the complete rare gas shell of the anion (8). According to Zachariasen[4]), therefore, we must expect a highly symmetrical configuration. The BX_3 molecule may be approached, thus, by another molecule BX_3 in a direction about perpendicular to the plane in which the first BX_3 molecule lies, in such a way that a halogen ion of the second

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[1]) H. Braune and P. Pinnow, Z. physik. Chem. B **35**, 239 (1937).

[2]) R. Linke and W. Rohrmann, Z. physik. Chem. B **35**, 256 (1937).

[3]) H. Ulrich and W. Nespital, Z. Elektroch. **37**, 559 (1931). W. Nespital, Z. physik. Chem. B **16**, 153 (1932).

[4]) W. H. Zachariasen, J. Am. Chem. Soc. **53**, 2123 (1931).

molecule will be the closest to the B^{+++} ion of the first molecule (fig. 7). This may cause an extra contribution to the boiling point, making the T_L we took too high and the found k_3 too low. It is obvious that the effect is least in BI_3; the polarizability of the halogen ion X is about proportional to the 5th power of the ionic radius r_X, the distance to which the X ion can approach the B ion is proportional to r_X, thus the total action to

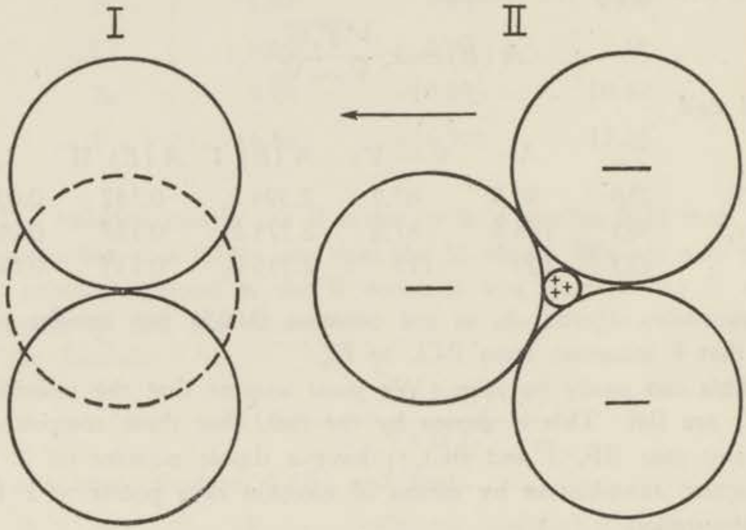

Fig. 7.

$$\frac{\sqrt{\varphi_X \alpha}}{r_X^6} = r_X^{-3/2},$$

in other words, in the case of the largest halogen ion the effect is the smallest. If we persue the calculation more precisely we must put

$$\alpha = A\,(E)\,r_X^5$$

in which $A\,(E)$ decreases from F to I, strengthening the course in the effect [1].

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[1] Here, and in the following calculations of Chapter II F we consider only the action between the cation of molecule I and the nearest anion of molecule II. As a simplification we neglect thus all other actions.

If we should conceive the interaction as purely Coulomb we get the same. The effect then goes with r_X^{-1}, we get an analogous course as in the case of London energy.

With the formula

$$T_L = 236 \frac{\{A\,(E)\ \ (V - V_B)\}^2}{V}$$

we can now ascertain what is the contribution to the boiling point of this interaction. We find

	$A\,(E)$	$V - V_B$	V	T_L (calc)	T_S (exp)	$T_P + T_M$
BF_3	0.161	30.6	52.8	109	172	63
BCl_3	0.142	67.2	90.5	238	286	48
BBr_3	0.137	87.3	108.6	311	363	52
BI_3	0.135	117	139	424	483	59

In this table for the $A\,(E)$ value of BF_3 we use 0.161 in connection with the fact that the $A\,(E)$ value calculated from the boiling point and the boiling point volumes give a better description of reality than those, calculated from the refraction data and in agreement with the fact that $A\,(E)$ values of F compounds calculated in the first way are about 0.05 lower than those calculated from the refraction. For V_F is chosen 10.2 as the fluorine ion lies here in about the same field as in SiF_4. It is found that the T_P values increase slightly from Cl to I. With T_P we indicate the contribution to the boiling point of flat molecules due to an action perpendicular to the plane of the molecule.

We can now extrapolate graphically (fig. 8) the T_P values to F and find for T_P for BF_3: 34°. 29° of the boiling point of BF_3 must be attributed to interaction in the old sense of the word, i. e. an action of the central ion and the halogen ions in the plane of the molecule. The boron ion would thus not fit into the cavity formed by three fluorine ions. Moreover, this is indicated by the fact that BF_3 is capable of forming complexes, but it is especially shown by the fact, that the molecular volume at the boiling point calculated is much larger than the experimental volume. This shows that a special contraction has taken place, which points to extra interaction. We calculate for BF_3 as molecular volume

52.8 and find from Biltz' values 47.0[1]). There is thus a contraction of 5.8 compared with the other halides of boron.

The T_P values decrease percentually from Cl to I. This explains why the k_3 values calculated increase. In absolute size, however, the T_P values increase. From this we may conclude, that for this perpendicular attraction effect the Coulomb and the London effect play a subordinate part. In these cases T_P will decrease from F to I. If the perpendicular attraction effect is regarded as the action of a boron ion upon the dipole μ induced in the halogen ion of molecule II the effect will follow a course proportional to

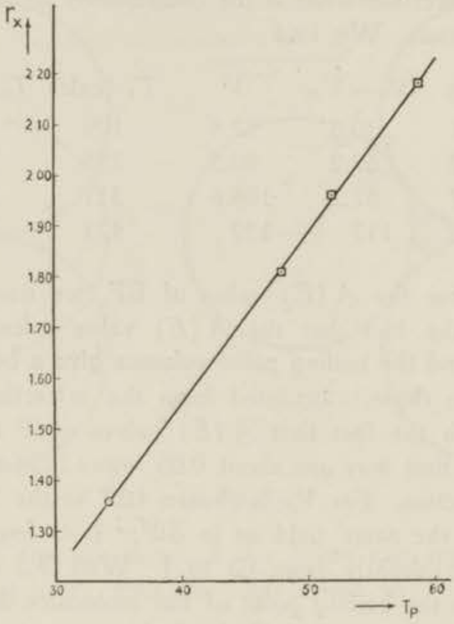

Fig. 8.

$$\frac{e\mu}{r_X^2} = \frac{e^2\alpha}{r_X^4} \sim A\,(E)\; r_X$$

$A\,(E)$ does not decrease as rapidly as r increases, and thus, when this effect predominates, T_P will increase somewhat, as here is actuelly seen.

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[1]) W. Biltz, Raumchemie der festen Stoffe, Leipzig 1934, p. 30.

The origin of the T_P values may thus be sought in three effects: the Coulomb attraction, the London attraction and the induced dipole attraction of the central ion of a flat molecule upon a halogen ion of another molecule in a sense about perpendicular to the plane of the molecule first considered. The first two influences decrease when the halogen ions become larger, the last increases in that case, and it is therefore impossible to predict beforehand, what will be the course of the T_P values.

On the other hand we may not draw conclusions from the course of the T_P values as to the nature of the perpendicular attraction effect. In the case in question T_P increases slightly with the size of the halogens and we might suppose that the third effect referred to, would be the most important. But such a conclusion is not allowable, as there are too many sources of error, giving a somewhat uncertain character to the calculation. Moreover, we must remember that in these flat molecules the polarizability is different in the plane of the molecule and perpendicular to it. With the refraction we measure only a sort of mean value. This may also disturb the calculation. Small deviations in T_L may be the cause that the course of T_P changes its sign.

In this connection it is interesting to call attention to the formula for the boiling point of completely halogenated ethylene derivatives. These molecules are also flat, the boiling points may be represented by

$$T_S = k\frac{(V - 2\,V_c)^2}{V} + T_P$$ [1]

in which $k = 4.39$ and T_P represents a constant equal to 66°.

The error is at most 3°. Van Arkel ascribes this T_P value to the effect of the partial dipoles, but considering the foregoing it is natural to conceive these values as the result of the perpendicular attraction effect.

We will now first compare this effect, with the effect of the central ion in normal cases, by which we mean those, in which there is no interaction.

For the present we will regard the perpendicular attraction effect as a London effect.

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[1] A. E. van Arkel, Rec. trav. chim. 51, 1081 (1932).

The molecule I (fig. 9) represents a BX_3 molecule, perpendicular to the plane of it (EF) another molecule II may approach, as drawn [1]).

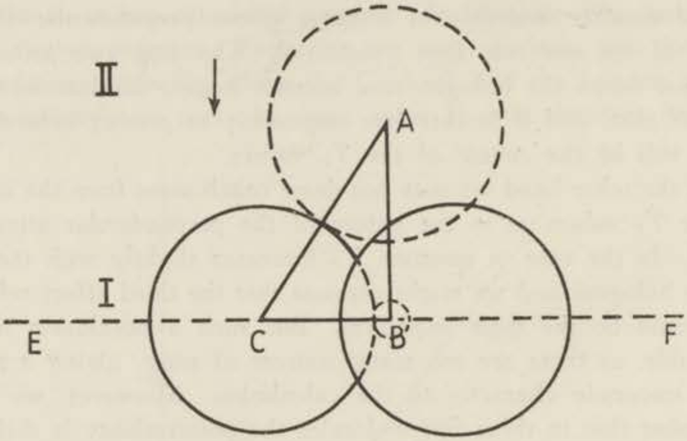

Fig. 9.

Now $AC = 2\,r_X$, $CB = 1.15\,r_X$ so that $AB \sim 1.6\,r_X$. The X ion can approach thus to a distance of about $1.6\,r_X$.

We now imagine a molecule II [1]) that approaches BX_3 in the

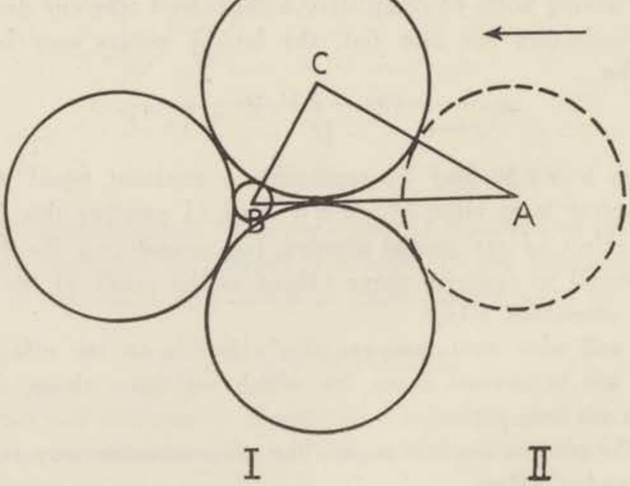

Fig. 10.

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[1]) Only one anion of molecule II is drawn.

plane of the considered molecule I (fig. 10). The distance AB is now much greater. ABC is again a rectangular triangle in which $\angle CAB = 30°$. $AC = 2\,r_X$, therefore $AB = 2.3\,r_X$. If we suppose, that the interaction of B and A is purely result of London attraction, the attraction in the plane of the molecule is only $\left(\frac{1.6}{2.3}\right)^6$ of the perpendicular attraction.

If the latter is of the order of magnitude of 45° in the boiling point (cf. p. 71) the attraction in the plane is then of the order of magnitude of 4°. Actually, however, it is much less. In the first case there may be a considerable electrostatic (= Coulomb + induction) attraction, which in the second case is screened off, as here the electrostatic field cannot penetrate. In the „completely screened" compounds (C derivatives, Si derivatives with Cl, Br, I etc.) the London influence of the central ion, therefore, is at most of the order of magnitude of a few degrees, so that in normal cases van Arkel and de Groot's calculation[1]), in which the London attraction of central ions is neglected, is completely justified.

We will further compare the perpendicular attraction effect of BF_3 with the interaction in SiF_4 and by comparing them together we will try to get a better insight into the nature of these effects. In the boiling points they are represented by 34° and 28° respectively. We should observe at once that in BF_3 and SiF_4 this means about $^1/_5$ and $^1/_6$ of the total boiling point, which makes it probable that London attraction is not the cause, considering the very small polarizability of the central ion. In BF_3 the distance at which the F ion of molecule II can approach the central ion of molecule I is $1.6\,r_X$ as we have already calculated. In SiF_4 we have a situation like fig. 11. EF is a plane through 3 F ions.

We know $DC = 1.6\,r_X$ and $BD = 1.15\,r_X$.

We can now take for $AB = 1.3\,r_X$ (cf. p. 27) from which follows $AD = 0.6\,r_X$, so that the distance $AC = 2.2\,r_X$. We take the interaction contribution to the boiling point as proportional to the interaction energy[2]).

The φ's of the B^{+++}-ion and of the Si^{++++}-ion are of the same

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[1]) A. E. van Arkel and W. de Groot, Physica **12**, 211 (1932).

[2]) cf. A. E. van Arkel, Rec. trav. chim. **52**, 719 (1933).

order of magnitude. We only know the ionization potential of the B^{+++}-ion, but a comparison of the various ionization potentials shows, that the φ's we need are of the same order of magnitude [1]); finally we must remember that in the following calculation we only need to use the root of φ.

Taking the $\sqrt{\varphi}$ values equal one to another and the radii of the F ions in both compounds too, the ratio of the energy due

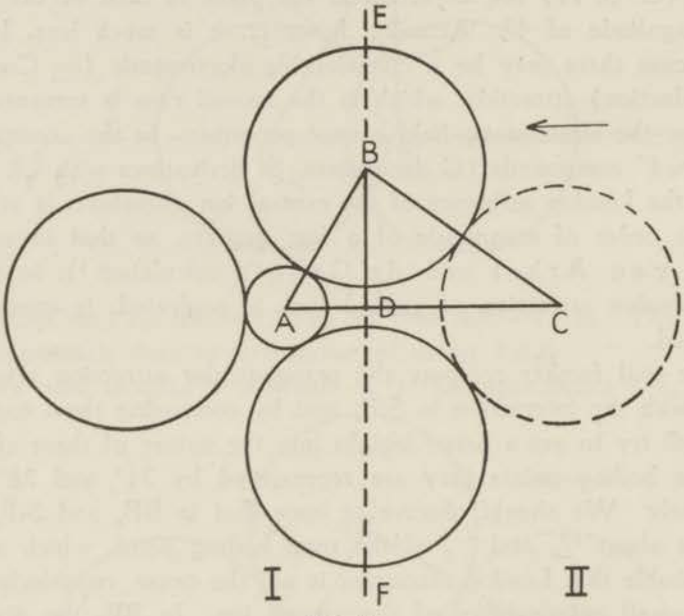

Fig 11.

to perpendicular attraction in BF_3 and the interaction energy in SiF_4 can be calculated. This is $\frac{0.05}{(1.6\,r_x)^6} : \frac{0.1}{(2.2\,r_x)^6} = 3.4$. The ratio of the contribution to the boiling point is of the order of magnitude 1.2 so that a predominating London effect may be rejected. If the effects are Coulomb ones we come to the ratio $\frac{3}{1.6\,r_x} : \frac{4}{2.2\,r_x} = 1.03$

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[1]) A. E. van Arkel and J. H. de Boer, La valence et l'Electrostatique, Paris 1936, p. 63.

if the effects are due to the attraction of the induced dipoles, the ratio considered becomes $\frac{9 \times 0.161}{(1.6\,r_X)^4} : \frac{16 \times 0.168}{(2.2\,r_X)^4} = 1.7$.

On the basis of this values we cannot decise about the nature of the effects. Probably both the Coulomb action and the induced dipole action occur. In SiF_4 the contraction enters into the boiling point volume. We have already shown, that non-Coulomb forces are not perceptable in the boiling point volume [1]).

But we must remember that the T_P values increase from BF_3 to BI_3, which indicates the occurrence of induced dipole action. The last agreement, however, is open to criticism, as we have shown above.

We may conclude, therefore, that the perpendicular action effect in BF_3 and the interaction in SiF_4 are not due to London forces, while it is probable that they are of an electrostatic nature, i. e. they are partially due to the Coulomb action, partially to induced dipole attraction.

It is known that BH_3 does not exist. We must here expect an unusually strong interaction, at any rate in the old sense of the word. Double molecules will be formed and thus B_2H_6 actually does exist.

Unfortunately similar reasoning cannot be applied to the halides of the other elements in the 3rd column of the Periodic system. Many of these substances are solid at 20° and even in the vapour double molecules are found. Ketelaar [2]) has shown that Al_2Cl_6 is so constructed, that we may suppose it to have arisen from two flat $AlCl_3$ molecules which approach eachother in a sense perpendicular to the plane of both molecules, while the Al ions are specially attached to one another. This would be a perpendicular attraction effect which, however, is certainly not electrostatic. This would lead us to suppose it quite possible that the perpendicular attraction

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[1]) The found contraction of BF_3 (cf. p. 72) is due to interaction in the plane of the molecule. If the perpendicular action is a Coulomb one, we may expect a contraction in all the halides of boron. This contraction may cause an error in the Kopp volume of boron, and thus, give our calculations a very uncertain character.

[2]) J. A. A. Ketelaar, Z. Krist. A. 90, 237 (1935).

effect in the B derivatives is of a different nature to what we have imagined hitherto.

We may further remark that AlF_3 will show a very great interaction. Therefore, it is much less volatile than $AlCl_3$: compare to this BF_3 which boils at a lower temperature than BCl_3[1]).

G. General remarks.

We have now determined the refraction of various halogen ions in different tetrahedral molecules and in the boron derivatives. The following table shows the results. To concentrate these in one figure, we have divided the refraction values by the value of the free ions R_0. The latter values are taken from Fajans'[2]) latest calculations. These values, unlike our values, cannot be reduced to the boiling point.

	R_F	R_{Cl}	R_{Br}	R_I	$\left(\frac{\alpha}{\alpha_0}\right)_F$	$\left(\frac{\alpha}{\alpha_0}\right)_{Cl}$	$\left(\frac{\alpha}{\alpha_0}\right)_{Br}$	$\left(\frac{\alpha}{\alpha_0}\right)_I$
C	1.67	6.64	9.90	16.83	0.68	0.74	0.78	0.87_6
B	1.96	6.97	10.03	16.90	0.80	0.77	0.79	0.88
Si	2.04	7.14	10.32	17.25	0.84	0.79	0.82	0.90
Ge	2.1?	7.49	10.92	18.00	0.86?	0.83	0.86	0.94
Sn	—	8.2?	11.7?	18.9?	—	0.90?	0.92?	0.98?
Ti	—	9 ?	—	—	—	1 ?	—	—
free ions	2.44	9.06	12.66	19.21	1.00	1.00	1.00	1.00

Figure 12 gives the course of $\frac{R}{R_0} = \frac{\alpha}{\alpha_0}$ (which we will call the reduced polarizability) with the ionic radius in various series.

We will now examine the general expression for the local electric force E in a halogen ion in a tetrahedral model.

According to the theory developed above, we must make a distinction between screened and not entirely screened molecules. We may join both cases as follows. We call the distance from the centre of the central ion to that of the halogen ion ρ thus

$$\rho = r_A + r_X$$

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[1]) A. E. van Arkel and J. H. de Boer, La valence et l'Electrostatisque, Paris 1936, p. 40.

[2]) K. Fajans, Z. physik. Chem. B 24, 103 (1934).

in which r_A is the radius of the cation and r_X the radius of the anion. In the case of complete enclosure

$$r_A = 0.225\, r_X.$$

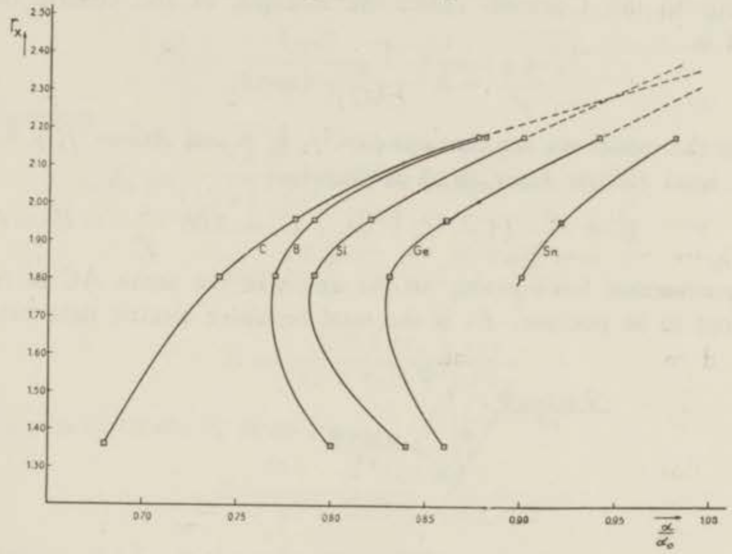

Fig. 12.

In the angles of a tetrahedron (fig. 13) we imagine the centres of rigid spheres, that represent the anions. We consider the dipoles

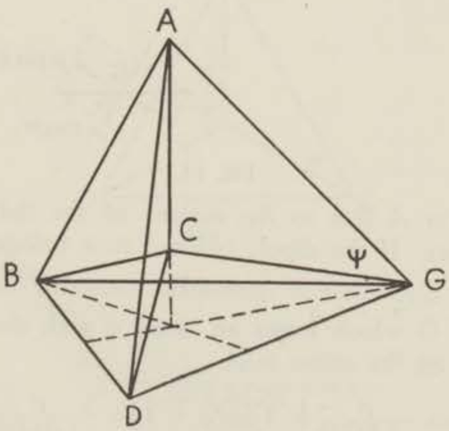

Fig. 13.

to be localized in these angles too. We take, thus, the dipole distance infinitely small. With this very simple model we now calculate the strength of field in A. Then $AC = \rho = r_A + r_X$. Owing to the Coulomb effect the strength of the electric field in A is

$$\frac{4\,e}{\rho^2} - 3\,\frac{e}{(AG)^2}\cos\psi.$$

From the model we see that $\cos\psi = {}^1/_3 \sqrt{6}$ and $AG = {}^2/_3\,\rho\,\sqrt{6}$. The total electric force in A is therefore

$$E = \frac{e}{\rho^2}\left(4 - {}^3/_8 \sqrt{6}\right) - E_T = 3.08\,\frac{e}{\rho^2} - E_T.$$

The attractive force acting on the anion in the sense AC is considered to be positive. E_T is the total repulsive electric field acting on the anion in A due to the actions of the induced dipoles in the other anions. If the dipole induced in a halogen ion is μ then

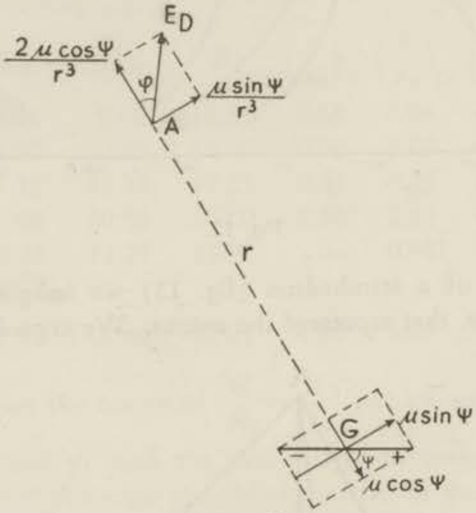

Fig. 14.

$$\mu = \alpha E.$$

A dipole μ in G which forms an angle ψ with the line AG gives a force acting on the anion in A

$$E_D = \frac{\mu}{(AG)^3}\sqrt{3\cos^2\psi + 1} = \frac{\mu}{(AG)^3}\sqrt{3}$$

E_D forms an angle φ with GA so that $\operatorname{tg}\varphi = \frac{1}{2}\operatorname{tg}\psi$ (fig. 14).

The vectors in the lower part of fig. 14 represent dipoles, those in the upper part the electric fields due to these dipoles.

Now

$$E_T = 3\,E_D \cos(\psi - \varphi)$$

$$E_T = \frac{3\,\alpha E}{(^2/_3\,\rho\sqrt{6})^3}\sqrt{3}\cos(\psi - \varphi)$$

Therefore

$$E_T = \frac{3\,\alpha E}{(^2/_3\,\rho\sqrt{6})^3}\sqrt{3} \times {^5/_9}\sqrt{3} = 1.15\,\frac{\alpha E}{\rho^3}$$

Thus

$$E = \frac{3.08\,\mathrm{e}}{\rho^2} - 1.15\,\frac{\alpha E}{\rho^3}$$

$$E = \frac{3.08\,\mathrm{e}\,(r_A + r_X)}{(r_A + r_X)^3 + 1.15\,\alpha}$$

We can calculate E, thus, by

$$E = \frac{3.08\,\mathrm{e}\,\rho}{\rho^3 + 0.45\,R_D\,(X)\,.\,10^{-24}},$$

in which $R\,(X)$ is the refraction of the anion.

We will now settle the formula for the boron derivatives.

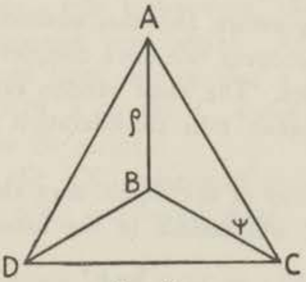

Fig. 15.

Owing to the Coulomb effect the electric field of force in A (fig. 15) is

$$\frac{3\,\mathrm{e}}{\rho^2} - 2\,\frac{\mathrm{e}}{(AC)^2}\cos\psi\,.$$

The model shows that $\cos\psi = \frac{1}{2}\sqrt{3}$ and $AC = \rho\sqrt{3}.$

$$E = \frac{e}{\rho^2}\left(3 - \frac{\sqrt{3}}{3}\right) - E_T = 2.43\,\frac{e}{\rho^2} - E_T$$

Here also

$$\mu = \alpha E$$

Further

$$E_D = \frac{\mu}{(AC)^3}\sqrt{3\cos^2\psi + 1} = \frac{\mu}{(AC)^3}\,\tfrac{1}{2}\sqrt{13}$$

This force forms an angle φ with AC so that $\operatorname{tg}\varphi = \tfrac{1}{2}\operatorname{tg}\psi$

$$E_T = 2\,E_D \cos(\psi - \varphi)$$

$$E_T = \frac{2\,\alpha E}{(\rho\sqrt{3})^3}\,\tfrac{1}{2}\,\sqrt{13}\cos(\psi - \varphi)$$

$$E_T = \frac{2\,\alpha E}{(\rho\sqrt{3})^3}\,\tfrac{1}{2}\sqrt{13}\,{}^{7}/_{26}\sqrt{13} = 0.67\,\frac{\alpha E}{\rho^3}$$

$$E = \frac{2.43\,e}{\rho^2} - 0.67\,\frac{\alpha E}{\rho^3}$$

$$E = \frac{2.43\,e\,\rho}{\rho^3 + 0.67\,\alpha} = \frac{2.43\,e\,\rho}{\rho^3 + 0.27\,R_D\,(X)\,.\,10^{-24}}$$

With this formula and the one we deduced for the tetravalent compounds we may calculate E, though only in a rough approximation. We are fully aware, that this method of calculation cannot be very accurate. Moreover, we have completely ignored the effect of the other molecules. The most serious error, however, is this, that we have not taken into consideration where the dipole is localized [1]).

However the position of the dipole may change the dependence of E upon ρ and R will remain in the form

$$E = \frac{C_1\,\rho}{\rho^3 + C_2 R}$$

---

[1]) According to van Arkel (Physica **1**, 343 (1934)) in CCl_4, at any rate, the whole dipole of the C-Cl bond is localised at a distance ⅛ b from the centre of the molecule, if b represents the radius of the spherical molecule. The same assumption is made by Smyth and Mc Alpine (J. Chem. Phys. **1**, 190 (1933)). This dipole, however, is of course equal to the dipole of C-Cl, considered as ions, diminished by the induced dipole in the chlorine ion. The last is the dipole, that we have considered hitherto.

in which we assume that all tetrahedral molecules can be expressed by the same constant C_1 and C_2.

The same result can be obtained from the formulas given by Klemm 1) as he applies a calculation of the same type.

From this formula we may now draw important conclusions. We here write $C_2 R = C_3 r_X{}^n$. In methane derivatives $n = 5$, for the Si derivatives and others this no longer holds. The comparatively slight variation of $A\ (E)$, however, shows that n is not so far from 5. At all events n is of the order of magnitude of 4 to 6.

E shows a maximum with variation of r_A. The condition

$$\frac{\partial E}{\partial r_A} = 0$$

yields

$$\rho^3 + C_3\, r_X{}^n - 3\, \rho^3 = 0$$

$$\rho = \sqrt[3]{4\, C_3\, r_X{}^n}$$

$$r_A = \sqrt[3]{4\, C_3\, r_X{}^n} - r_X$$

From this it follows, that in the case of sufficiently large halogen ions, the refraction of the last will diminish when the central ion becomes larger 2).

In general, the halogen ions F, Cl, Br and I are too small to demonstrate the effect. For I, however, the difference between the various series becomes very slight. An extrapolation given in figure 12 by dotted lines, shows that a halogen ion with an ionic radius > ± 2.29 Å in the C series will have a greater refraction than in the Si series.

For $r_X < 2.29$ Å the CX_4 compound yields the greatest field, for $r_X > 2.29$ Å the SiX_4 compound does.

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1) W. Klemm, Z. physik. Chem B **12**, 20 (1931).

2) As we have seen the polarizability increases more rapidly than the volume. But, of course, there is a limit. From the equation

$$\frac{\varepsilon - 1}{\varepsilon + 2}\, V = \frac{4\pi}{3}\, N\alpha$$

it follows that for $\varepsilon \rightarrow \sim \alpha$ reaches a maximum of about $\frac{1}{4} v$ (v is the volume per molecule $= \frac{V}{N}$).

In essence this effect means the rapidly increasing polarizability of the anions. We call this effect the inversion effect I. It is not realized in any series of known compounds.

What is to be expected now, with variations of r_X in the case of constant r_A? It appears that E varies simultaneously, as $\frac{\partial E}{\partial r_X} < 0$ for

$$\rho^3 + C_3 r_X^n - \rho (3 \rho^2 + n C_3 r_X^{n-1}) =$$
$$-2 \rho^3 + C_3 (1 - n) r_X^n - n r_A C_3 r_X^{n-1} < 0$$

From this formula it follows that in the case of an increase of the radii of the halogen ions, there is never an extreme value of the field, the field diminishes constantly.

Thus an inversion effect of this kind (inversion effect II) does not exist at all. We wish to lay stress here on the fact, that in this respect figure 12 is extremely deceptive. The $\frac{\alpha_0}{\alpha}$ values show a minimum in the case of a constant central ion. It would seem probable, that the relative deviation of the refraction from those of the free ions, as expressed by the reduced polarizability, would vary simultaneously with the field. In this case extreme values of the $\frac{\alpha}{\alpha_0} - r_X$ curves should indicate the existance of an inversion effect II. But this effect is not actually present.

The occurrence of extreme values for $\frac{\alpha}{\alpha_0}$ is a proof, that no simultaneous connection exists between $\frac{\alpha}{\alpha_0}$ and E and we shall point this out later (p. 86).

At the same time the inversion effect II, however, deserves a further consideration. We will divide it into II A and II B. Let us take the molecule X_3AX, we then introduce ion Y so that $r_Y > r_X$ and a molecule Y_3AZ is formed. We now distinguish two cases.

A. $Z = Y$ then we have the inversion effect II A, which, as we have seen, never actually occurs.

B. $Z = X$ giving inversion effect II B which almost always does occur.

The local field in Z now only changes because 3 X ions are replaced by larger Y ions. The Coulomb effect, therefore, decreases and the field of the central ion is less counteracted, the local field in Z increases, the refraction decreases. At the transition from X to Y the polarizability of these ions is also greatly increased and the dipoles induced in these ions will increasingly counteract the field of the central ion and increase the refraction of the ion Z. With constant r_A, thus, the refraction of a particular ion X will first decrease and then increase again, if the rest of the halogen ions are made larger. The refraction thus shows a minimum and this we call the reverse effect II B. We shall later see numereous examples of this (p. 138). The essential here is that the distance AZ remains constant. If it becomes larger the induced dipoles cannot exercise a predominating influence and therefore inversion effect II A never occurs.

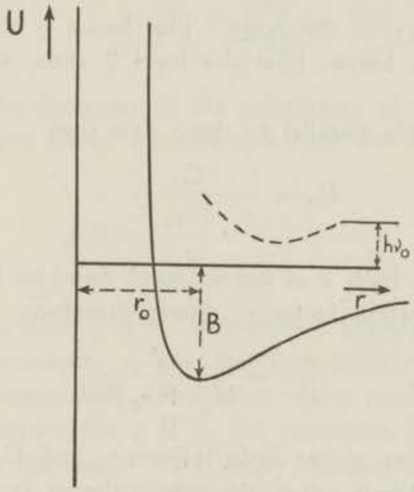

Fig. 16.

We can also use the energy of the tetrahedron model. By differentiating a general formule for the energy to r_A and r_X, we obtain the same results. For the sake of brevety we have omitted these calculations.

Figure 16 represents the energy as a function of the atomic distance, when a molecule is formed. When the atoms come from an exited state (level 2) the energy of the molecule is given by the dotted line.

For the free ions $R_D = \frac{C_1}{\nu_0^2}$

(We write here for the denominator ν_0^2 instead of $\nu_0^2 - \nu_D^2$ in which ν_0 represents an effective ultra violet absorbtion frequency).

For the ions which form a molecule

$$R_D = \frac{C_2}{(g\frac{B}{h} + \nu_0)^2}$$

if B is the energy of the bond. The factor g is introduced because we do not know, how the level 2 runs, when r becomes smaller.

If it runs exactly parallel to the r axis then

$$R_D = \frac{C_2}{(\frac{B}{h} + \nu_0)^2}$$

As, however, the level 2 is not so much bend as level 1, we may introduce a correction factor g. Now, therefore,

$$\frac{\alpha}{\alpha_0} = \frac{\nu_0^2}{(g\frac{B}{h} + \nu_0)^2}$$

If we assume, that g has little influence, and $C_1 = C_2$ which is permissible, considering that the whole theory is very rough, we see at once, that for a particular anion (this means that we have a particular ν_0) $\frac{\alpha}{\alpha_0}$ is the measure for the energy of the bond.

If, on the other hand, we consider various anions, the ν_0 will also play a part. ν_0 is in I extremely small but in F it is very large.

$\frac{\alpha}{\alpha_0}$ is therefore no longer a measure for comparising energies of the bond with one another.

This rough theory explains the „apparent inversion effect II A". By development in a series we find

$$\frac{\alpha}{\alpha_0} = 1 - \frac{2\,g\,B}{\nu_0 h} - -$$

In F ν_0 is large, so that $\frac{\alpha}{\alpha_0}$ in cases of small B values (SiF_4, GeF_4 etc.) has a stronger tendency to approach 1 than in Cl which corresponds to a smaller ν_0.

One more regularity can be explained. If we take $\Delta R = R_{\text{free ion}} - R_{\text{bound ion}}$ in the C series we find

	ΔR
F	0.74
Cl	2.46
Br	2.92
I	2.93

We see, that the decreases of the refractions of the anion in I, Br and even in Cl are about the same and after that it declines rapidly.

Now

$$\Delta R = \frac{C}{\nu_0^2} - \frac{C}{(g\frac{B}{h} + \nu_0)^2}$$

We know, that from I to F, B increases greatly, in consequence of which ΔR increases. ν_0 also increases greatly in this direction, causing ΔR to dimininish. The latter effect predominates, but the former is the reason for ΔR in the transition from I to Cl still remaining about the same. This theory, that is indeed very rough, shows, that the refractions of both cations and anions decrease when a molecule is formed, which is not in agreement with Fajans' conception concerning the cations. The decrease of the last, however, will be very small as ν_0 is very high.

Klemm[1]) has plotted the quotient of the refraction and the zero volume $\frac{R}{V_0}$ against the boiling point temperature T_S and through the points obtained he can draw curves for substances with the same number of molecules.

Generally speaking, this is possible as long as no peculiarities occur. There are some deviations and it is very remarkable to see, that these are just the same, as those we mentioned above.

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[1]) W. Klemm, J. prakt. Ch. **143**, 106 (1935).

$TiCl_4$ and SnI_4 have an $\frac{R}{V_0}$ value, that is too high. We mentioned the abnormal large dispersion of both substances, so that R_D here is too high to serve for comparison with other substances. For BF_3, SiF_4, GeF_4 (and CO_2) $\frac{R}{V_0}$ is too small. CF_4, however, is normal. From the foregoing, we have seen that BF_3, SiF_4 and GeF_4 show interaction, CF_4 not. Klemm also ascribes these deviations to the fact, that except „unpolare Kräfte" electrostatic ones occur. His hypothesis, thus, is in complete agreement with ours.

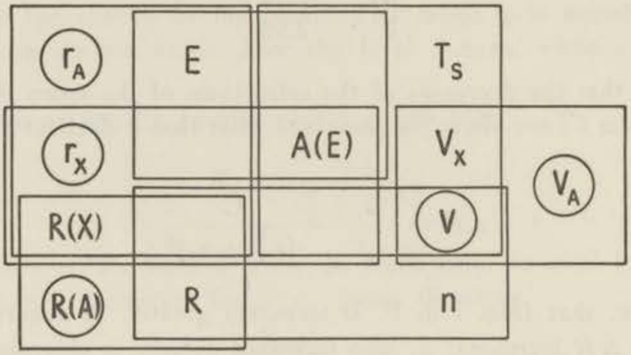

Fig. 17.

Finally, we wish to make the following remark. It might be of some use to calculate the numerical values of the electric field or of the energy, with the formula derived above, from the known ionic radii and the refraction of the anion and to try to find after this, an empirical (or theoretical) relation between the $A(E)$ values and these quantities. But considering that $A(E)$, as we have repeatedly pointed out, has scarcely an actual physical significance, and calculations of this kind only lead to results, that are very approximate, such a thing would only be of formal significance. The result, however, would be, that we could calculate the boiling points and the refraction index of a given substance from the radius of the anion, the radius, the refraction and the Kopp volume of the cation and the total boiling point volume $\left(\text{or the density at boiling temperature } d = \frac{M}{V}\right)$.

We may draw the diagramme on page 88 (fig. 17). The quantities are represented by their usual notation. Each rectangle represents a relation. From $(n-1)$ quantities within a certain rectangle the n-th quantity may be calculated.

We have here 12 quantities between which 7 equations exist. By knowing r_A, r_X, V, V_A and $R\,(A)$ both T_S and n can be calculated. The theory developed above only holds, when no interaction occurs, unless of course the latter can be accurately calculated, both as regards its influence on the boiling point and on the volume.

If n is known T_S may be calculated, in which only 4 of the known quantities are needed and on the other hand, if T_S is known n may be calculated.

CHAPTER III.

EXPERIMENTAL METHODS AND DISCUSSION OF ERRORS.

In the first chapter we have shown that our purpose is to measure the (molecular) refraction of a number of organic pure liquids and liquid mixtures with sufficient accuracy. We always determined these quantities at a temperature of 20° C, as the majority of examples in the literature are measured at this temperature and in this way we can compare the substances one with another. The (molecular) refraction of a liquid is determined by its refractive index and density.

A. Determination of the refractive index.

The refractive index was always determined with an Abbe refractometer with heatable prisms. The prisms were kept at a constant temperature of 20° C during the measurements, by pumping water through them from a thermostat regulated to 20° C. A thermometer was also attached to the prism to control the temperature, as there is a possibility, that the heating water changes in temperature on the way from the thermostat to the refractometer. By means of this refractometer the refractive index can be determined to four decimal places with a maximum error of 2 units in the last decimal. As we shall see later, this is sufficiently accurate for our purposes.

At first sight, it might seem better to use a Pulfrich refractometer, which brings the accuracy to 4 units in the 5th decimal, but the reason for our choice is the following: many of our measurements are made on mixtures with one component of low vapour pressure, but one that is very volatile. In the usual construction of the Pulfrich refractometer the mixture to be examined is exposed to the atmosphere which can so far change its composition that a subsequent determination down to five decimals is quite meaningless. The composition and thus the refractive index will change during the measurements.

With an Abbe refractometer the measurements can be made without the liquid being perceptably exposed to the atmosphere. Into the bulb, to be described below (p. 95), in which the liquid is prepared, a capilary tube with bent point is thrust. The top is closed by a finger and the tube removed from the bulb. The tube forms thus a sort of micropipet. To insert the capillary tube into the bulb it is necessary to remove the stopper and when the liquid has been pipetted out to replace it. With a little practice this manipulation can be done in less than a second. To ascertain whether the composition of the liquid has been perceptably changed by this process, we have tested several mixtures consisting of a very volatile component and one of low vapour pressure (propanone and CBr_4, CCl_4 and CBr_4, propanone and CHI_3) by extracting a sample eight times in the usual way, always removing and replacing the stopper. The refractive index of the liquid in the bulb did not change perceptably in the case of these three mixtures, so that it may be assumed practically with certainty, that this method will yield the true refractive index.

The liquid having been thus brought into the capillary tube, can then be introduced directly into the small cavity between the two halves of the prism of the refractometer. In this way the liquid is not exposed to the atmosphere either, it spreads between the two halves of the prisms and the value of n_D can be read directly, after equilibrium has been reached. As the amount of liquid is very minute, this occurs almost immediately. It should be here especially noted, that the refractometer is not used in the ordinary way, there the liquid is placed on the lower half of the prism and then shut off. In our method the two halves of the prism are first closed and then the liquid is introduced.

In the Abbe refractometer we tested, whether the air was sufficiently excluded to prevent the change of the composition of the liquid. The three mixtures mentioned above could be kept in the closed prism for five minutes at 20° C without any change in the refractive index. As the measurements only take a few seconds, we may say, that the accuracy of our results is sufficiently guaranteed.

Our measurements were made in the following way. After the prism had been brought to 20° C the mixture to be examined was prepared in the bulb, in a manner to be described later. The refractive index was first determined, then the liquid was tapped off for the density determinations and the refractive index of the remainder determined again. Only when these two determinations had a maximum difference of one unit in the fourth decimal the determination was considered to be correct. Very occasionally the difference might be greater, owing to unknown circumstances. Such measurements were regarded as unreliable and were not made use of.

This method of work is not only suitable for measuring the refractive index of mixtures, it is also excellently adapted for pure substances which quickly decompose in the air. On this account we only measured the values of $CHCl_2I$ and CCl_3I in the Abbe refractometer and not in the Pulfrich one, in which we measured the n_α^{20} and n_β^{20} values of all other methane derivatives we examined.

Taking all these precautions into consideration and regarding the capacity of our refractometer, we feel justified in stating, that the maximum error will not exceed 2 units in the fourth decimal.

We tested this at once. A number of substances of guaranteed purity and of which the refractive index is exactly known (in literature) were measured with our apparatus. We append a table of the accepted values and the values found by us.

	Literature	Found
Distilled water	1.3330	1.3332
Propanone	1.3589	1.3588
Tetrachloromethane	1.4603	1.4604
Benzene	1.5014	1.5012
Pyridine	1.5094	1.5094
Nitrobenzene	1.5529	1.5527
Bromobenzene	1.5599	1.5598
α-Bromonaphtalene	1.6588	1.6588

As can be seen, the largest divergence is actually two units in the 4th decimal. As the substances used are fairly evenly distributed over the field covered by our research, in the further measurements we made use of the values given by the refractometer without any correction.

In so far as we wished to measure the refraction of pure substances, that did not evaporate in the atmosphere there were advantages in using a Pulfrich refractometer, because this it not only more accurate, but because we can also determine in this way refractive indices at different wave-lengths. We measured in these cases the H_{α}-, the H_{β}- and the Na-D-line. The temperature was again 20°. The Pulfrich refractometer used, was one with heating apparatus („Neukonstruktion 1895"). This yields an accuracy of 4—5 units in the fifth decimal.

The two prisms $n_D = 1.62$ and $n_D = 174$ were tested before use with very pure standard substances, for the H_{α}-, D- and H_{β}-line, which showed that the values found differed from those in literature within the above mentioned limit. The following were used as test substances: propanone, tetrachloromethane, benzene, bromobenzene and α-bromonaphtaline. These substances about cover the field, that we needed. The prisms could therefore be used without further corrections.

The temperature gradient of the refractive index of the substances we worked with is of the order of magnitude of 0.0005 per degree, so that the maximum change of temperature of 0.1° (which we acquired by means of the thermostat) in the heating apparatus yields an error of 5 units in the last decimal.

For the Abbe refractometer the deviation arising from the error in temperature regulation does not exceed the error arising from the inaccuracy of the apparatus. To sum up therefore we may state that the refractive indices found by us, both with the Abbe and the Pulfrich refractometer, for both simple substances and mixtures, have a maximum error of 2 units in the fourth decimal.

B. Determination of the density.

The determination of the density was always made with an Aubry pyknometer of a capacity of about 5 cm^3. This is a simple flask with a capillary neck on which is a mm scale. The flask is closed by a glass stopper.

It was absolutely essential for our research, that during the measurements no change should take place in the liquid. Hubbard[1]) carried out an elaborate research as to which kind of pyknometer was the most suitable for this purpose and he strongly recommended an Aubry. It is obvious, that it can be used for either pure substances or for mixtures. Before using them, the capacity and mm scale of the pyknometer were tested, as well as the fitting of the stopper. If the stopper does not fit tightly, the substance will evaporate slightly, which is of no consequence in the case of a pure substance, but is of the highest importance in the case of a mixture. If one of the components is very volatile, the mixture will change during the measurements. We therefore used propanone to test the stoppers of the pyknometers as this was the most volatile substance we used in our research. The pyknometers were filled with propanone, well closed and weighed and heated to 20° C for six hours. After this they were again weighed and only those pyknometers, that had a maximum loss of 0.3 milligram per hour were used for our experiments. As stability of the liquid in the pyknometer is always reached within 20 minutes, the maximum error due to evaporation is 0.1 milligram or of the order of magnitude of 0.02 $^0/_{00}$ or less.

Hubbard[2]) has designed a method to fill the flasks with capillary neck without any change occuring in the liquid, which we followed, modified so as to eliminate even more of the possible errors. Hubbard weighs off the first component of the mixture to be made in a weighing flask and then adds the second component to it. He then applies a correction for that part of the first component that will have evaporated during the opening of the weighing flask. He now knows the composition of the mixture. This is then sucked up from the bottom into a reservoir and from this reservoir it is forced through a capillary tube into the pyknometer by a slight pressure.

It is obvious that in passing from the weighing flask to the reservoir the composition of the liquid may change as it is exposed

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[1]) J. C. Hubbard, Z. physik. Chem. 74, 210 (1910).

[2]) J. C. Hubbard, loc. cit.

to the air for a moment. Moreover, as Hubbard himself acknowledges, it is extremely difficult to shake the mixture into a homogeneous phase in the flask without a certain amount getting between the rim and the stopper, where the volatile component may easily evaporate. We, therefore, used a different method for filling the pyknometers. The filling apparatus (fig. 18) resembles an ordinary separatory funnel, but the glass stopper A is pierced and provided with a glass cock B. The stopcock C is not placed at a distance from the reservoir D, as is usual, but close to it. Finally, the tube E ends in a capillary. This apparatus is used in the first place for preparing the mixture. The whole apparatus is weighed and then the least volatile component is introduced into the bulb D. It is then weighed again, the second component is introduced at A and the bulb weighed once more. The composition of the mixture can be calculated from these three weighings, applying, if desired, Hubbards correction for evaporation of the first component during the addition of the second. As need hardly to be said, during the measurements the bulb is closed by stopper A and the stopcocks B and C are always closed.

Fig. 18.

The capacity of bulb D is about 40 cm^3. For each measurement the bulb was almost filled with liquid. This avoids the possibility of the most volatile component collecting at the top and effecting the composition of the mixture. By now shaking the whole apparatus vigorously we get a homogeneous mixture. Stopper A was fitted so accurately, that no liquid could get in between, so that the second difficulty pointed out by Hubbard, was completely eliminated. Greasing the stopper must be avoided, because grease is soluble by most of the substances we examined.

We can transfer the mixture prepared directly into the pyknometer by pressure. The apparatus is coupled at F to a gas container filled with air by a tube containing anhydrous calcium chloride and fused sodium hydroxide to dry the passing air. Thus by opening B we get a small over-pressure of dried carbondioxide freed air above the mixture. In some cases it was necessary, to work with carbondioxide freed air, viz., in those, in which we measured mixtures containing pyridine. By opening stopcock C the mixture is forced through the capillary E. The pyknometer is therefore filled with liquid that has not been exposed to the air. We now take care, that the end of capillary E rests upon the bottom of the pyknometer and that it is gradually filled from the bottom. We continue until the pyknometer overflows. We are now assured ,that it contains exclusively liquid, that has not been exposed to the air so that its composition is unchanged. By a capillary tube connected with the water jet pump the liquid is removed till the meniscus falls exactly in the scale on the neck of the pyknometer. This apparatus can of course be used equally well for filling the pyknometer with various pure liquids, which we used in our research.

By connecting tube F to the water jet pump and opening stopcocks B and C the pyknometers can be almost quantitively emptied. The liquid does not then disappear into the pump but remains in bulb D, so that practically the whole of the liquid is preserved. This was of great importance, as some substances were to be used again as the basis of new material.

Some of the substances we used decomposed perceptably in the atmosphere. In these cases the apparatus was first thoroughly rinsed with dry carbondioxide. The material was introduced into the apparatus in a carbondioxide atmosphere. The slight over-pressure that was needed in this case was provided by a Kipp apparatus producing the same gas. Of course this carbondioxide was properly dried before being introduced into the apparatus.

C. Discussion of errors.

1. Pure substances. Refraction is represented by

$$\frac{n^2-1}{n^2+2}\,\frac{M}{d}$$

in which M is the molecular weight of the substance. If the error in n is equal to Δn the error in

$$\frac{n^2 - 1}{n^2 + 2}$$

is equal to

$$\frac{6\,n\,\Delta\,n}{(n^2 + 2)^2}$$

and the relative error is

$$\frac{6\,n\,\Delta\,n}{(n^2 - 1)\,(n^2 + 2).}$$

In the measurements with the Abbe refractometer the maximum error is two units in the fourth decimal, and, therefore in the most unfavorable case ($n = 1.4$) the relative error in the refraction is $\frac{6 \times 1.4 \times 0.0002}{0.96 \times 3.96}$, that is in the order of magnitude of 0.4 °/₀₀. The measurements in the Pulfrich refractometer have a maximum error of one unit in the fourth decimal and thus a relative error in the refraction of 0.2 °/₀₀. The error in density may be put at about 0.1 °/₀₀.

This can easily be seen as follows: The scale in the neck of the pyknometer can certainly be accurately read to 0.2 divisions. This corresponds to an error in volume of 4×10^{-4} cm^3 which is actually of the order of magnitude of 0.1 °/₀₀.

We may regard the molecular weight M as always being known with sufficient accuracy, so that this does not involve any increase of the error. As n and d are entirely independent of eachother, the total error which may arise from reading errors cannot exceed 0.3 °/₀₀ when using the Pulfrich refractometer. In all this, it is assumed, that in the weighing no perceptable errors have been made. All weighing is carried out on a balance with an accuracy of 0.1 milligram, yielding a maximum error of 0.02 °/₀₀ for each weighing, which is negligible compared to the error consequent on the determination of n and d.

Generally speaking, the refraction of the substances we examined lies between 20 and 40, and taking the above into consideration we may regard the second decimal in our results as certain op to one unit. An accuracy up to the third decimal is quite superfluous. For example: for the value 29.29 of CCl_3Br we should therefore read 29.29 ± 0.01. Unless otherwise specified our refractions are always given with this amount of error.

2. Mixtures. For some solids it was also desirable to know the refraction. It is possible, of course, to determine n and d in a solid condition, but in the first place here birefringence of the crystals occur, so that n cannot be determined unambiguously and in the second place we have all our arrangements made for the liquid condition. We have, therefore, made a concentrated solution of the substances in question in suitable solvents of which the refraction is accurately known.

These mixtures follow approximately the mixture law

$$\nu_1 R_1 + \nu_2 R_2 = \frac{n_0^2 - 1}{n_0^2 + 2} \; \frac{\nu_1 M_1 + \nu_2 M_2}{d_0}$$

The index 1 refers to the solvent, the index 0 refers to the mixture, ν represents the molfraction of the components. n_0 and d_0 are the determinated quantities and thus R_2 may be calculated

$$R_2 = \frac{n_0^2 - 1}{n_0^2 + 2} \; \frac{\nu_1 M_1}{\nu_2 d_0} + \frac{n_0^2 - 1}{n_0^2 + 2} \; \frac{M_2}{d_0} - \frac{\nu_1}{\nu_2} R_1$$

The error in the first term is $\frac{\nu_1}{\nu_2} \times 0.5\,{}^0/_{00}$, in the second term $0.5\,{}^0/_{00}$ and in the third term $\frac{\nu_1}{\nu_2} \times 5\,{}^0/_{00}$ as we have used the Abbe refractometer. Supposing the three terms to be of the same order of magnitude, the total error in R_2 is therefore $\left(\frac{2\,\nu_1}{\nu_2} + 1\right) 0.5\,{}^0/_{00}$. As ν_1 is actually large compared to ν_2 and $0.5\,{}^0/_{00}$ certainly on the large side, we may consider the total error in R_2 as $\frac{\nu_1}{\nu_2} \times 1\,{}^0/_{00}$. This is, of course, a maximum value; if one or two of the terms are small, compared to the other(s) the relative error decreases considerably. The relative error is here dependent, as might be expected upon the expression $\frac{\nu_1}{\nu_2}$. If this expression is large, i.e. if we extrapolate a great deal to calculate R_2 the relative error will also be large.

CHAPTER IV.

THE EXPERIMENTAL WORK CONCERNING THE METHANE DERIVATIVES.

A. Preparation.

It is obviously absolutely necessary for our research, that the chemical substances used should be of the greatest possible purity. Generally speaking, the density and even more the refractive index are extremely sensitive to impurities. We took, therefore, every possible precaution to have our materials pure. When they were obtainable commercially they were purified in the way described below, unless there was sufficient guarantee, that further purification would be unnecessary. Some of the materials we have prepared ourselves. Our methods of preparation and purification are described in detail below.

The succession in which the carbon compounds are treated is according to the principle of the latest possible registration and therefore corresponds to the order in Beilstein's handbook.

CH_2Cl_2. For this we used a preparation „Schering—Kahlbaum reinst". This was several times distilled, each time the middle fraction only being used again. These distillations were continued until a constant density ($d_4^{20} = 1.3243$), a constant boiling point (39.6° at 758 mm pressure) and a constant refractive index in the Abbe refractometer ($n_D^{20} = 1.4244$) were found. This required three distillations.

$CHCl_2F$. This substance was prepared principally by the method devised by Swarts[1]). 24 gr. SbF_3, 7 cm³ Br_2 and 33 cm³

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[1]) F. Swarts, Bull. Acad. Roy. de Belgique (3), 24, 474 (1892), Ber. 26 Ref. 781 (1893).

$CHCl_3$ were heated in a bulb with a reflux cooler to about 70°, the boiling temperature of the mixture. A rapid reaction followed. Unmodified $CHCl_3$ flows back into the reaction mixture, the $CHCl_2F$ formed escapes through the cooler and is lead into two U-tubes which are cooled in a mixture of propanone and solid CO_2. The content of the U-tubes ($\pm$ 20 cm^3) is again warmed up in a small bulb to about 25° and the $CHCl_2F$ is received in a small Ladenburg bulb. This is suspended in cold water which is slowly heated. The CHF_2Cl distils over at 14.5° at 760 mm and is received in a tube cooled with propanone and solid CO_2. The yield is about 16 cm^3. By distilling it three times at a very low temperature the trace of $CHCl_3$, that may be present, can be removed. It is then fractionally distilled until a constant density at 9° (1.405) and constant refractive index n_D^9 in the Abbe refractometer (1.3723) were reached. This required one distillation only.

CCl_3F. This was prepared also principally by Swarts' method [1]), except that we used $SbCl_5$ as catalyst instead of Br_2. The reaction mixture of 90 gr. SbF_3, 5 cm^3 $SbCl_5$ and 90 cm^3 CCl_4 was heated to 55° in a bulb with a reflux cooler through which water of 30° flowed. The CCl_4 is thus retained in the vessel. The product is conducted through 3 washing-flasks, the first is used empty and reverse, the second contains a solution of KOH, the third concentrated H_2SO_4. The washing-flasks all stand in water of 30°. The substance is condensed in a tube placed in propanone and solid CO_2 (temp. — 75°).

The resulting product was 55 cm^3. CCl_3F can be distilled by hand warmth and it was purified by repeated distillation (5 times). In the first two distillations there was always some CCl_4 left. Finally constant density ($d_4^{20} = 1.4827$) and constant boiling point 24.9°—25.1° at 760 mm) were obtained.

CH_2ClBr. This substance was prepared by the method given by Besson [2]), modified on several points. We tried several

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[1]) F. Swarts, Ber. **26**, Ref. 291 (1893) Bull. Acad. Roy. Belg. (3), 24, 309 (1892).

[2]) A. Besson, Ber. **25**, Ref. 15 (1892), Compt. rend. **113**, 773 (1891).

methods and finally found, that the following was the best. CH_3Cl was conducted through a reverse washing-flask and then through a washing-flask filled with Br_2, which was heated by a very small flame. The mixture of Br_2 and CH_3Cl was conducted through a tube heated in a gas oven and filled with pumice stone. Here CH_2ClBr and $CHClBr_2$ are formed. (It is important not to heat to much. Heating to gentle red-heat as given by Besson is to much and leads to carbonisation). This mixture is cooled and collected under water. It is now washed with Na_2SO_3 solution and dried with $CaCl_2$. It is then distilled. The reaction mixture distilled over between 66° and 73°, after that the temperature rose rapidly to over 110°. The first fraction was now purified by freezing out in a mixture of solid carbondioxide and propanone of —55° C. $CHClBr_2$ melts at —32° C and CH_2ClBr is still liquid at this temperature. A solid substance separated out. Finally fractional distillation was applied till constant boiling point (67.8°—67.9° at 750 mm), constant density $d_4^{20} = 1.9441$ and constant refractive index $n_D^{20} = 1.4840$ were reached.

$CHCl_2Br$. This substance was prepared in an analogous way. We conducted vapour of Br_2 and CH_2Cl_2 through a glass tube heated in a gas oven. We took care to have a preporderance of Br_2, which will thus come unchanged out of the tube. In this way CCl_2Br_2 is not formed. The product obtained was washed first with NaOH solution and then with water. After it had been dried with $CaCl_2$ the product was distilled, it passes over at ± 90°. The distillate is purified by repeated fractionation, and finally a product is attained with constant boiling point (89.6° at 750 mm), constant density $d_4^{20} = 1.9802$ and a constant refractive index $n_D^{20} = 1.4965$.

CCl_3Br. This substance was prepared according to a method similar to that of Briscoe, Peel and Rowlands[1]) for producing CBr_4.

5 cm³ $CHCl_3$ and 10 cm³ Br_2 were dissolved in 600 cm³ cold N-NaOH solution. The mixture of chloroform and bromine was

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[1]) H. V. A. Briscoe, J. B. Peel and J. R. Rowlands, J. Chem. Soc. 131, 1766 (1929).

slowly added, while constantly keeping cool. Too high a temperature leads to the formation of bromate and therefore diminishes the production of CCl_3Br. The mixture is shaken for a whole day. In the two layer system produced the lowest layer consists chiefly of the required CCl_3Br. Four portions of CCl_3Br were prepared in this way, producing 25 cm^3 of the rough product. This was purified by being alternately fractionated with a Ladenburg bulb and crystallized out in a cooling mixture of $CaCl_2$ and ice. (m.p. CCl_3Br — 21° C). In melting again a more pure fraction is always obtained. This was repeated three times, after which the substance showed a constant boiling point of 104.1° at 759 mm, a constant density $d_4^{20} = 2.0118$ and a constant refractive index in the Abbe refractometer $n_D^{20} = 1.5061$.

CH_2Br_2. This substance was obtained by reduction of bromoform with a solution of sodium arsenite [1]).

540 gr. $CHBr_3$ and 10 cm^3 of a sodium arsenite solution (made of 230 gr. As_2O_3 and 445 gr. NaOH dissolved in 1.4 liter water) were gently heated with reflux on a steam bath till the reaction began. The remainder of the arsenite solution is then slowly added during one hour. It is then heated four hours more on the steam bath. After this we distil the reaction mixture. The lowest layer of the distillate is principally CH_2Br_2. This is dried with $CaCl_2$ and distilled again untill a constant boiling point 97.2° at 774 mm and constant refractive index $n_D^{20} = 1.5420$ and constant density $d_4^{20} = 2.4960$ are reached.

$CHBr_2F$. This substance we prepared by Swarts' method [2]). 60 cm^3 $CHBr_3$, 42 gr. SbF_3 and 3.5 cm^3 $SbCl_5$ were heated in a bulb provided with a Vigreux on an oil bath. The reaction begins at an oil bath temperatur of 140° at which the thermometer in the Vigreux indicates 30°. The bath temperature was raised to 180° by which the product distilled over between 60° and 70°. It was cleaned with KOH and $KHSO_3$ respectively and then dried. After this it was repeatedly fractionated, but the boiling point did

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[1]) Org. Syntheses, IX, p. 56.

[2]) F. Swarts, Bull. Ac. Roy. Belg. 113 (1910).

not become sharp (64°—66°). According to Booth and Bixby[1]) this is due to volatile antimony compounds which can only be removed by distillation under reduced pressure. This we accomplished also, the pressure was ± 10 cm, under which the $CHBr_2F$ boils at room temperature. An ice and salt mixture was used for the recollection. After this treatment a constant boiling point of 64.9° at 760 mm was reached. Density d_4^{20} and refraction index n_D^{20} became constant after a renewed distillation at 2.4210 and 1.4686 respectively.

$CHClBr_2$. The fraction boiling above 110° in the preparation of CH_2ClBr was fractionally distilled. But as a boiling range of 117°—119° constantly re-appeared it was impossible to obtain in this way a pure substance. We therefore purified the substance by repeated crystallization in a mixture of solid carbondioxide and propanone (melting point of $CHClBr_2 = -32°$ C) by which means we finally obtained a product with constant density $d_4^{20} = 2.4510$ and constant refractive index $n_{20}^{D} = 1.5483$ and boiling point 118.6°—118.8° at 757 mm.

$CHBr_3$. A preparation „Brocades en Stheeman" was frozen out five times, so as to remove any possible traces of alcohol, which is usually added for stabilisation. These five times were sufficient to produce a constant density ($d_4^{20} = 2.8893$) and a constant refractive index $n_D^{20} = 1.5973$ in the Abbe refractometer. The determinations were always made immediately after freezing as $CHBr_3$ is unstable. For this reason it cannot be purified by distillation.

CBr_3F. 75 gr. AgF and 100 gr. CBr_4 were mixed in a bulb and heated on an oil bath to 120°. The reaction is strongly exothermic, so that we had to mix the substance rapidly. The product that comes over, is coloured brown by Br_2, which was shaken out with water and K_2CO_3. After being dried with $CaCl_2$ the product was fractionated several times until a constant boiling point 107° at 762 mm, constant density $d_4^{20} = 2.7574$ and constant

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[1]) H. Booth and E. M. Bixby, Ind. Eng. Chem. 24, 637 (1932).

refractive index $n_{20}^{D} = 1.5365$ had been obtained. The substance was also prepared from 100 gr. CBr_4 and 50 gr. SbF_3 with catalyst $SbCl_5$ at 120° according to Swarts' method. The mass first becomes liquid and after 15 minutes the CBr_3F distils over. It was purified in the same way as above.

CBr_4. This was prepared by a method, given by Briscoe, Peel and Rowlands[1]), from bromoform and bromine in alcaline solution. 5 cm^3 $CHBr_3$ was dissolved with 10 cm^3 Br_2 in 600 cm^3 cold N-NaOH solution. The bromoform-bromine mixture was added slowly with constant cooling. Too high a temperature promotes the formation of bromate and, thus, decreases the production of CBr_4. The mixture is shaken for a whole day. Then white CBr_4 precipitates. After being washed and drawn off this substance was cleansed by a method given by Korvezee[2]). The substance was dissolved in absolute alcohol and again precipilated by dilution with water. After being drawn off it was finally cleansed by sublimation in a vacuum of ± 2 cm. This gave a product with a melting point of 93.4° corresponding exactly to Korvezee's value[3]).

Besides the preparation we made ourselves, we used a preparation „Fraenkel und Landau, reinst" which was purified in a similar way.

CH_2FI. For this we used the preparation described by van Arkel and Janetzky[4]). The method of preparation and the degree of purity are minutely described by them.

CH_2ClI. This was prepared from CH_2I_2 and ClI by Sakurai's method[5]). To 150 gr. CH_2I_2, which had been cooled to just above its melting point (+ 4° C) 5 to 10 % of the theoretical quantity ClI is added, while constantly being shaken. This was then distilled

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[1]) H. V. A. Briscoe, J. R. Peel and J. R. Rowlands, J. Chem. Soc. **131**, 1766 (1929).

[2]) A. E. Korvezee, Rec. trav. chim. **53**, 464 (1934).

[3]) A. E. Korvezee, loc. cit.

[4]) A. E. van Arkel and E. Janetsky, Rec. trav. Chim. **56**, 167 (1937).

[5]) J. Sakurai, J. Chem. Soc. **47**, 198 (1885).

on an oil bath at 100°—110° at 20 mm pressure with a Vigreux and a long cooler. The receiver was an U-tube cooled in a carbondioxide propanone mixture. The distillation was continued till CH_2I_2 came over constantly (boiling point of CH_2ClI at 20 mm is 25°, of CH_2I_2 at 20 mm is 70°). After this the remainder was again cooled, ClI added and the whole process repeated several times. When in this way about a half has been distilled off the large amount of I_2 generated begins to have a disturbing effect. The remainder is therefore washed out with dilute NaOH solution and dried (fraction A). The receiver now holds CH_2ClI and CH_2I_2, which after freeing it from I_2 is fractionated again. The reclaimed CH_2I_2 is now added to fraction A and with this the whole treatment is repeated.

In this way we get portions of CH_2ClI. we repeated it 3 times by which from 110 gr. CH_2I_2 50 % of the theoretical yield was obtained. This method of work is certainly extremely elaborate, but it is the only way to avoid getting too much CH_2Cl_2. The CH_2ClI was fractionated, the fractions with higher and lower boiling points proved to be very small. Refractionating the product passed over between 108.7° and 109.2° at 760 mm.

$CHCl_2I$ was prepared by a method described by Borodine[1]), somewhat modified. 250 gr. CHI_3 and 170 gr. $HgCl_2$ were ground together in a mortar. The mixture was heated to 160° in an oil bath in a CO_2 current. After the first violent reaction is over the temperature is gradually raised to 200°. After that hardly anything passes over. The distillate is fractionated in a CO_2 current: first chloroform passes over and a liquid with a lower boiling point, perhaps $C_2H_2Cl_2$, generated by the disintegration of $CHClI_2$, then up to 132° comes ± 45 % of the theoretical quantity $CHCl_2I$. The residue is exposed to the influence of sunlight for a day under CO_2 atmosphere. Hereby $CHClI_2$ is decomposed almost quantitavely but $CHCl_2I$ is not attacked. Fractionating this portion we find 15 % more of the theoretical yield. Refractionating the total yield in a CO_2 atmosphere (not in a CO_2 current) the fraction between 127°—132° was collected. The largest amount passed

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[1]) A. Borodine, Ann. **126**, 239 (1863).

over at 131° at 780 mm. After repeating the distillation a fraction between 131° and 131.5° was measured. The $CHCl_2I$ is a clear yellow fluid which quickly becomes red by oxydation, when exposed to the air.

CCl_3I was prepared in principle from Besson's[1]) receipt. 100 gr. anhydrous AlI_3 were introduced in small quantities into a mixture of 500 gr. CCl_4 and 500 gr. CS_2, that had been previously carefully dried at a temperature of 0°. The portions of AlI_3 were made so small, that the reaction did not take place violently. We kept the whole reaction mixture in the dark for two days. After that we decoloured the liquid which has been made purple by the I_2 with a dilute $Na_2S_2O_3$ solution, dried it again and evaporated the CCl_4-CS_2 mixture off. The remaining liquid is again coloured purple; the substance is now decoloured once more, dried and distilled in vacuum. The last treatment was repeated until the refractive index of the distillate is constant. The liquid boils with 1 mm pressure at 46° and was light yellow as was described by Besson.

CHI_3. For this we used a preparation „Brocades en Stheeman cryst." melting point 119° C.

B. Critical review of present measurements and earlier results on the densities and refractive indices.

In this part we will systemetically discuss all possible halogenated methane derivatives concerning their refractive indices and densities, in the order given in Chapter IV A. All measurements were made at 20° in the liquid condition; we did not consider the substances, which are gaseous at that temperature, with the exception of $CHFCl_2$, as this had a special theoretical significance for us. We did not measure, thus, CH_4, CH_3F, CH_2F_2, CHF_3, CF_4, CH_3Cl, CH_2ClF, $CHClF_2$, $CClF_3$, CCl_2F_2, CH_3Br and $CHBrF_2$.

Of some of the compounds of the methane series the density and refraction were already known exactly. Unless there was some reason, we did not determine these values again. In this Chapter,

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[1]) A. Besson, Bull. Soc. chim. (3) 9, 174 (1893).

we shall try by the discussion of our observations and those of other authors to arrive at the most probable value for the molecular refraction and the error made in the determination. For some substances different values have been measured for density and refraction at different temperatures. In such cases we have only regarded the literature values for d_4^{20} and n^{20}. Old deviating values are not taken. For the less carefully examined substances sometimes the values were only known at temperatures other than 20° C. These are given for comparison.

Of the remaining substances of our group of compounds another part cannot be taken into consideration as they are solid at 20°. The value for the molecular refraction would therefore have to be determined from measurements of solutions of these substances in suitable solvents. This gives at once a greater inaccuracy. Some compounds are also extremely unstable in solution so that it is impossible to make measurements with an accuracy necessary for our purposes. Moreover, the exclusion of these compounds (which have a high boiling point) has the advantage, that all the substances investigated lie within a limited range.

It would have been better to make all refraction determinations at the boiling point of the compound in question [1]), but in connection with the experimental difficulties which this would involve, and especially as then no data from literature could be used, we decided to confine ourselves to a temperature of 20° C. The molecular refraction shows a course with the temperature, even though a very slight one. By making our choice as described above, we shall more or less eliminate the dependence of the molecular refraction on temperature, as will be seen later. For this reason, CCl_2Br_2, $CClBr_3$, $CHBr_2I$, CBr_3I, $CHClI_2$, CCl_2I_2, $CHBrI_2$, $CBrI_3$ and CI_4 do not come under our consideration. There remain two known solid representatives of this group i.e. CBr_4 and CHI_3. Of these it was very necessary to our theory to know the refraction. We have been able to determine this by various contrivances. They are discussed in Chapter VI.

CH_2Cl_2. The density of this substance has been determined by various authors at different temperatures. A review of these

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[1]) cf. Chapter II A.

researches is given by Timmermans and Mme Hennaut—Roland[1]).

Timmermans found by interpolation d_4^{20}: 1.32579. Görke, Köppe and Staiger[2]) found d_4^{20} : 1.3222, Clark and Roberts[3]) d_4^{20}: 1.3478 and Patterson and Thompson[4]) : 1.3361.

Timmermans showed, than the last two products were not quite pure. We have repeated the density determination and found for a very pure preparation d_4^{20} : 1.3243, which lies between Timmermans' and Görke's values. We shall take this value as correct.

In the refractive indices there is also a difference. From the values of Timmermans and Mme Hennaut—Roland we find

n_α^{20} : 1.42196
n_D^{20} : 1.42446
n_β^{20} : 1.43022

while Görke found

n_α^{20} : 1.4216
n_D^{20} : 1.4237
n_β^{20} : 1.4296

We therefore determined these refractive indices again and found

n_α^{20} : 1.42215
n_D^{20} : 1.42440
n_β^{20} : 1.43025

agreeing well with Timmermans' values.

CHFCl$_2$. As this substance boils at 14.5° the density and refractive indices were measured at 9°. For d_4^{0} we found: 1.405. After the pyknometer had been taken out of the thermostat we

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[1]) J. Timmermans and Mme. Hennaut — Roland, J. Chim. phys. **29**, 529 (1932).

[2]) W. D. Harkins, G. L. Clark and L. T. Roberts, J. Am. Chem. Soc. **42**, 700 (1920).

[3]) S. Patterson and D. Thomsom, J. Chem. Soc. **93**, 370 (1908).

[4]) H. Gorke, E. Köppe and F. Staiger, Ber. **41**, 1163 (1908).

cooled it first in ice to 0° C and then dried it on the outside and weighed it. During the weighing the liquid in the pyknometer did not boil, but some may have evaporated. We have therefore not given here the 4th decimal of the density. Swarts 1) found for d^0 : 1.426, which may be considered as in agreement with our measurements.

With the Pulfrich fractometer we found for the refractive indices

n_α^9 : 1.37017
n_D^9 : 1.37240
n_β^9 : 1.37694

$CHCl_3$. For the density of this substance at 20° was found

1.4888 (Schoorl) 2)
1.4889 (Mathews) 3)
1.4890 (Görke) 4)
1.48913 (Zmaczynski) 5)
1.48921 (Timmermans) 6)

For our calculation we will take d_4^{20} : 1.4890. For the refractive indices several authors have found (by means of Timmermans' value for $\frac{dn}{dt}$ recalculated to 20°).

		n_α^{20}	n_D^{20}	n_β^{20}
Timmermans 7)	(15°)	1.44296	1.44563	1.45185
Brühl 8	(18.85°)	1.44255	1.44504	—
Görke 9)	(20°)	1.4431	1.44550	1.4517
Schoorl 10)	(20°)	—	1.44588	—
Hubbard 11)	(25°)	1.44347	1.44604	1.45247

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1) F. Swarts, Ber. **26**, Ref. 781 (1893).

2) N. Schoorl and A. Regenbogen, Rec. trav. Ch. 41, 1 (1922).

3) J. H. Mathews, J. Am. Chem. Soc. **48**, 562 (1926).

4) N. Gorke, E. Köppe and F. Staiger, Ber. **41**, 1161 (1908).

5) A. Zmaczynski, J. Phys. Chem. **27**, 503 (1930).

6) J. Timmermans and F. Martin, J. Chim. phys. **23**, 747 (1926).

7) J. Timmermans and F. Martin, loc. cit.

8) J. W. Brühl and H. Schroder, Z. physik. Ch. **51**, 520 (1905).

9) H. Gorke, E. Köppe and F. Staiger, loc. cit.

10) N. Schoorl and A. Regenbogen, loc. cit.

11) J. C. Hubbard, Z. physik. Ch. **74**, 226 (1910).

We may therefore take for our calculation

n_α^{20} : 1.4428
n_D^{20} : 1.4456
n_β^{20} : 1.4520

CCl_3F. For the density of this substance we found d_4^{20} : 1.4897 which may be considered as in agreement with Swarts' 1) value $d^{17.2} = 1.4944$ and Desreux' $d^{15} = 1.4995$.

Swarts found for the refractive index $n_D^{18.5} = 1.3895$.

With the Pulfrich refractometer we found

n_α^{20} : 1.38273
n_D^{20} : 1.38490
n_β^{20} : 1.38988

CCl_4. This substance has also been repeatedly examined. A list of densities and refractive indices found by various authors is given by Timmermans and Martin 3).

For d_4^{20} was found

1.59410	(Timmermans) 4)
1.5944	(Mathews) 5)
1.5945	(Görke) 6)
1.59472	(Patterson) 7)

As basis for our calculation we take d_4^{20} : 1.5944. For the refractive indices we find the following values recalculated at 20° by means of the $\frac{dn}{dt}$ values according to Timmermans.

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1) F. Swarts, Ber. **26**, Ref. 291 (1893).

2) V. Desreux, Bull. Soc. chim. Belg. **44**, 249 (1935).

3) J. Timmermans and F. Martin, J. chim. phys. **23**, 747 (1926).

4) J. Timmermans and F. Martin, loc. cit.

5) J. H. Mathews, J. Am. Chem. Soc. **48**, 562 (1926).

6) H. Gorke, E. Köppe and F. Staiger, Ber. **41**, 1161 (1908).

7) S. Patterson and D. Thomson, J. Chem. Soc. **93**, 371 (1908).

		n_α^{20}	n_D^{20}	n_β^{20}
Timmermans[1]	(15°)	1.45735	1.46030	1.46690
Görke[2]	(20°)	1.4571	1.4603	1.4669
Mathews[3]	(20°)	—	1.46048	—
Hubbard[4]	(25°)	1.45744	1.46007	1.46680

As basis for our calculation we take:

n_α^{20} : 1.4573
n_D^{20} : 1.4603
n_β^{20} : 1.4669

CH_2ClBr. For the density we here found d_4^{20} : 1.9441, which is very low compared to the value d^{19} : 1.9907 given by Henry[5]. For the refractive index we found the following result. The Abbe refractometer gave $n_D^{20} = 1.4840$, while with the Pulfrich refractometer we found:

n_α^{20} : 1.48117
n_D^{20} : 1.48409
n_β^{20} : 1.49214

$CHCl_2Br$. Here we found for d_4^{20} : 1.9802. From the values of Timmermans and Martin[6] we calculate by interpolation d_4^{20} : 1.9945.

The agreement is not good. Walden and Swinne[7], however, found $d_4^{25} = 1.9687$, from which we calculated by means of the dilatation coefficient of Timmermans and Martin $d_4^{20} = 1.9797$, which agrees well with our value.

Jacobson and Neumeister[8] found $d^{15} = 1.9254$ which is very different.

We found lower refractive indices than Timmermans and

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[1] J. Timmermans and F. Martin, loc. cit.

[2] H. Gorke, E. Köppe and F. Staiger, loc. cit.

[3] J. H. Mathews, loc. cit.

[4] J. C. Hubbard, Z. phys. Chem. **74**, 226 (1912).

[5] L. Henry, J. prakt. Chem. (2), **32**, 431 (1885).

[6] J. Timmermans and F. Martin, loc. cit.

[7] P. Walden and R. Swinne, Z. physik. Chem. **82**, 280 (1913).

[8] O. Jacobson and R. Neumeister, Ber. **15** (1882).

Martin, as could be expected, as our density was lower than theirs:

	T. and M.	Own measurements
n_α^{20}	1.49503	1.49273
n_D^{20}	1.49850	1.49639
n_β^{20}	1.50677	1.50478

CCl_3Br. We found with the Abbe refractometer $n_D^{20} = 1.5061$, with the Pulfrich refractometer

n_α^{20} : 1.50288
n_D^{20} : 1.50610
n_β^{20} : 1.51512

For the density was found d_4^{20}: 2.0118. It is striking to point out, that the data given in the International Critical Tables for this substance, i.e. $n_D^{20} = 1.5300$ and $d_4^{14.5} = 1.959$, are certainly erroneous. The value given by Thorpe[1]) $d_4^0 = 2.0550$ is probably correct.

CH_2Br_2. It is remarkable that on this substance very few reliable measurements have been made. Perkin[2]) has made a research which yields very different values to those of Timmermans and Mme Hennaut—Roland[3]).

Timmermans found

d_4^{20} : 2.4970
n_α^{20} : 1.53742
n_D^{20} : 1.54188
n_β^{20} : 1.55227

We measured the substance again and found d_4^{20} : 2.4960. With the Pulfrich refractometer we found

n_α^{20} : 1.53723
n_D^{20} : 1.54179
n_β^{20} : 1.55182

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[1]) T. E. Thorpe, J. Chem. Soc. **37**, 203 (1880).

[2]) H. Perkin, J. Chem. Soc. **45**, 421, 527 (1884), J. prakt. Chem. (2), **131**, 510 (1885).

[3]) J. Timmermans and Mme. Hennaut—Roland, J. chim. phys. **29**, 529 (1932).

with the Abbe refractometer we found $n_D^{20} = 1.5420$. We take for our calculation

n_α^{20} : 1.5373
n_D^{20} : 1.5419
n_β^{20} : 1.5520

$CHBr_2F$. For the density we found d_4^{20} : 2.4210, while Swarts[1]) had found $d^{18.5}$: 2.4256, which may be considered a satisfactory agreement. With the Abbe refractometer we found n_D^{20} : 1.4686, with the Pulfrich refractometer

n_α^{20} : 1.46499
n_D^{20} : 1.46850
n_β^{20} : 1.47671

$CHCl_2Br$. For the density we found d_4^{20} : 2.4510 which is not in agreement with the values of Jacobson and Neumeister[2]) who found d^{15} : 2.4450. For the refractive index we found with the Abbe refractometer n_D^{20} : 1.5483, with the Pulfrich

n_α^{20} : 1.54382
n_D^{20} : 1.54815
n_β^{20} : 1.55868

$CHBr_3$. The density of this substance has been determined by several authors. They have found d_4^{20} : 2.8899 (Patterson)[3]), 2.8905 (Timmermans)[4]), 2.8905 (Desreux)[5]). We determined the density also and found d_4^{20} : 2.8899.

We shall take the mean value as correct $d_4^{20} = 2.8902$. Timmermans and Martin[6]) and Gladstone[7]) find for the refractive indices

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[1]) F. Swarts, Bull. Ac. Roy. Belg. 113 (1910).

[2]) O. Jacobson and R. Neumeister, Ber. **25**, 601 (1882).

[3]) S. Patterson and D. Thomson, J. Chem. Soc. **93**, 367 (1908).

[4]) J. Timmermans and F. Martin, J. Chim. Phys. **25**, 411 (1928).

[5]) V. Desreux, Bull. Soc. Chim. Belg. **44**, 249 (1935).

[6]) J. Timmermans and F. Martin, loc. cit.

[7]) J. H. Gladstone, J. Chem. Soc. **59**, 253 (1891).

	T. and M.	Gl.
n_{α}^{20}	1.59250	—
n_D^{20}	1.59768	1.5974
n_{β}^{20}	1.61060	1.6101

With the Abbe refractometer we found $n_D^{20} = 1.5973$ and with the Pulfrich

n_{α}^{20} : 1.59234
n_D^{20} : 1.59767
n_{β}^{20} : 1.61050

Our results agree with those of Timmermans.

CBr_3F. For the density we found $d_4^{20} = 2.7574$, not in very good agreement with Desreux[1]), who found 2.7648. With the Abbe refractometer we found $n_D^{20} = 1.5257$, with the Pulfrich

n_{α}^{20} : 1.52106
n_D^{20} : 1.52556
n_{β}^{20} : 1.53639

CH_3I. Timmermans and Delcourt[2]) found $d_4^{20} =$ 2.27900 while Patterson and Thomson[3])found 2.27899.

For our calculations we take d_4^{20} : 2.2790. For the refraction indices was found (recalculated to 20°)

		n_{α}^{20}	n_D^{20}	n_{β}^{20}
J. Timmermans and Y. Delcourt[4])	(15°)	1.52575	1.53119	1.54403
A. Karvonen[5])	(20°)	1.52592	1.53111	1.54409

The values of Cotton and Mouton[6]) are higher, those of Gladstone[7]) lower. Smyth and Mc Alpine[8]) give the value $n_D^{20} = 1.53067$.

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[1]) V. Desreux, Bull. Soc. Chim. Belg. **44**, 249 (1935).

[2]) J. Timmermans and Y. Delcourt, J. Chim. Phys. **31**, 85 (1934).

[3]) S. Patterson and D. Thomson, J. Chem. Soc. **43**, 369 (1908).

[4]) J. Timmermans and Y. Delcourt, loc. cit.

[5]) A. Karvonen, Ann. Ac. Sc. Fennicae, A3, No. 10, 1105 (1917).

[6]) A. Cotton and N. Mouton, Ann. Chim. Phys. (8),**28**, 236 (1913).

[7]) J. H. Gladstone, J. Chem. Soc. **59**, 293 (1891).

[8]) C. P. Smyth and K. B. Mc Alpine, J. Chem. Phys. **1**, 499 (1933).

As basis of our calculation we take

n_α^{20} : 1.52583
n_D^{20} : 1.53115
n_β^{20} : 1.54406

CH_2FI. We found for the density $d_4^{20} = 2.366$ and $d_4^{18.5} = 2.370$. With the Abbe refractometer we found $n_D^{20} = 1.4910$ and $n_D^{18.5} = 1.4918$. These values have been published already [1].

With the Pulfrich refractometer we found

n_α^{20} : 1.48665
n_D^{20} : 1.49111
n_β^{20} : 1.50281

CH_2ClI. With the Abbe refractometer we found $n_D^{20} = 1.5823$. With the Pulfrich

n_α^{20} : 1.57630
n_D^{20} : 1.58224
n_β^{20} : 1.59611

For the density we found $d_4^{20} = 2.4226$. There are various values for the density in the literature [2] i.e. $d_{11}^{11} = 2.447$ and $d_{14.5}^{14.5} = 2.444$. Recalculated this yields $d_4^{11} = 2.446$, $d_4^{14.5} = 2.442$.

$CHCl_2I$. With the Abbe refractometer we found $n_D^{20} = 1.5840$. For the density we found $d_4^{20} = 2.392$. In spite of all our precautions to avoid colouring, as described in Chapter III, the preparation was slightly coloured by free I_2 during the density measurements, so that giving four decimals for the density is quite meaningless. Our value for the density lies just between the value of Borodine [3], who found $d^0 = 2.454$ and $d^{21.5} = 2.403$, which extrapolated to 20° yields $d^{20} = 2.407$ and of Auger [4], who found $d^0 = 2.41$, which for d^{20} yields a value of about 2.37.

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[1] cf. A. E. van Arkel and E. Janetzky, Rec. trav. Chim. **56**, 167 (1937).

[2] J. Sakurai, J. Chem. Soc. 47, 198 (1885).

[3] A. Borodine, Ann. **126**, 239 (1863).

[4] M. V. Auger, Compt. rend. **146**, 1038 (1908).

CCl_3I. This substance decomposes rapidly in the air, so that we have only made measurements with the Abbe refractometer. We find n_D^{20} :1.5854 and for density d_4^{20} : 2.355. There is no point in giving four decimals for the density for the same reason as in $CHCl_2I$. Besson[1]) gives for the density $d^{17} = 2.36$.

CH_2I_2. The density of this substance was determined at 20° by Harkins and Feldman[2]). They found $d_4^{20} = 3.3190$. Timmermans[3]) found by interpolation between 15° and 30°: $d_4^{20} = 3.3213$.

For our calculations we will use the values $d_4^{20} = 3.320$ with a possible error of $0.3\,^0/_{00}$. For the refractive indices Timmermans gives the following values

n_α^{20} : 1.73098
n_D^{20} : 1.74108
n_β^{20} : 1.76826

Timmermans measured these values with various prisms with a mutual agreement of 0.0001. Perkin[4]) measured the refractions at 8°4, Gladstone[5]) at 10.5. Extrapolation to 20° yields too many uncertainties for these values to be used.

C. Summary and preliminary discussion.

We have, thus, determined the values of the quantities d_4^{20}, n_α^{20}, n_D^{20} and n_β^{20} of the various halogenated methane dervatives with a very slight error.

The three last values we plotted on Hartmann's dispersion paper against the wave-length of the line H_α, Na_D and H_β. It proved possible in each case to draw a straight line through the three given points, the maximum deviations being 0.0002. In most cases the deviation was even smaller. This gives us a kind of check as to whether the found values agree with eachother. Moreover, we can find by extrapolation what is the refraction

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[1]) A. Besson, Bull. Soc. chim. (3), **9**, 174 (1893).

[2]) W. J. Harkins and A. Feldman, J. Am. Chem. Soc. **44**, 2665 (1922).

[3]) J. Timmermans and Mme. Hennaut—Roland, J. chim. phys. **29**, 529 (1932).

[4]) H. Perkin, J. Chem. Soc. **45**, 421, 527 (1884), J. pr. Chem. (2), **31**, 510 (1885).

[5]) J. H. Gladstone, J. Chem. Soc. **59**, 253 (1891).

index for $\lambda \rightarrow \sim$. By means of the value $n^{20}_{\sim}$ found and the values d_4^{20}, n_α^{20}, n_D^{20} and n_β^{20} we can calculate the (molecular) refraction of the substances examined, according to

$$R = \frac{n^2 - 1}{n^2 + 2} \; \frac{M}{d}$$

In the following table we give a list of the most probable values of density, refraction index and refractions of the liquid halogenated methane derivatives. The density is given to three decimals, the refractive index to four as the 4th and 5th decimal of these two values respectively are not completely reliable. All values are given at 20° except for $CHCl_2F$ for which the values are at 9°. Finally the value of m is calculated in connection with a remark in Chapter I (p. 37) given by the equation

$$R_D = (1 + m)\, R_{\sim}.$$

	M	$\varkappa_4^{20}$	n_β^{20}	n_D^{20}	n_α^{20}	$n_\sim^{20}$	R_β	R_D	R_α	$R_\sim$	m
CH_2Cl_2	84.94	1.324	1.4302	1.4244	1.4222	1.4086	16.58	16.38	16.30	15.84	3.4
$CHCl_2F$	102.92	1.405	1.3769	1.3724	1.3702	1.3590	16.85	16.67	16.58	16.13	3.4
$CHCl_3$	119.39	1.489	1.4520	1.4456	1.4428	1.4274	21.63	21.37	21.25	20.60	3.7
CCl_3F	137.37	1.490	1.3899	1.3849	1.3827	1.3708	21.85	21.61	21.50	20.90	3.4
CCl_4	153.84	1.594	1.4669	1.4603	1.4573	1.4422	26.77	26.44	26.29	25.54	3.5
CH_2ClBr	129.39	1.944	1.4921	1.4841	1.4812	1.4634	19.31	19.04	18.95	18.34	3.8
$CHCl_2Br$	163.85	1.980	1.5048	1.4964	1.4927	1.4727	24.53	24.19	24.04	23.19	4.3
CCl_3Br	198.29	2.012	1.5151	1.5061	1.5029	1.4822	29.73	29.29	29.13	28.11	4.2
CH_2Br_2	173.85	2.496	1.5520	1.5419	1.5373	1.5122	22.26	21.92	21.76	20.91	4.8
$CHBr_2F$	191.84	2.421	1.4767	1.4685	1.4650	1.4452	22.38	22.05	21.91	21.10	5.0
$CHClBr_2$	208.30	2.451	1.5587	1.5482	1.5438	1.5190	27.43	27.00	26.82	25.80	4.7
$CHBr_3$	252.76	2.890	1.6105	1.5977	1.5923	1.5616	30.34	29.83	29.61	28.35	5.2
CBr_3F	270.75	2.757	1.5364	1.5256	1.5211	1.4949	30.64	30.12	29.90	28.63	5.2
CBr_4 [1]	331.66	—	—	—	—	—	—	39.0_0	—	—	—
CH_3I	141.95	2.279	1.5441	1.5312	1.5258	1.4951	19.67	19.28	19.11	18.17	6.1
CH_2FI	159.95	2.366	1.5028	1.4911	1.4867	1.4592	19.98	19.58	19.43	18.49	6.0
CH_2ClI	176.40	2.422	1.5961	1.5822	1.5763	1.5428	24.78	24.31	24.11	22.94	6.0
$CHCl_2I$ [2]	210.85	2.392	—	1.5840	—	—	—	29.50	—	—	—
CCl_3I [2]	245.30	2.355	—	1.5854	—	—	--	34.94	—	—	—
CH_2I_2	267.88	3.320	1.7683	1.7411	1.7310	1.6676	33.47	32.58	32.24	30.06	8.4
CHI_3 [1]	393.80	—	—	—	—	—	—	48.5_5	—	—	—

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[1] CBr_4 and CHI_3 are measured in solution as they are solid at 20° C. For this reason only the value R_D can be given (cf. Chapter VI).

[2] For the reason why we can give for $CHCl_2I$ and CCl_3I only d_4^{20}, n_D^{20} en R_D cf. p. 115.

Now we can give the manner in which density and refraction change with substitution. This is expressed in the following table. A plus sign means that the physical quantity in question increases and a minus sign means that it decreases.

1. *Refractive index.*

		by H	F	Cl	Br	I
Substitution of	H	0	—	+	+	+
	F	+	0	+	+	+
	Cl	—	—	0	+	+
	Br	—	—	—	0	+
	I	—	—	—	—	0

2. *Density.*

		by H	F	Cl	Br	I
Substitution of	H	0	±	±	+	+
	F	±	0	+	+	+
	Cl	±	—	0	+	+
	Br	—	—	—	0	+
	I	—	—	—	—	0

3. *Refraction.*

		by H	F	Cl	Br	I
Substitution of	H	0	+	+	+	+
	F	—	0	+	+	+
	Cl	—	—	0	+	+
	Br	—	—	—	0	+
	I	—	—	—	—	0

The following may be said concerning the density. For the present we only consider the density at the boiling point. It is then given by $d = \frac{M}{V}$, in which M is the molecular weight and V the molecular volume. We now substitute an halogen ion by another. The increase of $M : \Delta M$ is equal to the difference of the atomic weights. The increase of $V : \Delta V$ is equal to the difference of the atomic volumes according to Kopp. The new density becomes

$$d' = \frac{M + \Delta M}{V + \Delta V}$$

The density will remain the same with substitution if the equation

$$M \Delta V = V \Delta M$$

is satisfied. If this is the case the density is

$$d = \frac{M}{V} = \frac{\Delta M}{\Delta V}$$

For each substitution, therefore, $\frac{\Delta M}{\Delta V}$ gives the ,,critical substitution density" i.e. the density that remains constant when the substitution is made. These ,,critical substitution densities" can be calculated from the atomic weights and the Kopp volumes:

	by	H	F	Cl	Br	I
Substitution of	H	—	3.3	2.2	3.3	3.7
	F	—	—	1.4	3.4	3.8
	Cl	—	—	—	7.0	5.5
	Br	—	—	—	—	4.7
	I	—	—	—	—	—

If the density of the original substance is higher than these values the substitution will decrease the density. Unfortunately, there is not much known of the dilatation coefficient, so that we cannot calculated the densities at the boiling temperature. But we can give similar ,,critical substitution densities" at 20°. We find for the substitution H → F 2.4, for H → Cl 2.1 to 2.3, for F → Cl 2.5, for instance.

These figures are completely empirical and exclusively fit the values of the liquid methane derivatives we examined. It is now clear, why a substitution of H by F and a substitution of H by Cl may lead to an increase or decrease; in these cases the critical substitution densities lies fairly low. In all other possible substitutions the ,,critical substitution density" is so high that all replacing of halogen ions by heavier ones must lead to an increase of density. It is true, that we cannot determine the last, but the theoretical values at the boiling points lie very high, so that we may expect the same of the empiricle values at 20°.

Especially the series $CH_2ClI \rightarrow CCl_3I$ must be noted. The density decreases very slowly and regularly, the refractive index increases very slowly and regularly again. It suggests that there can be a „critical substitution refractive index" too, though we did not find it in the examples examined. For the substitution H → F it lies very low, for all the other substitutions very high. From the fact that the refractive index in the series CH_2ClI → CCl_3I increases so slowly, we can conclude, that perhaps for the substitution H → Cl it will be about 1.6. So we can expect by substituting H by Cl in CH_2I_2 (and perhaps ($CHBr_3$) that the refractive index will decrease. Unfortunately $CHClI_2$ and $CClBr_3$ are solids at 20° and very unstable at higher temperature, so that we cannot make comparisons.

As regards the value of m we may note the following. We see here the same phenomenon ,that m increases at the introduction of heavier halogen ions, that is to say the dispersion increases (cf. p. 38).

As a mean value for all the methane derivatives as well as for all the symmetrical tetrahedral molecules, mentioned op p. 37 the equation

$$R_D = (1.043 \pm 0.018)\, R_{\sim}$$

holds. (CH_2I_2 is left out of consideration).

This is a very fortunate circumstance. In all these compounds R_D, thus, is about proportional to P_E.

CHAPTER V.

INTERPRETATION OF THE MEASUREMENTS.

In the first part of this chapter we shall develop a method for calculating the amount that each halogen ion separately contributes to the refraction of the halogenated methane derivatives and we shall inquire in how far it is permissible to draw conclusions as to the polarizability from refraction data for the Na_D-, the H_α- and the H_β-line and the wave-length extrapolated to infinity and also in how far the results of these measurements, which we carried out at 20° may be applicable to the boiling point and the gaseous phase. In the second part of the chapter we shall apply the results to the illucidation of various physical and chemical properties of these compounds.

A. General theory.

I. Preliminary remarks.

We will now consider the bond refractions, that is, we shall split every refraction value found into four parts of which each part must be attributed to a particular bond. This corresponds, thus, to the ,,atomic refraction'' of the halogen ion in question added to $\frac{1}{4}$ of the ,,atomic refraction'' of the C ion. Generally speaking we must assume that the refraction of a hydrogen or halogen ion is different in the different halogenated methane derivates and we shall fully develop below the classification of the variations found in the refraction values. Let us take the series CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, CH_4.

We will first consider the refraction of these compounds only in a phenomenological way. We assume, that the molecular refraction is additively composed from the bond refractions. Here, however, we definately abandon the supposition that these bond refractions are constant ¹).

In CCl_4 a chlorine ion is placed in the field of the central C ion, that is counteracted by 3 other chlorine ions. We represent the bond refraction of this chlorine ion by Cl_{ClClCl}.

(Moreover this clorine ion is naturally influenced by the other molecules, but we leave that out of consideration at present, to return to it later (p. 124)).

Now

$$R_{CCl_4} = 4\,Cl_{ClClCl}.$$

In $CHCl_3$ we may represent the refraction of the chlorine ion by Cl_{ClClH} the refraction of the hydrogen ion may be represented by H_{ClClCl} and

$$R_{CHCl_3} = 3\,Cl_{ClClH} + H_{ClClCl}$$

By analogy,

$$R_{CH_2Cl_2} = 2\,Cl_{ClHH} + 2\,H_{HClCl}$$

$$R_{CH_3Cl} = Cl_{HHH} + 3\,H_{HHCl}$$

$$R_{CH_4} = 4\,H_{HHH}$$

The difficulty is now to determine these values separately. In the most favourable circumstances there are in such a series five known quantities (the R's), while there are 8 unknown. As the differences between the different Cl and H values are small, however, as will be shown later, we may make the assumption, that

$$Cl_{ClClCl},\ Cl_{ClClH},\ Cl_{ClHH} \text{ and } Cl_{HHH}$$

form an arithmetical series and therefore, generally speaking,

$$Cl_{Cl_{3-a}H_a} = Cl_{ClClCl} + a\,\Delta_{Cl}^{H}$$

Δ_{Cl}^{H} is thus the change in refraction, that takes place in one chlorine ion by replacing another chlorine ion by a hydrogen ion.

By analogy we write

$$H_{H_{3-a}Cl_a} = H_{HHH} + a\,\Delta_{H}^{Cl}$$

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¹) cf. J. M. Stevels, Trans. Far. Soc. 33 ...... (1937).

We now shall abbreviate Cl_{ClClCl} to Cl and in general X_{XXX} to X. X, thus, represents the refraction of the X ion in the compound CX_4 [1]). If we include the above in our equations we have

$$
\begin{aligned}
R_{CCl_4} &= 4\,Cl \\
R_{CHCl_3} &= 3\,Cl + 3\,\Delta^{H}_{Cl} + H + 3\,\Delta^{Cl}_{H} \\
R_{CH_2Cl_2} &= 2\,Cl + 4\,\Delta^{H}_{Cl} + 2\,H + 4\,\Delta^{Cl}_{H} \\
R_{CH_3Cl} &= Cl + 3\,\Delta^{H}_{Cl} + 3\,H + 3\,\Delta^{Cl}_{H} \\
R_{CH_4} &= 4\,H
\end{aligned}
$$

The coefficients of Δ we get by multiplying the number of ions which undergo the change by the number of ions that exercise their influence. It is evident, that the coefficient of Δ^{H}_{Cl} is always the same as that of Δ^{Cl}_{H}. We can now include $\Delta^{H}_{Cl} + \Delta^{Cl}_{H}$ in one symbol viz:

$$\Delta^{H}_{Cl} + \Delta^{Cl}_{H} = (HCl)$$

(HCl) is the result of the mutual action of the ions H and Cl and our equations now become

$$
\begin{aligned}
R_{CCl_4} &= 4\,Cl \\
R_{CHCl_3} &= 3\,Cl + H + 3\,(HCl) \\
R_{CH_2Cl_2} &= 2\,Cl + 2\,H + 4\,(HCl) \\
R_{CH_3Cl} &= Cl + 3\,H + 3\,(HCl) \\
R_{CH_4} &= 4\,H
\end{aligned}
$$

We see, that from 5 data we only need to calculate 3 unknowns. On the one hand this has the advantage, that we can to some extent check our assumption regarding the linear course of the refraction value of the chlorine and hydrogen ions in this series, while, on the other hand, it has the advantage that where only 3 or 4 values of the R's are known we can still reach a result.

Of course, we cannot expect that the (XY) symbols can always be determined as accurately as may be done for the R's. We must

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[1]) X has here, thus, the same significance as R_D^{20} (X). We only use the notation X, when we do not need to express dependence of the refraction on the wave-length and the temperature.

not forget, that all manner of other influences (dipole actions etc.) are included in the (XY) values. But in many cases we can determine the (XY) values fairly accurately. We shall see, that we can draw important conclusions from their sign and orde of magnitude. We will now consider the most general case. How would the refraction of CXYZW be constructed according to this theory? It is obvious that

$$\begin{aligned} R_{CXYZW} = X &+ \Delta_X^Y + \Delta_X^Z + \Delta_X^W \\ &+ Y + \Delta_Y^X \qquad\qquad + \Delta_Y^Z + \Delta_Y^W \\ &+ Z \qquad + \Delta_Z^X \qquad + \Delta_Z^Y \qquad + \Delta_Z^W \\ &+ W \qquad\qquad + \Delta_W^X \qquad + \Delta_W^Y + \Delta_W^Z \end{aligned}$$

so that

$$\begin{aligned} R_{CXYZW} = X + Y + Z + W + (XY) + (XZ) + (XW) + \\ + (YZ) + (YW) + (WZ) \end{aligned}$$

or more general

$$R_{CX_1X_2X_4X_3} = \sum_{n=1}^{4} X_n + \frac{1}{2} \sum_{\substack{n=1 \\ m=1}}^{4} (X_n X_m)$$

in which $(X_n X_m) = 0$ for $n = m$.

One great disadvantage of this method of description is that we can never determine $\Delta_{X_n}^{X_m}$ separately.

We shall explain a method later, by which we can say, at any rate approximately, what part of $(X_n X_m)$ is derived from $\Delta_{X_n}^{X_m}$ and what from $\Delta_{X_m}^{X_n}$.

All compounds were measured in a liquid state, and it is a question, therefore, whether the mutual influence of the molecules had no influence which would disturb the results. This is not the case, however, as may be seen from the following: Let us take an ion X_n: this lies in the field of the central C ion. The field is counteracted by other ions of the same molecule. X_n, however, comes into the neighbourhood of ions of other molecules and statistically it will come near to an ion X_m of another molecule just as often as the molecule itself carries X_m ions. The negative ions of the other molecules strengthen the field of the central ion of the molecule in question. They polarize this ion X_n in the sense that the polarization due to the central ion is increased.

$\Delta^{X_m}_{X_n}$, thus, represents the modification of the refraction of the ion X_n by the presence of the ion X_m, both by X_m in the molecule itself and by X_m in the other molecules. It is obvious, that in the gaseous condition the latter influence is almost absent, so that the X_n ion is here in a less strong field and the refraction will therefore be higher. This is a well known fact, that applies to innumarable non-polar substances. Fajans and Joos[1]) and many later investigators[2]) have already pointed this out. Stuart and Volkmann pointed out, that the decrease of the refraction with the condensation shows no relation to the dipole moment of the considered substance.

The decrease of the refraction is expressed in the formula of Raman and Krishnan[3]).

According to these authors, refraction is given by

$$\frac{n^2-1}{n^2+2}\frac{M}{d}=\frac{A}{1-Bd}$$

in which $A=\frac{4\pi}{3}N\frac{\alpha_1+\alpha_2+\alpha_3}{3}$ and $B=\frac{N}{M}d\frac{\alpha_1 S_1+\alpha_2 S_2+\alpha_3 S_3}{3}$

N is the number of Avogadro, S_1, S_2 and S_3 are the deviations of the internal field in the three coordination directions from the field in a spherical „Hohlraum".

In an isotropic medium $S_1+S_2+S_3=0$, so that in the case of an isotropic molecule $B=0$.

According to Höleman, in the gaseous state for an isotropic

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[1] K. Fajans and G. Joos, Z. Physik **23**,1 (1924).

[2] H. A. Stuart and H. Volkmann, Z. Physik **83**, 461 (1933).

P. Hölemann, Z. physik. Chem. **B 32**, 354 (1936).

K. Fajans, Z. physik. Chem. **B 24**, 108 (1934).

H. A. Stuart, Molekülstruktur, Leipzig 1934, p. 110—112. Many quotations of literature are to be found here.

[3] C. V. Raman and K. S. Krishman, Proc. Roy. Soc. London (A) **117**, 589 (1928).

molecule $B = 0$, but not in the liquid state. He derives the formula [1])

$$R_{liq} = \frac{R_{gas}}{1 - \frac{1}{4\pi} S R_{gas} \frac{d^2}{M}}$$

in which $S = \sum_i S_i$. For $S > 0$ which is probably the case usually $R_{liq} < R_{gas}$.

This decrease is due to the same effect, to which the positive temperature coëfficient of the refraction of liquids is due. The higher the temperature, the less the molecules will disturb the symmetrical field in which a molecule lies. As mentioned already gases have not a considerable temperature coëfficient (Chapter I).

This dependence of the temperature, of course, is of quite a different kind to that which is expressed in the Kramers formula, and which is due to another phenomenon. Obviously the first effect is of a much greater order of magnitude.

The difference between the refraction in the gaseous and liquid condition is always extremely small. We may therefore conclude that the influence of the ,,other molecules'' upon the refraction in the liquid state is very small.

II. Calculation of the mutual actions for the Na-D-line.

a. *Mutual action* (HF).

This quantity cannot be calculated directly as no values are known for the refraction of the methane derivatives only containing fluorine. Moreover, none of these compounds are liquid at 20°, so that we did not measure them. Later we shall calculate the (HF) values in a round about way.

b. *Mutual action* (HCl).

R_{CH_2Cl}, R_{CHCl_3} and R_{CCl_4} are known for the liquid state. We assume for R_{CH_4} the value 6.60 [2]) and thus find the equations

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[1]) P. Höleman, Z. physik. Chem. Ber. 32, 354 (1936).

[2]) St. Friberg, Z. Physik 41, 378 (1927).

CH_4 $4\,H = 6.60$ (1)
CH_2Cl_2 $2\,Cl + 2\,H + 4\,(HCl) = 16.38$ (2)
$CHCl_3$ $3\,Cl + H + 3\,(HCl) = 21.37$ (3)
CCl_4 $4\,Cl = 26.44$ (4)

Now we can calculate

$H = 1.65$ (1)
$Cl = 6.61$ (4)

from (2) we obtain $4\,(HCl) = -0.14$
from (3) $3\,(HCl) = -0.11$
So $(HCl) = -0.04$

c. *Mutual action* (HBr).

$R_{CH_2Br_2}$, R_{CHBr_3} and R_{CBr_4} are known.
We find the equations

CH_4 $4\,H = 6.60$ (1)
CH_2Br_2 $2\,Br + 2\,H + 4\,(HBr) = 21.92$ (2)
$CHBr_3$ $3\,Br + H + 3\,(HBr) = 29.83$ (3)
CBr_4 $4\,Br = 39.0$ (4)

From these we calculate

$Br = 9.75$ (4)
$4\,(HBr) = -0.88$ (2)
$3\,(HBr) = -1.07$ (3)

We see, that there is already a deviation from our assumed linearity. There are some sources of error to be pointed out which might disturb the results. The CBr_4 is a solid substance which is measured in various solvents and the value of it is calculated on the assumption that the simple law of mixtures holds for the refraction

$$R_{12} = \nu_1 R_1 + \nu_2 R_2$$

in which R_{12} is the refraction of the mixture, R_1 and R_2 the refraction of the components 1 and 2 respectively, ν_1 and ν_2 the molfractions of the components. In how far this mixture law is of general application is not known. In connection with the measurements made, 39.0 was chosen as most probable value for the hypothetical liquid at 20° C. The value $Br = 9.75$ agrees completely with the theory of boiling points (p. 40).

This assumption of linearity is really only a method of description, of easy calculation. As long as the deviations are small this does no harm. We shall see, accordingly, that with the mutual action (HI) there will be abnormalities too. As the possible error in the Br value enters only 2 times in CH_2Br_2 and here the coefficient of (HBr) is larger than in $CHBr_3$ we will consider the value, calculated from CH_2Br_2, as correct. Thus $(HBr) = -0.22$.

d. Mutual action (HI).

R_{CH_3I}, $R_{CH_2I_2}$ and R_{CHI_3} are known.
We find the equations:

$$\begin{array}{ll} CH_3I & I + 3H + 3(HI) = 19.28 \\ CH_2I_2 & 2I + 2H + 4(HI) = 32.58 \\ CHI_3 & 3I + H + 3(HI) = 48.5_5 \end{array}$$

from this we find

$$\begin{array}{rl} I + 3(HI) = 14.33 & (1) \\ 2I + 4(HI) = 29.28 & (2) \\ 3I + 3(HI) = 46.90 & (3) \end{array}$$

Unfortunately, the value for I is not known. As was to be expected the equations 1—3 do not conform to our simple assumption of linearity; we cannot find a value for I and (HI) which fits them. We shall have to be satisfied with a kind of mean value to arrive at something like the order of the magnitude of this value.

The sources of error are here the same as in the foregoing series, here CHI_3 is a solid substance. We now find from

$$\begin{array}{ll} (3) - (1) & 2I = 32.57 \\ 4(3) - 3(2) & 6I = 99.79 \\ 3(2) - 4(1) & 2I = 30.57 \end{array}$$

Mean value for I is 16.29.

This value is in complete agreement withing the theory of boiling points (p. 40).

From this we may calculate

$$\begin{aligned} 3\,(HI) &= -1.98 \\ 4\,(HI) &= -3.31 \\ 3\,(HI) &= -1.97 \\ \hline 10\,(HI) &= -7.26 \\ (HI) &= -0.73 \end{aligned}$$

It is striking that CH_3I and CHI_3 correspond completely to one another.

e. *Mutual action* (ClBr).

This can be directly calculated from $CClBr_3$

$$R_{CCl_3Br} = 3\,Cl + Br + 3\,(ClBr).$$

From this we find 3 (ClBr) = — 0.29.

Assuming (HCl) = — 0.04 and (HBr) = — 0.22 we now calculate from

CH_2ClBr : $R_{CH_2ClBr} = Cl + Br + 2\,H + 2\,(HCl) + 2\,(HBr) + (ClBr)$

$CHCl_2Br$: $R_{CHCl_2Br} = 2\,Cl + Br + H + 2\,(HCl) + (HBr) + 2\,(ClBr)$

$CHClBr_2$: $R_{CHClBr_2} = Cl + 2\,Br + H + (HCl) + 2\,(HBr) + 2\,(ClBr)$

$$\begin{aligned} (ClBr) &= -0.10 \\ 2\,(ClBr) &= -0.13 \\ 2\,(ClBr) &= -0.28. \end{aligned}$$

We find thus as mean 8 (ClBr) = — 0.80. (ClBr) = — 0.10.

f. *Mutual action* (ClI).

This can be calculated at once from CCl_3I

$$R_{CCl_3I} = 3\,Cl + I + 3\,(ClI).$$

From this we find

$$3\,(ClI) = -1.16.$$

On the assumption (HCl) = — 0.04 and (HI) = — 0.73 we now calculate from

CH_2ClI : $R_{CH_2ClI} = Cl + I + 2\,H + 2\,(HCl) + 2\,(HI) + (ClI)$
$CHCl_2I$: $R_{CHCl_2I} = 2\,Cl + I + H + 2\,(HCl) + (HI) + 2\,(ClI)$

$$(ClI) = -0.35$$
$$2\,(ClI) = -0.85$$

respectively.

We have thus as mean $6\,(ClI) = -2.36$ or $(ClI) = -0.39$.

g. Mutual action (FH), (FCl), (FBr) *and* (FI).

Of these only (FCl) and (FBr) can be directly determined. We know the refraction of CF_4 only in a gaseous condition, from this we find for the F ion 1.82. In the liquid state the refraction per F ion is certainly lower. We take the value, given by van Arkel and de Boer[1]), $F = 1.71$, which is in complete agreement with the theory of boiling points (cf. p. 40).

From CBr_3F : $R_{CBr_3F} = 3\,Br + F + 3\,(FBr)$
we calculate

$$3\,(FBr) = -0.84$$
$$(FBr) = -0.28.$$

From CCl_3F : $R_{CCl_3F} = 3\,Cl + F + 3\,(FCl)$

we calculate

$$(FCl) = +0.02.$$

By means of (FCl) and (FBr) we can now calculate (HF) from

$CHCl_2F$: $R_{CHCl_2F} = H + 2\,Cl + F + 2\,(HCl) + 2\,(FCl) + (HF)$

and

$CHBr_2F$: $R_{CHBr_2F} = H + 2\,Br + F + 2\,(HBr) + 2\,(FBr) + (HF)$.

From this we find

$$(HF) = +0.12$$
$$(HF) = +0.19$$

respectively.

Considering the innumerable sources of error which appear before we arrive at these values the agreement may be considered satisfactory. By means of $(HF) = +0.16$ we calculate from

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[1]) A. E. van Arkel and J. H. de Boer, Z. physik. Chem. **122**, 101 (1926).

$CH_2FI : R_{CH_2FI} = 2\,H + F + I + 2\,(HF\ (HF) + 2\,(HI) + (FI)$

$$(FI) = -\,0.60$$

This value is of course very doubtful.

h. Theoretical part.

Recapitulating we thus find the following table for the mutual actions

	H	F	Cl	Br	I
H	—	+ 0.16	— 0.04	— 0.22	— 0.73
F	+ 0.16	—	+ 0.02	— 0.28	— 0.60
Cl	— 0.04	+ 0.02	—	— 0.10	— 0.39
Br	— 0.22	— 0.28	— 0.10	—	?
I	— 0.73	— 0.60	— 0.39	?	—

This table seems to have no regularity, but we must not forget, that as standard value for X_n we have all through taken the value of the refraction of X_n in CX_{n_4}. (ClBr) is chosen, for instance, dependent upon the value of Cl in CCl_4 and Br in CBr_4 and (ClI) dependent upon the value of Cl in CCl_4 and I in CI_4 etc. so that (ClBr) and (ClI) etc. are not mutually comparable. To do this we must compare everything with a certain norm for which the following may serve.

The meaning of (X_nX_m) is $\Delta_{X_n}^{X_m} + \Delta_{X_m}^{X_n}$

If we now remember what $\Delta_{X_n}^{X_m}$ represents, we know from the above that it is the change, which the refraction of the ion X_n undergoes from the influence of the ion X_m, compared to the state in the compound CX_{n_4}. We now have the compound $CX_n^{(1)}\,X_n^{(2)}\,X_n^{(3)}\,X_n^{(4)}$ and consider the ion $X_n^{(1)}$. We now replace $X_n^{(4)}$ by X_m and examine what happens to the refraction of $X_n^{(1)}$. First we remove $X_n^{(4)}$ so that the field of the central C ion is less counteracted, ion $X_n^{(1)}$ comes into a stronger field, the refraction of $X_n^{(1)}$ decreases with an amount given by

$$\Delta_{X_n^{(1)}} = -\,C_{X_n^{(4)}}\,\frac{R^2_{X_n^{(1)}}}{r^4_{X_n^{(1)}}}$$

We can understand this in the following way: We consider in one case an ion $X_n^{(1)}$, that is caught in the field of the configuration $\overset{X_n^{(3)}}{\underset{X_n^{(2)}}{-C-}}$.

We now suppose that the field of the C ion is the most important and, therefore, we have according to Fajans[1])

$$\Delta R_1 = -C\,\frac{R^2_{X_n^{(1)}}}{r^4_{X_n^{(1)}}}$$

in which formula ΔR_1 represents the decrease of the refraction of the ion $X_n^{(1)}$, when it is caught in the field of the contiguration $\overset{X_n^{(3)}}{\underset{X_n^{(2)}}{-C\cdot-}}$ from the hypothetical free state. $R_{X_n^{(1)}}$ represents the refraction of the ion considered $X_n^{(1)}$ [2]) and $r_{X_n^{(1)}}$ represents the distance from the central ion to the halogen or hydrogen ion $X_n^{(1)}$. $r_{X_n^{(1)}}$ is proportional to the radius of the latter ion as we must assume in methane derivaties anion-anion contact (cf. Chapter II A).

We now consider the case in which the ion $X_n^{(1)}$ is caught in the field of the configuration $X_n^{(4)}\overset{X_n^{(3)}}{\underset{X_n^{(2)}}{-C-}}$. In this case the decrease is less, for the field is counteracted by the presence of $X_n^{(4)}$ and this can be described by an additional factor to C, so that the decrease is now

$$\Delta R_2 = -\left(C - C_{X_n^{(4)}}\right)\frac{R^2_{X_n^{(1)}}}{r^4_{X_n^{(1)}}}$$

and we find for

$$(\Delta_{X_n})_1 = \Delta R_1 - \Delta R_2 = -C_{X_n^{(4)}}\,\frac{R^2_{X_n^{(1)}}}{r^4_{X_n^{(1)}}}\,.$$

It must be noted that Fajans proposed his formula for the decrease of the refraction in the halogen ions only for the halides

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[1]) K. Fajans, . physik. Chem. A 130, 724 (1927).

[2]) R_{X_n} has, thus, the same significance as $R\ (X_n)$.

of the alkaline metals. Here we use the same formula with another constant C. This suggestion seems to fit very well with the measured mutual actions.

$C_{x_n}^{(4)}$ is a constant which shows what the „influence" of the ion $X_n^{(4)}$ is.

It is clear that $C_{x_n}^{(4)}$ will be greater the more ion $X_n^{(4)}$ counteracts the field. In the following we shall omit the indices (1), (4) etc. as having no more use.

Now for halogens in methane derivatives $R_{x_n} \sim r^3_{x_n}$ (cf. p. 35). We may write now

$$(\Delta_{x_n})_1 = -\beta_{x_n}^{(4)}\, r_{x_n}^6$$

If we now put ion X_m into the place of $X_n^{(4)}$, the field of the central ion is more counteracted, the refraction of $X_n^{(1)}$ again increases with an amount

$$(\Delta_{x_n})_2 = +\beta_{x_m}\, r_{x_n}^6$$

The total change in the refraction of $X_n^{(1)}$ consequent on the replacing of ion $X_n^{(4)}$ by X_m is therefore

$$\Delta_{x_n}^{x_m} = (\Delta_{x_n})_1 + (\Delta_{x_n})_2 = (\beta_{x_m} - \beta_{x_n})\, r^6_{x_n}$$

We now replace $r_{x_n}^6$ by A_{x_n} and find for

$$(X_n X_m) = \Delta_{x_n}^{x_m} + \Delta_{x_m}^{x_n} = (\beta_{x_m} - \beta_{x_n})\, A_{x_n} + (\beta_{x_n} - \beta_{x_m})\, A_{x_m}$$

$$(X_n X_m) = (\beta_{x_m} - \beta_{x_n})\, (A_{x_n} - A_{x_m})$$

The formula immediately gives for $X_n = X_m$

$$(X_m X_n) = 0$$

as must naturally be the case. As now the A_{x_n}'s are known we can calculate the β's from our $(X_n X_m)$ values.

We shall for the present count the A_H value as unknown, as R_H is not proportional to r_H^3, the latter being not exactly known. We find

A_F	5.5
A_{Cl}	36.3
A_{Br}	56.7
A_I	101.6

As we use the A values only in comparison with each other, it is permissible to use for r_X the ionic radii given by Pauling which we suppose to be proportional to the actual radii (cf. p. 29).

We therefore find the equations

$$\begin{aligned}
(\beta_F - \beta_H) & \ (A_H - 6) && = +0.16\\
(\beta_F - \beta_{Cl}) & \times 30 && = +0.02\\
(\beta_F - \beta_{Br}) & \times 50 && = -0.28\\
(\beta_F - \beta_I) & \times 95 && = -0.60\\
(\beta_{Cl} - \beta_H) & \ (A_H - 36) && = -0.04\\
(\beta_{Cl} - \beta_{Br}) & \times 20 && = -0.10\\
(\beta_{Cl} - \beta_I) & \times 65 && = -0.39\\
(\beta_{Br} - \beta_H) & \ (A_H - 56) && = -0.22\\
(\beta_I - \beta_H) & \ (A_H - 101) && = -0.73
\end{aligned}$$

We now assume $\beta_I = 0$, because we always determine differences.

We have nine equations between five unknown values β_H, β_F, β_{Cl}, β_{Br} and A_H. It is easy to calculate them.

We may now find

	$-\beta \cdot 10^4$	A
H	100	30
F	63	6
Cl	60	36
Br	8	56
I	0	101

We are now able to calculate all mutual actions by these values and find now:

	emp.	theor.
(HF)	+ 0.16	+ 0.09
(HCl)	— 0.04	— 0.02
(HBr)	— 0.22	— 0.24
(HI)	— 0.73	— 0.71
(FCl)	+ 0.02	— 0.01
(FBr)	— 0.28	— 0.28
(FI)	— 0.60	— 0.60
(ClBr)	— 0.10	— 0.10
(ClI)	— 0.39	— 0.39

The agreement may be considered good as an error of ± 0.03 can be expected as can be shown. This will be discussed later (p. 142). The refraction of the liquid compounds $CX_1X_2X_2X_4$ therefore, generally speaking, can be represented by

$$R = \sum_{n=1}^{4} X_n + \frac{1}{2} \sum_{\substack{n=1 \\ m=1}}^{4} (\beta_n - \beta_m)\ (A_m - A_n).$$

We can now calculate what change of refraction an ion undergoes from the presence of other ions. We can calculate $\Delta_{X_n}^{X_m}$ in absolute value:

$$\Delta_{X_n}^{X_m} = (\beta_{X_m} - \beta_{X_n})\ A_n.$$

We therefore find the following

	by	H (Δ^H)	F (Δ^F)	Cl (Δ^{Cl})	Br (Δ^{Br})	I (Δ^I)
change of	H (Δ_H)	0	+ 0.11	+ 0.12	+ 0.28	+ 0.30
	F (Δ_F)	— 0.02	0	0	+ 0.03	+ 0.03
	Cl (Δ_{Cl})	— 0.14	— 0.01	— 0	+ 0.19	+ 0.21
	Br (Δ_{Br})	— 0.52	— 0.31	— 0.29	0	+ 0.04
	I (Δ_I)	— 1.01	— 0.63	— 0.60	— 0.08	0

With the aid of this table we can calculate the refraction of each halogen ion separately. The refraction of an ion X_n is given by

$$X_n + \sum_{m} \Delta_{X_n}^{X_m} \qquad \text{(a)}$$

We have found, thus, a method for splitting up the refraction of a methane derivative into the refractions of the halogen ions.

Another method to split up the refractions in principle has been developed by Mrowka[1]). He applies the relation between the diamagnetic susceptibility χ and the polarizability α

$$\chi = C \sqrt{p\,\alpha}$$

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[1]) B. Mrowka, Z. physik. **80**, 495 (1933).

which formula has been derived by Kirkwood and Vinti[1]). C is composed of general physical constants and p is the number of electrons of the atom (ion) considered. We can measure the total susceptibility $(\chi^+ + \chi^-)$ and the total refraction $(R^+ + R^-)$ and by means of four equations, calculate χ^+, χ^-, R^+ and R^- separately.

Fajans[2]) has shown, that this method is not very accurate. So it cannot be applied to our data, as we are concerned here with an very small effect.

In the first place we see that the refraction of a particular ion is more and more increased when the central ion carries larger ions. At first sight this is quite unexpected. If we regard the bound ions as non-polarized negetively charged spheres, the larger these ions become, the less counteracted will be the field of the central ion, the energy of the bond will be greater and the refraction of the ion in question will diminish.

Van Arkel and de Boer[3]) have formerly calculated for methane and ethane derivatives, assuming a constant atomic refraction for the halogens, that the hydrogen ions will have a higher refraction, when they occur in a greater amount and these authors explain it on grounds such as given above: the more the field of the central ion is counteracted by small ions the greater will be the refraction of the hydrogen ion. These authors only considered the chlorine derivatives of the methane series. We find here, applying the formula (a), a course that runs in an exactly opposite direction. In the series $CH_4 \rightarrow CCl_4$ we find for the refraction per ion

	H	Cl
CH_4	1.65	—
CH_3Cl	1.77	6.19
CH_2Cl_2	1.89	6.33
$CHCl_3$	2.01	6.47
CCl_4	—	6.61

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[1]) J. G. Kirkwood, physik. Z. 33, 57 (1932).
J. P. Vinti, Phys. Rev. 41, 813 (1932).

[2]) K. Fajans, Z. Phys. Chem. B 24, 127 (1934).

[3]) A. E. van Arkel and J. H. de Boer, Z. physik. Chem. A 122, 101 (1926).

The numbers themselves are, of course, not quite exact, it is only the course in the table that is significant. According to Van Arkel and de Boer[1]) the refraction in hydrogen decreases from CH_4 to $CHCl_3$. A similar course as given in the table we have in the series $CH_4 \rightarrow CBr_4$ and $CH_4 \rightarrow CI_4$.

A description, which takes into consideration the Coulomb forces only is thus certainly not permissible, we must remember several effects. We are only considering the liquid state and therefore the surrounding molecules will exercise an influence upon a particular ion X, and it is so, that growing halogen ions of the surrounding molecules will diminish the field in the ion X. In the first mentioned halogen ions are small they counteract the electric field in X due to the central ion to a great extent. The refraction will be hereby increased. Assuming only Coulomb forces the refraction of a particular ion X, with an increase of the radius of the other substituents of the methane derivative will decrease in consequence of the action of the ions of the same molecule and increase in consequence of the action of the ions of the other molecules. It may obviously be assumed that the first influence is far stronger than the latter. The total effect, therefore, is that in consequence of the Coulomb action the refraction of the ion X decreases as the radius of the other substituents increases. This does not agree with the values found by us.

We must not forget, however, the following: the larger the halogen ions the more they can be polarized. The induced dipole will counteract the field of the central ion. This effect increases passing to larger halogen ions. The refraction of the ion X will therefore be increased. From the ions of other molecules a dipole effect may also be expected, namely a decrease of the refraction of ion X, but this will be negligible compared to the first dipole effect, as we must assume that the dipoles in other molecules lie at a distance, which is much larger than that of the dipoles in the molecule itself. The total effect of the dipole action is thus an increase of the refraction of the ion X in question as the substituents increase in size.

Thus we have two effects which counteract one another. The

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[1]) A. E. van Arkel and J. H. de Boer, loc. cit.

Coulomb action will cause the refraction of X to decrease, while the dipole action will cause the refraction of X to increase, if we change the other substituents successively from F to I.

We now examine a particular halogen ion X and replace the other substituents gradually by larger ones. The refraction of X will first decrease and finally the dipole effect will cause it to increase once more. Thus, there is a certain minimum. From our figures we can deduce that this effect is reached in the carbon derivatives already for hypothetical halogen ions smaller than hydrogen. The „preponderantly Coulomb" behaviour of the refraction is not realised in the carbon derivatives. The refraction is principally determined by the polarization effect. This behaviour is thus expressed in the increase of the $\Delta_{X_n}^{X_m}$ values from $\Delta_{X_n}^{H}$ to $\Delta_{X_n}^{I}$, or which is essentially the same thing, the increase from β_H to β_I.

III. Calculation of the mutual actions for a wave-length extrapolated to infinity.

So far we have discussed the mutual action applying the refraction of the Na-D-line. We will now consider the wave-length extrapolated to infinity. Unfortunately we cannot determine these mutual actions so accurately as the refraction itself has been found by a considerable extrapolation. Moreover, we have not such extensive material at our disposal as in case of the Na-D-line as in various substances only the Na-D-line can be determined without serious difficulties. We calculate $R_\sim$ for CH_4 from Friberg's dispersion formula ¹) for this substance. For CH_4 we find 6.44 from which we find for H : 1.61. We then calculate from

$$R_{CH_2Cl_2} = 15.84$$
$$R_{CHCl_3} = 20.60$$
$$R_{CCl_4} = 25.54$$

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¹) St. Friberg, Z. Physik. 41, 378 (1927).

$$\begin{aligned} \mathrm{Cl} &= 6.44 \\ 4\,(\mathrm{HCl}) &= -0.28 \\ 3\,(\mathrm{HCl}) &= -0.18 \\ (\mathrm{HCl}) &= -0.06. \end{aligned}$$

We can further compare this series CH_aBr_{4-a}

$$\begin{aligned} R_{CH_2Br_2} &= 20.91 \\ R_{CHBr_3} &= 28.76. \end{aligned}$$

This yields equations with two unknowns for which we find $\mathrm{Br} = 9.25$ and $(\mathrm{HBr}) = -0.20$.

Of course these values are extremely precarious, we have no means of checking them by other compounds. We have already found, that $CHBr_3$ deviated from linearity. The refraction for the Na-D-line R_{CHBr_3} proved to be 0.41 lower than calculated. We have therefore in this case added 0.41 to the experimental value of $R_{CHBr_3} = 28.35$ to obtain the theoretical value for the linearity. These values for Br and (HBr) are well confirmed in the mixed chlorine and bromine containing methane derivatives. We find from

$$\begin{aligned} R_{CH_2ClBr} &= 18.34 & (\mathrm{ClBr}) &= 0 \\ R_{CHCl_2Br} &= 23.19 & 2\,(\mathrm{ClBr}) &= -0.13 \\ R_{CHClBr_2} &= 25.80 & 2\,(\mathrm{ClBr}) &= -0.24 \\ R_{CCl_3Br} &= 28.11 & 3\,(\mathrm{ClBr}) &= -0.31 \end{aligned}$$

Considering all the causes of inaccuracy, the agreement may be considered good. We find as mean value $(\mathrm{ClBr}) = -0.09$.

The mutual actions of F may be determined as follows. From $R_D\,(\mathrm{F}) = 1.71$ we may estimate $R_{\sim}\,(\mathrm{F}) = 1.67$. From $R_{CHCl_2F} = 16.13$ we find, (assuming $(\mathrm{ClF}) = 0$ which is quite acceptable, as we found it for the Na-D-line too) $(\mathrm{HF}) = +0.19$.

From this we can again calculate from

$$\begin{aligned} R_{CBr_3F} &= 28.68 & 3\,(\mathrm{FBr}) &= -0.74 \\ R_{CHFBr_2} &= 21.10 & 2\,(\mathrm{FBr}) &= -0.47 \end{aligned}$$

in good agreement. As mean value we find $(\mathrm{FBr}) = -0.24$.

From $R_{CH_3I} = 18.17$ and $R_{CH_2I_2} = 30.06$ we calculate $\mathrm{I} = 14.63$

and (HI) = — 0.50. Here a similar correction is introduced as in the series CH_nBr_{4-n}, i.e. R_{CH_3I} is diminished by 0.21 and $R_{CH_2I_2}$ is increased by 0.42. Our only other data are R_{CH_2FI} and R_{CH_2ClI} but we do not feel justified in determining (FI) and (ClI) further by means of the very doubtful values of X and (X_nX_m), as we have no means of checking them further.

IV. Calculation of the mutual actions for the H_α-line and the H_β-line. Survey of Results.

We apply the same method of calculation here. For the sake of brevity we will leave out the calculations. The results will be found in the table below. H = 1.64 [1] and F = 1.70 is taken for the H_α-line and H = 1.66 [1] and F = 1.72 for the H_β-line with the assumption (FCl) = 0 for both H_α- and H_β-line.

All our results are collected in the following table:

	β	D	α	$\lambda \rightarrow \sim$
H	1.66	1.65	1.64	1.61
F	1.72	1.71	1.70	1.67
Cl	6.69	6.61	6.58	6.44
Br	9.92	9.75	9.67	9.25
I	16.90	16.29	16.11	14.63
(HF)	+ 0.09	+ 0.16	+ 0.16	+ 0.19
(HCl)	— 0.03	— 0.04	— 0.04	— 0.06
(HBr)	— 0.22	— 0.22	— 0.21	— 0.20
(HI)	— 0.81	— 0.73	— 0.71	— 0.50
(FCl)	0	0	0	0
(FBr)	— 0.27	— 0.28	— 0.26	— 0.24
(FI)	—	— 0.60	—	—
(ClBr)	— 0.10	— 0.10	— 0.10	— 0.09
(ClI)	—	0.39	—	—

We see that the X values decrease from the H_β-line to $\lambda \rightarrow \sim$ as was to be expected in accordance with the theory of dispersion. Dispersion is highest in iodine and lowest in hydrogen and fluorine.

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[1] St. Friberg, Z. Physik. 41, 378 (1927).

As regards the mutual actions we see, that all these in first approximation are the same as those of the Na-D-line, considering the accuracy with which they can be determined. And yet the following regularity is undeniable: in (HF) and (HCl) the value increases at the transition to a larger wave-length, in (HBr) the values are about constant and in (HI) they diminish. It is not easy to account for this at first sight. The whole would seem to suggest that we can describe mutual actions also by using the H_α- or H_β-line or the wave-length extrapolated to infinity. In the foregoing we have used the Na-D-line as a basis of our calculation. This was done for the following reasons: 1° because this line will be the least disturbed by infra-red and ultra-red absorbtion, as Fajans and Joos have shown and 2° because we have here much larger and more accurate material for comparison.

V. Influence of temperature on the mutual actions.

We must now investigate whether the mutual actions at 20° retain their value at the boiling point, as we shall often use them in calculations which apply to this temperature.

We represent the refraction of any compound at boiling point by

$$R^B = \sum_n R^B_{X_n} + \tfrac{1}{2} \sum_{nm} (X_n X_m)$$

in which R^B represents the total refraction of the compound, R_{X_n} the constant value for the refraction of a particular halogen ion X_n and $(X_n X_m)$ are the mutual action terms.

The refraction shows a positive temperature coëfficient, generally speaking it rises 1 ‰ per 10°. We can therefore represent the refraction at 20° C by

$$R^{20} = \sum_n R^B_{X_n} - (T_s - 293)\,\gamma + \tfrac{1}{2} \sum_{nm} (X_n X_m).$$

in which $\gamma = R \,.\, 10^{-4}$.

$$R^{20} = \sum_n R^B_{X_n} - (\sum_n T_{X_n} + T_D - 293)\,\gamma + \tfrac{1}{2} \sum_{mn} (X_n X_m).$$

T_{X_n} is the cohesion contribution of the halogen ion X_n to the boiling point and T_D is the dipole contribution. T_D is in compounds with one H ion 45°, with two H ions 85° and with three H ions 81° 1)).

This means per H ion a contribution of 45°, 42° and 27° respectivily. We take 36° with variation $\Delta T'_H = \pm 9°$.

We now call $T'_{X_n} = T_{X_n} - 73$ and $T'_H = T_H + 36 - 73 = T_H - 37$.

Then we can write

$$R^{20} = \sum_n (R^B_{X_n} - \gamma T'_x) + \tfrac{1}{2} \sum_{nm} (X_n X_m)$$

$$R^{20} = \sum_n R^{20}_{X_n} + \tfrac{1}{2} \sum_{nm} (X_n X_m)$$

At 20° we find, therefore, about the same mutual action as at the boiling point, while the connection between the standard values at 20° and the boiling point are given by

$$R^{20}_{X_n} = R^B_{X_n} - \gamma T'_{X_n}.$$

We have made use of this equation earlier 2)).

The refraction in the compounds examined varies between about 16 and 30. If we, therefore, take as standard value $\gamma = 23 \times 10^{-4}$ the deviation is $|\Delta\gamma| = 7 \times 10^{-4}$. If then the mutual action at the boiling point is to be the same as at 20° $|\Delta\gamma T'_x|$ must be small compared to the mutual actions. This is shown by the following table.

	$\lvert T'_x \rvert$	$\lvert \Delta\gamma T'_x \rvert$
H	10	0.01
F	37	0.03
Cl	14	0.01
Br	43	0.03
I	83	0.06

These values certainly are small compared to the values found for $(X_n X_m)$. We see that the values (HCl) = — 0.04 and (FCl) = — 0.02 are very uncertain and they are therefore not used in the calculation of the β's and A's. The fact that for (HCl)

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1) A. E. van Arkel, Rec. trav. chim. **51**, 1081 (1932).

2) cf. also J. M. Stevels, Chem. Weekblad **34**, 334 (1937).

and (FCl) we find — 0.04 and + 0.02 experimentally and — 0.02 and — 0.01 theoretically is not at all disturbing, on the contrary, it strongly supports the theory. The compounds which determine (FCl) have a γ of the order of magnitude of 18×10^{-4}, in other words the R_X^{20}-values for these compounds are of the order of magnitude of $5 \times 10^{-4}\ T'_X$ higher than the standard values and thus we find the empirical $(X_n X_m)$ value too high.

(HCl) is disturbed by the dipole effect (Chapter VI), so a small deviation of the theoretical value from the experimental can be expected.

Further we must investigate whether the variations in T'_H are of influence, in other words, if $|\gamma \Delta T'_H|$ is small compared to the mutual actions.

This proves to be the case, $|\gamma \Delta T'_H|$ is namely 0.02. To summarise we may say, therefore, that the $(X_n X_m)$ value at 20° is about the same as at the boiling point. We may not draw quantitative conclusions from the mutual actions. The dipole effect, moreover is not very injurious to the $(X_n X_m)$ values either (cf. Chapter VI).

B. Application of the theory to some physical and chemical proporties of organic compounds.

I. Explanation of the exceptions to the rule of additivity of the boiling points of methane derivatives.

Taking as our starting point the formula

$$T_S = k \frac{\left[\sum_n \frac{\sqrt{\varphi_n \alpha_n}}{\sqrt{r_n^3}}\right]^2}{V}$$

we may write

$$T_S = k \frac{[\sum_n C_n \alpha_n]^2}{V}$$

We know that α_n in the carbon derivatives is variable. For the present we shall regard C_n as constant. If we call the variation in α_n $\delta\alpha_n$ it follows that T_S changes by δT_S.

$$\delta T_s = \frac{2k}{V} \sum_n \left[\sum_m C_m \alpha_m\right] C_n \delta\alpha_n$$

$$\delta T_s \sim \frac{V - V_c}{V} \sum_n C_n \delta\alpha_n$$

$$\delta T_s \sim \frac{V - V_c}{V} \sum_n \frac{C_n \alpha_n \delta\alpha_n}{\alpha_n}$$

$$\delta T_s \sim \frac{V - V_c}{V} \sum_n \frac{V_n \delta\alpha_n}{\alpha_n}$$

We now call $\frac{\delta\alpha_n}{\alpha_n} = S_n$ and then

$$\frac{\delta T_s}{T_s} \sim \frac{\sum_n V_n S_n}{\sum_n V_n}$$

This formula enables us to calculate the percentual deviation the actual boiling point will show compared to the boiling point calculated with certain standard values for the hydrogen and halogen ions.

The formula is of course not absolutely correct, as we know that C_n is not constant. In fact

$$C_n = \frac{\sqrt{\varphi_n}}{\sqrt{r_n^3}} = \text{const. } r_n^{-2} \sim \alpha_n^{-2/5}$$

$$\delta C_n = \text{const. } \alpha_n^{-7/5} \delta\alpha_n$$

in which r_n is proportional to $V^{1/3}$.

We must therefore write

$$\delta T_s = \frac{2k}{V} \sum_n \left[\sum_m C_m \alpha_m\right] \left[C_n \delta \alpha_n + \alpha_n \delta C_n\right]$$

$$\delta T_s \sim \frac{(V - V_c)}{V} \sum_n \frac{\left[C_n \alpha_n \delta \alpha_n - \text{const. } \alpha_n^{3/5} \delta \alpha_n\right]}{\alpha_n}$$

$$\delta T_s \sim \frac{V - V_c}{V} \left[\sum_n \left(V_n - \text{const. } \alpha_n^{3/5}\right) S_n\right]$$

Now

$$\alpha_n^{3/5} \sim V_n$$

and thus

$$\frac{\delta T_s}{T_s} = k' \frac{\sum\limits_n V_n S_n}{\sum V_n}$$

We shall now suppose that the standard values for the contribution to the boiling points of the various halogen ions correspond to the mean values of the refraction of these halogen ions.

The mean refraction of the halogen X is represented by $\overline{X}$, we may write

$$\overline{X_n} = X_n + \sum_p g_{x_p} \Delta_{X_n}^{X_p}$$

in which g_{x_p} indicates the mean number of times that X_p occurs in the whole series of the known substances. Naturally the g's are normalized, so that

$$\sum_p g_{x_p} = 3.$$

The total change of refraction of a halogen ion X_n in regard to the refraction of the ion in CX_{n_4} is given by

$$\Delta_{x_n} = (\sum_m \beta_{x_m} - 4\,\beta_{x_n})\,A_n$$

in which the X_m's represent the ions of the molecule in question including X_n. We call the deviation of the actual refraction value from the standard value δR_n.

Then,

$$\delta R_n = (X_n + \Delta_{x_n}) - \overline{X} = \Delta_{x_n} - \sum_p g_{x_p} \Delta_{X_n}^{X_p}$$

$$\delta R_n = (\sum_m \beta_{x_m} - 4\,\beta_{x_n})\,A_n - (\sum_p g_{x_p}\,\beta_{x_p} - \sum_p g_{x_p}\,\beta_{x_n})\,A_n$$

$$\delta R_n = (\sum_m \beta_{x_m} - 4\,\beta_{x_n} + 3\,\beta_{x_n} - \sum_p g_{x_p}\,\beta_{x_p})\,A_n$$

$$\delta R_n = (\sum_m{}' \beta_{x_m} - \sum_p g_{x_p} \beta_{x_p}))\,A_n$$

in which the accent of the Σ' sign indicates that β_{x_n} must not be included.

Now, therefore,

$$S_n = \frac{\delta\,\alpha_n}{\alpha_n} \sim (\sum_1^4{}' \beta_{x_m} - \text{const.})\,r_n$$

because

$$\frac{A_n}{\alpha_n} \sim r_n\ ^{1})$$

Finally

$$\frac{\delta\, T_s}{T_s} = k'' \frac{\sum\limits_n V_n\, Q_n}{\sum\limits_n V_n}$$

in which

$$Q_n = \Big(\sum_{4}^{1}{}'\, \beta_{X_m} - \text{const.}\Big)\, r_n$$

If H, F, Cl, Br and I occur to the same extent the constant becomes

$$\frac{3}{5}(\beta_H + \beta_F + \beta_{Cl} + \beta_{Br} + \beta_I) = -139 \times 10^{-4}.$$

In principe we can determine k'' and $\sum\limits_p g_{X_p}\, \beta_{X_p}$ from the compounds having the greatest deviations. Here very little and very unreliable material is known. An error of 1 degree in the boiling point means a deviation of the order of magnitude of 10 to 40 % in $\frac{\delta\, T_s}{T_s}$.

Moreover, three of the boiling points, that show deviations are determined by extrapolation of the vapour pressure curve, so that they are quite uncertain. Further it is a question, if the relation $\frac{T_s}{T_{cr}} =$ constant, which is introduced in this calculation, holds with sufficient accuracy. Finally we showed above that we may not use the β values for exact calculations.

Though it is impossible to calculate the value of the deviations, it is possible to indicate which compounds will show them. The simultaneous occurence of H and F causes a relatively large increase in the polarizability of the H ion, while that of the F ion is practically unchanged. The total London energy will be larger therefore, and the true boiling point is higher than the additively calculated one, which can be seen in the following table.

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1) Of course, here we have to do with an effective r_n in the case of hydrogen.

	b. p. exp.	b. p. calc.
CHF_3	189	180
CHF_2Cl	233	231
$CHFCl_2$	288	283

In the simultaneous occurence of H and I the relative increase of the polarizability of the hydrogen ion is greater, but the relative diminution of that of the iodine ion is much greater so that we may expect a lower boiling point than the calculated one. From the table on p. 135 we may expect that in the case of the occurence of H and I this effect is much more marked than the first mentioned one and therefore compounds with the combinations H, F and I will have a lower boiling point than the additively calculated ones. This can be seen in the following table.

	b. p. exp.	b. p. calc.
CH_2FI	326	332
CHF_2I	295	300
$CHFI_2$	374	420
CHI_3	492	540

In $CHFI_2$ the effect must be very large, which, in spite of the doubtful value for the boiling point (it is found by extrapolation of the vapour pressure temperature curve, which was only determined up to 50 degrees under the boiling point) is quite obvious, as it is very improbable, that the error made by the extrapolation exceeds more than 30 degrees. The same holds for CHI_3.

We must remember, moreover, that the occurence of F and I will also produce a lowering of the boiling point as the polarizability of F is relatively slightly raised and the polarizability of I much diminished. This effect also influences the three above mentioned F and I containing methane derivatives. Unfortunately CF_3I, in which this effect could be so well tested, as it is not disturbed by the dipole effect is not known. To a less extent, the same is to be expected of Cl and I, and indeed CCl_3I boils 4° lower than the additive calculation predicted (b. p. calc. 419, b. p. found 415). All deviations of the known boiling points of the methane derivatives $> 3°$ are now explained. From the grounds developed above we may expect that CH_2F_2 will boil at a higher temperature and CF_3I, CF_2I_2 and CFI_3 at a lower than the additively calculated boiling points, when we use a constant T_D value.

We come now, however, as a consequence of the theory developed above, to the conclusion, that the T_D values of the methane series, are no constants.

The simultaneous occurence of H and F causes an increase of the London energy, while H with Cl, Br and I causes a decrease and in even increasing extent. Van Arkel and de Boer have found that the dipole contribution in a particular type CH_aX_b was constant when assuming an additive London contribution to the boiilng point. The consequence of the above, therefore, is that we must assume a dipole contribution which always increases as we introduce heavier halogen atoms. In the series $CH_aF_{4-a} \rightarrow CH_aI_{4-a}$, thus, the T_D value constantly increases slowly in complete agreement with what we found for the series containing silicon.

Finally we can explain, why there is a sudden decrease of the T_D values in the series $SiHF_3 \rightarrow SiHI_3$, when passing from $SiHBr_3$ to $SiHI_3$. Generally speaking the T_D values increase in the silicon series, when we introduce larger halogen ions. Only $SiHI_3$ is an exception. From $SiHBr_3$ tot $SiHI_3$ T_D is lowered from 42.5° to 34° (cf. p. 33). Assuming that the theory developed above for the carbon series holds for the silicon series too, we must expect that the London contribution is relatively more and more lowered, if compared to the additivily calculated one, when we introduce heavier halogen ions.

In $SiHI_3$ therefore, the London contribution is much smaller than the additively calculated one, so the T_D value determined in the last way, seems to be lowered suddenly. Unfortunately, SiH_3I and SiH_2I_2 are not known so that we cannot find this effect elsewhere.

Perhaps this is an indication, that the large deviations of the boiling points of $CHFI_2$ and CHI_3 have a real significance.

II. The dipoles of the halogenated organic compounds.

a. Chlorine containing methane derivatives.

The structure of the chlorine and hydrogen containing methane derivatives, has been determined by various authors both by *X* rays and by electron rays. The following values have been found:

		dist. Cl-Cl in Å	angle Cl-C-Cl	dist. C-Cl in Å
CH_3Cl	2)			1.77 ± 0.02
	3)			1.85 ± 0.06
	4)			1.80 ± 0.1
CH_2Cl_2	2)	2.92 ± 0.02	111 ± 2°	1.77 ± 0.03
	3)	3.16 ± 0.06	112 ± 3°	1.86 ± 0.04
	4)	2.23 ± 0.1	124 ± 6°	(1.83)
$CHCl_3$	2)	2.93 ± 0.02	111 ± 2°	1.78 ± 0.03
	3)	3.04 ± 0.04		
	4)	3.11 ± 0.05	116 ± 3°	(1.83)
CCl_4	1)2)	2.87 ± 0.01	(109° 28′)	1.760 ± 0.005
	3)	2.98 ± 0.03	(109° 28′)	1.82 ± 0.02
	4)	2.99 ± 0.03	(109° 28′)	1.83 ± 0.02

We see, that the distance C-Cl in all these compounds is practically the same when we compare the values given by a particular author, while the distance Cl-Cl in CH_2Cl_2 and $CHCl_3$ seem to be different to those in CCl_4 5). From this we may calculate that the angle Cl-C-Cl in these compounds is larger than the normal angle between two bonds in an undeformed tetrahedron (109°28′). This effect has been attributed to the fact that the two Cl ions more or less repulse one another, whereby a neat explanation can be given, why the dipole moment of $CHCl_3$ is smaller than of CH_3Cl. The dipole moments, however, of these two compounds differ too much to be explained by an effect of this kind.

Sutton and Brockway 6) assuming a moment equal to 0

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1) L. Pauling and L. O. Brockway, J. Chem. phys. **2**, 867 (1934).

2) L. E. Sutton and L. O. Brockway, J. Am. Chem. Soc. **57**, 473 (1935).

3) R. Wierl, Ann. Phys. (5), **8**, 521 (1931), **13**, 453 (1931).

4) P. Debye, L. Bewilogua and F. Ehrhardt, Physik. Z. **30**, 84, 524 (1929).

L. Bewilogua, Physik. Z. **32**, 265 (1931).

5) cf. also H. A. Stuart, Physik. Z. **32**, 793 (1931).

6) L. E. Sutton and L. O. Brockway, loc. cit.

for the C-H bond have calculated by means of the angles, found with X rays, what the moment of the C-Cl bond is in chlorated methane derivatives. They found for μ_{CCl} in CH_3Cl 1.85 D, for μ_{CCl} in CH_2Cl_2 1.35 D and for μ_{CCl} in $CHCl_3$ 1.28 D. The sequence is exactly opposite to what we should expect from our refraction values. The refraction per Cl ion increases from CH_3Cl to CCl_4, that is, the polarization decreases and therefore the dipole moment of the C-Cl bond increases. If we consider our refraction values further, we see that the values for the Cl ions do not vary very greatly, showing that the Cl ions in the compounds in question are all bound approximately in the same way. But the H ions show a great variety, so that it is natural to assume, that in the description of this effect we may roughly take the dipole μ_{CCl} to be a constant and the dipole μ_{CH} to be highly variable. We have found, that the polarizability of the H ion in CH_3Cl is lower than in $CHCl_3$. The dipole μ_{CH} in CH_3Cl will therefore be smaller than in $CHCl_3$.

The dipole $\mu_{(\mathrm{CH})}$ has its negative side in the H ion [1]), so the total dipole of CH_3Cl is $\mu_{\mathrm{CCl}} - \mu_{(3\,\mathrm{CH})}$ in which $\mu_{(3\,\mathrm{CH})}$ gives the dipole due to 3 H ions.

Eucken and Meyer [2]) do not accept the negatively charged hydrogen. They consider the dipole moment of CH_3Cl ($\mu = 1.9$) as the sum of the partial dipole moments $\mu_{(\mathrm{CCl})} = 1.5$ and $\mu_{(3\,\mathrm{CH})} = 0.4$.

The dipole of $CHCl_3$ is $\mu_{(3\,\mathrm{CCl})} - \mu_{(\mathrm{CH})}$. Now $\mu_{(3\,\mathrm{CCl})}$ is somewhat smaller than $\mu_{(\mathrm{CCl})}$ due chiefly to the repulsion effect (the induction effect is here very small). $\mu_{(3\,\mathrm{CH})}$ is much smaller than $\mu_{(\mathrm{CH})}$, due partly to the repulsion effect but chiefly to the induction effect.

This would explain why CH_3Cl must have a very much larger dipole than $CHCl_3$. The total dipole of two C-X bonds, making an angle of about 109°28′ with one another is about 1.14 times the dipole of one of such a C-X bond. As the dipoles of CH_3X

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[1]) A. E. van Arkel and J. H. de Boer, La Valence et l'Electrostatique, Paris 1936, p. 119.

cf. H. G. Trieschmann, Z. physik. Chem. B 24, 22 (1936), who proves this for benzene derivatives.

[2]) A. Eucken and L. Meyer, Physik. Z. 30, 397 (1929).

and CHX_3 differ about 70 %, the sequence in de dipoles CH_3X, CH_2X_2, CHX_3 is always guaranteed.

It should here be remarked that Bauer[1]) succeeded in calculating the distances C-Cl and Cl-Cl in CH_2Cl_2 and $CHCl_3$ by means of an analysis of the diffraction photos of these substances with two independent parameters. His results follow:

	dist. C-Cl in Å	dist. Cl-Cl in Å	Angle Cl-C-Cl
CH_3Cl	1.77 ± 0.02		
CH_2Cl_2	1.78_5	2.91_3	109°22′
$CHCl_3$	1.78_1	2.91_0	109°34′

This indicates a rigid tetrahedral model; the repulsion effect does not occur at all, the distances C-Cl and Cl-Cl are the same in all molecules examined. The explaination of the difference between the dipole mements of CH_3Cl, CH_2Cl_2 and $CHCl_3$ must be attributed in this case to the induction effect, which according to our theory, is quite possible[2]).

b. Other methane derivatives.

The structure of the methane derivatives containing bromine and iodine has been determined by the X rays method by Dornte[3]).

His results are found in the following table.

	distance X-X	Angle X-C-X	distance C-X
CH_3Br	—	—	2.06 ± 0.05
CH_2Br_2	3.61 ± 0.1	125 ± 5°	2.03 ± 0.05
$CHBr_3$	3.46 ± 0.1	115 ± 5°	2.05 ± 0.05
CH_3I	—	—	2.28 ± 0.05
CH_2I_2	4.06 ± 0.1	125 ± 5°	2.28 ± 0.05
CHI_3	3.80 ± 0.2	115	—
	3.56[4])		

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[1]) S. H. Bauer, J. Chem. Phys. 4, 406 (1936).

[2]) We may ask how far the occurrence of atomic polarisation P_A disturbs the results, as our values only represent the electronic polarisation P_E. As P_A is always small compared to P_E, however, we do not need to be anxious about this point. Cf. C. P. Smyth, J. Chem. phys. **1**, 247 (1933); K. L. Wolf, Physik. Z. **31**, 227 (1930); Z. physik. Chem. B **2**, 39 (1929), **3**, 128 (1929); K. L. Wolf and O. Fuchs, Handbuch der Stereochemie, Leipzig 32, p. 215; O. Fuchs and K. L. Wolf, Dielektrische Polarisation, Leipzig 1935, p. 262.

[3]) R. W. Dornte, J. Chem. Phys. **1**, 630 (1933).

[4]) M. L. Huggins and B. A. Nobbe, Am. Mineral, **16**, 519 (1931).

Here we see, that the distance CX is constant and that there is a repulsion effect. Further the same considerations apply as in the chlorine compounds so that we may expect a sharp decline in the dipole moments when passing from CH_3X to CHX_3.

The following dipole moments are given:

	Cl	Br	I
CH_3X	1.86	1.79	1.60
CH_2X_2	1.57	1.39	1.10
CHX_3	1.15	1.09	0.91

The dipole moments of compounds CH_3X, generally speaking, is $\mu_{(CX)} - \mu_{(3\ CH)}$. We assume now, that $\mu_{(CX)} =$ constant in CF_4, CCl_4, CBr_4 and CI_4. $\mu_{(3\ CH)}$ increases from CH_3F to CH_3I, while $\mu_{(CX)}$ is not very variable in the different compounds.

The total dipole will actually decrease in the series CH_aX_{4-a} from Cl to I. Generally speaking, as the halogen ions become smaller, the total dipole will become larger, because $\mu_{(CH)}$ will be diminished. In this connection is it highly instructive to examine the following series[1])

	μ
$CHCl_3$	1.15
$CHFCl_2$	1.29
CHF_2Cl	1.40

An exception to this rule is formed by CH_3F for which we find $\mu = 1.81$, which is a little smaller that for CH_3Cl ($\mu = 1.86$). Experimentally we have found that (HF) $= + 0.16$ so that $\Delta^{F}_{H} > 0.16$ and thus certainly greater than Δ^{Cl}_{H} for which we found $+ 0.12$. The immediate consequence of this is, according to the above, that the dipole moment of CH_3F must be somewhat smaller than that of CH_3Cl. It follows from the fact that the refraction of the halogen ions (not hydrogen!) change relatively so little and from our assumption, that $\mu_{(CX)}$ is constant in the symmetrical derivatives, that $\mu_{(CX)}$ is practically constant.

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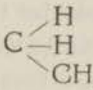
[1]) C. P. Smyth and K. B. McAlpine, J. Chem. Phys. 1, 190 (1933).

From this it follows that the mixed halogenated methane derivatives must have a dipole moment 0 too. $\mu_{(CX)}$ is practically constant and therefore in $CFBr_3$, for instance, the dipole $\mu_{(3\ CBr)}$ will compensate $\mu_{(CF)}$ etc. Van Arkel and Snoek[1]) have, in fact, found, that this is the case for CBr_3F and CCl_3Br. Other research[2]) however, led to dipole moments for CF_2Cl_2 : 0.51 and for $CFCl_3$: 0.45.
The method followed by van Arkel en Snoek is of quite another kind than that followed by Smyth and McAlpine, so that the results are not mutually comparible.

c. *The dipolemoments of the halogen alkanes.*

1. Monohalogen alkanes.

The arguments concerning the dipoles may be logically extended to the series which contain more than one C atom. (In order to join with the terminology, used in organic chemistry we shall speak in the following of atoms instead of ions).

Let ust first consider the series C_2H_5X. Here we again have a central C atom which carries the groups X, H, H and CH_3. One H is replaced by a CH_3 group. The dipole moment is that of CX diminished by that of the configuration  $C\begin{matrix}H\\H\\CH_3\end{matrix}$, thus,

$$\mu_{(CX)} - \mu_{\binom{2\ CH}{C\ (CH_3)}}$$

The C-H dipole is negative on the side of the H atom, the C-CH_3 dipole, when not zero, is positive on the side of the CH_3 group and thus $\mu_{(3CH)}$ is smaller than $\mu_{\binom{2\ CH}{C\ (CH_3)}}$ so that the total dipole is increased.

We can go even further. If we proceed in the series C_2H_5Cl to C_2H_5I only 2 H atoms are always in their refraction increased by the presence of halogen, while in the CH_3X series 3 H atoms are.

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[2]) A. E. van Arkel and J. L. Snoek, Z. Physik. Chem. B 18, 159 (1932).

[3]) C. P. S. Smyth and K. B. McAlpine, J. Chem. Phys. 1, 190 (1933).

In the C_2H_5X series, thus, the difference between the dipoles will diminish, but the course will remain:

	F	Cl	Br	I
CH_3X	1.81	1.86	1.78	1.59
C_2H_5X	1.92	2.03	2.02	1.90

These values are taken from Smyth and McAlpine 1).

The dipole moments of these compounds have been measured by a number of other experimenters and results are to be found in numerous reviews 2). The values here given are about the mean of those found by the various authors. They also agree with measurements given later 3).

A transition to higher monohalogen alkanes yields little more change in the dipole moment, as was to be expected from the above. The only difference is that the CH_3 group is replaced by the C_2H_5 group.

The number of influenced H atoms remains the same; this seems to be the principle criterion. The irregularities in the results are too great for us to establish an effect with certainty, the dipole are of about the same order in the C_2H_5X series as in the $n\text{-}C_3H_7X$ series and in the higher normal mono-halogen alkanes.

We may now consider the secondary monohalogen alkanes. The lowest terms that can be compared are the propyl compounds. The dipole of the primary compounds is

$$\mu_{(CX)} - \mu\left(\genfrac{}{}{0pt}{}{2\,CH}{C\,(C_2H_5)}\right)$$

and of the secondary

$$\mu_{(CX)} - \mu\left(\genfrac{}{}{0pt}{}{CH}{2\,C\,(CH_3)}\right)$$

Applying the above we see that the secondary compounds have a larger dipole moment than the primary ones. The difference between the dipoles of the Cl, Br and I compounds will diminish.

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1) C. P. Smyth and K. McAlpine, J. Chem. Phys. **2**, 501 (1934).

2) Trans. Far. Soc. **30**, 905 (1934).

Supplement O. Fuchs and K. L. Wolf, Dielectrische Polarisation, Leipzig 1935.

3) K. L. Ramaswamy, Proc. Indian Ac. Sci. A **4**, 108 (1936).

The dipole of the tertiary monohalogen butanes, for instance, is given by

$$\mu_{(CX)} - \mu_{(3\ C(CH_3))}.$$

There are no H atoms at all, attached to the halogen carrying carbon atom, the dipole moments of the compounds in the series $(CH_3)_3CCl \rightarrow (CH_3)_3CI$ are practically all alike. These statements are confirmed by the following results (the dipole effects are given according to the table for Dipole moments of the Faraday Society):

	Cl	Br	I
n-C_3H_7X	2.0	1.9	1.7
CH_3CHXCH_3	2.1	2.1	2.0
n-C_4H_9X	2.0	1.9	(1.7)
$(CH_3)_2CHCH_2X$	1.98	1.97	1.87
$CH_3CH_2CHXCH_3$	2.05	2.12	2.04
$(CH_3)_3CX$	(2.15)	2.15	2.13

The brackets show, that these is some uncertainty as deviating values are to be found in the literature. It is most instructive to notice the exellent agreement between the series of the normal and secondary propyl and butyl compounds.

The course of the dipole effect in the monohalogen alkanes can be understood satisfactorily, when we notice the refraction of the hydrogen atoms, which are carried by the carbon atom, that carries the halogen atom too.

2. Dihalogen alkanes.

The same thing applies here. Transition from the series CH_2X_2 to CH_3CHX_2 gives an increase of the dipole moment, the course in the dipole moment becomes smaller. Transition to $C_2H_5CHX_2$ etc. again has very little influence.

Of course, there is an increase with the change to $(CH_3)_2CX_2$; the course, moreover, becomes less. Replacing CH_3 by C_2H_5 again has little influence.

Unfortunately there is very little material known to test this theory. As might be expected, we find the following dipole moments CH_2Cl_2 : 1.57, CH_3CHCl_2 : 1.9, $C_2H_5CHCl_2$: 2.06 $(CH_3)_2CCl_2$: 2.1. Of these CH_3CHCl_2 and $C_2H_5CHCl_2$ should show the same dipoles; the results obtained for CH_3CHCl_2 differ greatly (1.8—2.05), only one determination has been made of $C_2H_5CHCl_2$, so that both values are very uncertain.

Everything therefore, corresponds very well to our expectations. There are no reliable data to demonstrate the decrease of the course when methyl groups are attached to the C atom.

3. Trihalogen alkanes.

Here again very few values are known. We can only mention $CHCl_3$: 1.15 and CH_3CCl_3 : 1.55 which answers our expectations.

III. The relation between refraction data and reactivity of halogenated methane derivatives.

Polanyi and co-workers [1]) have investigated the reaction of sodium vapour and hydrogen with many halogenated organic compounds and they can show in the first case the modification of the collision numbers i.e. the numbers, showing how many collisions must take place on the average, before an effective one is accomplished. The higher the collision number, the greater the energy of activation of the reaction is. The halogen compounds, which show the least energy of activation, are those which have halogen ions which are most weakly bound. This becomes apperent, when we compare these phenomena with the vibration frequencies of the ions. The restoring force constant here gives us a criterion for the strength of the bond, the lower the restoring force constant, the weaker the bond of the ion in question. The energy of activation and the restoring force constant are thus in immediate connection. This fact has been pointed out by Polyani and co-workers [2]).

On the other hand, however, the refraction is also a criterion of the strength of the bond. We have now found a method for

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[1]) H. von Hartel and M. Polanyi, Z. Physik. Chem. B **11**, 97 (1930).

H. von Hartel, N. Meer and M. Polanyi, Z. physik. Chem. B**19**, 139 (1932).

W. Heller and M. Polanyi, Trans. Far. Soc. **32**, 633 (1936).

[2]) R. A. Ogg and M. Polanyi, Trans. Far. Soc. **31**, 482 (1935).

W. Heller and M. Polanyi, Trans. Far. Soc. **32**, 633 (1936).

estimating the contribution of each individual halogen ion to the refraction, and therefore, on the basis of Fajans and Joos' hypothesis, in which direction the strength of the electrostatic field changes, or according to Wolf and Herzfeld, how the energy of the bond is modified, in other words, in what sense the energy is modified by progression in a particular series. It is clear that this must be connected [1]) with the restoring force constant of the vibration which corresponds to the valency bond and also with the energy of activation that is required for the reaction with sodium vapour which will break up this bond. We assume here, that the course of the refraction in the gaseous state is quite the same as in the liquid state, which is permissible, as was shown above, as the refraction of the liquid and the gaseous state do not differ much.

Polanyi and co-workers generally give the collision number of the reaction, i.e. the average number of collisions that is necessary before an effective one takes place.

From the above it can be seen that a decrease of the restoring force constant and collision number accompanies an increase of refraction. Polanyi and Ogg [2]) lay special stress upon the first two. We will first consider the halogens in the methane derivatives. In the series CH_3X according to the most recent calculations by Heller and Polanyi [3]) we find

	Coll. number	rest. force const.	refr. X
CH_3F	10^6	—	1.65
CH_3Cl	7100	3.12	6.19
CH_3Br	75	2.61	8.19
CH_3I	1	2.15	13.26

Unfortunately, there is not enough known of the series CH_2X_2, CHX_3 and CX_4 to serve for comparison. We may now give the following table of the methane derivatives so far as known:

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[1]) J. M. Stevels, Trans. Far. Soc. **33**, ... (1937).

[2]) R. A. Ogg and M. Polanyi, Trans. Far. Soc. **31**, 482 (1935).

[3]) W. Heller and M. Polanyi, Trans. Far. Soc. **32**, 633 (1936).

	Coll. number	rest. force const.	refr. X
CH_3Cl	7100	3.12	6.19
CH_2Cl_2	310	2.94	6.33
$CHCl_3$	22	2.47	6.47
CCl_4	2	2.00	6.61
CH_3Br	75	2.61	8.19
CH_2Br_2	—	2.56	8.71
$CHBr_3$	—	1.82	9.23
CBr_4	—	1.41	9.75
CH_3I	1	2.15	13.26
CH_2I_2	—	2.09	14.27

We should here again emphasize that too much importance must not be attached to the values for the refraction ,there are too many hypothetical elements introduced. But the course clearly indicates the anticipated change with the restoring force constant and the collision number.

There is also a striking correspondance between our theory and experiments, which were made by Cremer, Curry and Polanyi[1]). These authors have made a research on the reactions of various methane derivatives to hydrogen atoms e.g.

$$CCl_4 + H \rightarrow HCCl_3 + Cl$$
$$HCCl_3 + H \rightarrow H_2CCl_2 + Cl$$

and similar reactions.

They came to the conclusion, that the reaction velocity increases from CH_3Cl to CCl_4. The striking thing is, that the reactivity of the hydrogen in the methane derivatives is also increased when more chlorine ions are introduced (H_2 as well as HCl is generated in a greater amount). It seems as if in this case the molecule becomes more and more weakly bound.

This behaviour can be foreseen on the basis of our refraction

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[1]) E. Cremer, J. Curry and M. Polanyi, Z. physik. Chem. B 23. 445 (1933).

data. It has been shown that in the series CH_3Cl → CCl_4 the refraction values for both hydrogen and halogen increase, in other words both the hydrogen and chlorine ions will be more weakly bound.

This may be seen in table on p. 136.

Further the authors, in agreement with Chadwell and Titani[1]) found that the reactivity of the hydrogen ions in the series CH_3F → CH_3I increases. This also is in accordance with our refraction values, as is shown in the table below:

	Refr. H
CH_3F	1.76
CH_3Cl	1.77
CH_3Br	1.93
CH_3I	1.95

All this makes it clear, that a research on the refraction throws valuable light upon the reactivity of organic compounds.

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[1]) H. M. Chadwell and T. Titani, J. Am. Chem. Soc. **55**, 1363 (1933).

CHAPTER VI.

THE PROPERTIES OF MIXTURES OF TETRABROMOMETHANE AND OF TRIIODOMETHANE WITH VARIOUS ORGANIC LIQUIDS.

As we have already explained, it was important to us to know the refraction of CBr_4 and CHI_3 with some accuracy. These substances are solid at 20° and therefore we have measured them in various solvents. We have given the details of our method of preparing these solutions and of the precautions we took (Chapter III).

We naturally cannot expect that all these solutions yield the same result, as it is inevitable, that the molecules of the solvent will exercise some influence upon the molecules in solution and thus modify their refraction. We can eliminate this difficulty to some extent by using different solvents, so that we get some idea of the order of magnitude of this influence.

As the basis for our calculation we always take the mixture law

$$\nu_1 R_1 + \nu_2 R_2 = R_0$$

in which the meaning of ν_1, ν_2, R_1, R_2 and R_0 has been explained above (Chapter III). We always measure R_0 and calculate R_1 from it by means of the known values ν_1, ν_2 and R_2.

It will be seen that we can deduce from the measurements what the refraction would be in a hypothetical CBr_4 and CHI_3 if liquid at 20°.

We will first give a table of the measurements made. CBr_4 was measured in solutions of tetrachloromethane, benzene and propanone, as typical representatives of a class of compounds with a high polarizability without dipole, with small polarizability and many small partial dipole moments and with a very small polarizability and great dipole moment.

In the case of CHI_3 our choice was narrowly confined by the fact, that this substance dissolves very badly in other substances. It is only properly soluble in pyridine, to some extent in propanone, but here the results are extremely uncertain. A solution of about 0.04 molfractions in propanone yields a possible error, of 2.5 %. It must be repeated here, that the measurements were only made for the Na-D-line, because the mixtures consisted of a very volatile substance and one of low vapour pressure which in the Pulfrich refractometer may give rise to serious errors.

The table of our results follows:

mol. CBr_4	mol. CCl_4	n_D^{20}	d_4^{20}	R_D^{20}
0.01835	0.14433	1.4812	1.7737	38.92
0.03543	0.13744	1.4989	1.9239	38.82
0.02070	0.07935	1.5001	1.9370	38.30
mol. CBr_4	mol. benzene			
0.01835	0.13765	1.5231	1.1924	38.95
0.03363	0.19083	1.5288	1.2706	38.91
0.03998	0.15732	1.5375	1.4002	39.75
mol. CBr_4	mol. propanone			
0.04037	0.21555	1.4207	1.3036	38.80
0.03415	0.10266	1.4484	1.5460	39.17
mol. CHI_3	mol. pyridine			
0.02282	0.20404	1.5532	1.3369	48.26
0.02830	0.18250	1.5673	1.4506	48.43
0.03673	0.22893	1.5680	1.4610	48.56
0.03923	0.24034	1.5696	1.4689	48.53
0.04107	0.19330	1.5849	1.5892	48.10
mol. CHI_3	mol. propanone			
0.00537	0.21521	1.3743	0.8936	49.66
0.00980	0.31018	1.3799	0.9229	48.70

The degrees of purity of CBr_4 and CHI_3 has been fully discussed above (p. 104 and 106). The „solvents" used were also as pure as possible, the following preparations being used:

Benzene (Schering-Kahlbaum), pro analysi, thiophene free, „rein kristallisierbar" $n_D^{20} = 1.5012$, b. p. 80.2° at 760 mm.

Propanone (Brocades en Stheeman) guaranteed pure reagentia, $n_D^{20} = 1.3588$, b. p. 56.2° at 757 mm.

CCl_4 (Brocades en Stheeman), purified by fractionating twice, $n_D^{20} = 1.4603$, b. p. 76.7° at 760 mm.

Pyridine (Schering-Kahlbaum), puriss., $n_D^{20} = 1.5094$ b. p. 115.3° at 752 mm.

The R's calculated show a considerable irregularity. It is not possible with the method followed to determine R more precisely. The same inexactitude is found elswhere[1]), when a similar process has been applied for calculating R in various solvents of a particular substance.

On the basis of the figures calculated in our table the following values seem most probable for the refraction of the hypothetical case of liquid at 20°: for CBr_4: 39.0_0 and for CHI_3: 48.5_5. Both values are cumbered by a large error and this may be the reason, why the linearity of the refraction in the series $CH_4 \rightarrow CBr_4$ and $CH_4 \rightarrow CI_4$ shows considerable deviations. The fact, however, that the mutual actions can describe the mixed halogenated methane derivates so well is a guarantee of the accuracy of them.

If we introduce dipoles into a solvent, these dipoles will arrange themselves so that the positive side is directed towards the molecule under consideration. The positive field of the central ion is weakened and the refraction rises. The influence of the dipole on the refraction, however, is extremely small. This is shown by the fact that the $\Delta_{X_n}^{X_m}$'s can be deduced from the dipole containinq methane derivatives as well as from the non-polar ones.

Fajans[2]) states, that the deviations of the additivity of binary mixtures are only slight. Smyth, Engel and Wilson[3]) investigated various organic mixtures, as to the validity of the mixture law for the refraction.

The greatest deviation they found was 0.7 %. This proves, that

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[1]) cf. G. Briegleb, Z. Physik. Chem. B **14**, 108 (1931).

[2]) K. Fajans, Z. physik. Chem. B **24**, 108 (1934).

[3]) C. P. Smyth, E. W. Engel and E. B. Wilson, J. Am. Chem. Soc. **51**, 1736 (1929).

the refraction of certain molecules is practically independent of the surrounding molecules.

This means, that it is justifiable to determine the refraction values for CBr_4 and CHI_3 even in solution in dipole containing substances. The comparative magnitude of our deviations is due to the fact, that we must determine the refraction value by extrapolation, which gives rise to large errors.

The fact referred to above (p. 125) that the decrease of refraction when passing from the gaseous to the liquid state, shows no definite connection with the magnitude of the dipoles, makes it clear, moreover, that the latter have very little influence on the refraction.

SAMENVATTING.

Dit proefschrift behandelt de samenhang van polariseerbaarheid en cohaesie-energie.

In het eerste hoofdstuk wordt in het kort nagegaan, wat de betekenis is van het begrip polariseerbaarheid en vervolgens worden de verschillende methoden besproken, die kunnen dienen om deze grootheid te bepalen. Een van de belangrijkste methoden is de bepaling van de refractie. Deze werkwijze heeft het voordeel, dat we hiermee een groot aantal gevallen kunnen bestuderen.

Onze fundamentele hypothese is nu, in navolging van Fajans en Joos, dat de refractie gemeten voor een bepaalde lijn uit het zichtbare spectrum, een maat is voor de electronen poliseerbaarheid. Volgens Fajans en Joos is hier de *Na-D*-lijn het meest voor geschikt, omdat deze het minst gestoord wordt door de ultra-violette en infra-rode absorbtiegebieden. In zijn algemeenheid is dit niet het geval maar wel voor verbindingen van het type AX_3 en AX_4.

De cohaesie van vloeistoffen wordt hoofdzakelijk bepaald door 3 effecten:

1°. het Keesom-effect, de onderlinge attractie van de dipolen van de moleculen van de vloeistof;

2°. het Debye-effect, de attractie van de dipool van bepaalde moleculen en de ingeduceerde dipolen in andere moleculen;

3°. het London-effect, de onderlinge attractie van twee polariseerbare moleculen.

Bij dipoolloze stoffen treedt alleen het laatste effect op.

Van Arkel en medewerkers hebben, door toepassing van de formule van London voor de attractie van twee deeltjes, laten zien, dat het kookpunt van dipoolloze methaanderivaten voorgesteld kan worden door

$$T_s = k \frac{(V - V_C)^2}{V}$$

waarin V het volume van de stof is bij het kookpunt, V_C het volume volgens Kopp voor de koolstof en K een constante.

Essentieel voor deze betrekking is, dat voor deze verbindingen moet gelden

$$\alpha_X \sim V_X{}^{5/3}$$

waarin V_X is het volume volgens Kopp van het halogeen ion X en α_X de polariseerbaarheid daarvan.

Deze betrekking moet voorlopig als toevallig en zonder theoretische betekenis worden geacht.

Wanneer we nu overgaan tot andere tetraeder-vormige moleculen, dan kunnen we aantonen, dat in het algemeen met een vergroting van de straal van het kation een vergroting van α_X en een verkleining van V_X gepaard gaat, zodat de bovenstaande betrekking niet algemeen geldig kan zijn. We schrijven nu

$$\alpha_X = A\,(E)\,V_X{}^{5/3}$$

waarin $A\,(E)$ variabel is.

In werkelijkheid hebben we $A\,(E)$ steeds berekend volgens

$$\alpha_X = A\,(E)\,r_X{}^5$$

waarbij voor r_X werd aangenomen de ionenstraal volgens Pauling; dit heeft dus tot gevolg, dat we $V_X{}^{5/3}$ als een constante grootheid beschouwen bij variatie van het kation. Het kleine effect van de variatie van V_X is dus verdisconteerd in $A\,(E)$.

De $A\,(E)$-waarden hebben echter nog een andere betekenis. Volgens Fajans en Joos is de polariseerbaarheid van een ion afhankelijk van het electrostatische veld, waarin dat ion zich bevindt, volgens Herzfeld en Wolf van de bindingsenergie van dat ion.

Dit wordt dus uitgedrukt door de onbekende functie A van E.

Daar bij de Si-derivaten niet voldaan is aan de betrekking

$$\alpha_X \sim V_X{}^{5/3}$$

zijn deze niet voor te stellen door een eenvoudige formule als bij de koolstofderivaten, zoals van Arkel en de Boer reeds vonden.

Zij worden echter wel voorgesteld door de formule

$$T_s = k\,A^2\,(E)\,\frac{(V - V_{si})^2}{V}$$

waarin k een constante is en A (E) uit de refractie is te berekenen. Met deze formule kan men algemeen de London bijdrage tot het kookpunt berekenen voor alle tetraedervormige moleculen.

Soms treedt echter een verschil op met het werkelijke kookpunt. In de meeste gevallen is dit te wijten aan de dipoolbijdrage tot het kookpunt, een feit, waarop reeds van Arkel heeft gewezen.

Soms komt echter ook een afwijking bij dipoolloze stoffen voor. We kunnen laten zien, dat dit enerzijds het gevolg kan zijn van het feit, dat het kation niet meer past in de holte gevormd door de vier anionen. Dit geeft aanleiding tot een extra cohaesie, het kookpunt is dus hoger, het kookpuntvolume wordt kleiner. Voorbeelden zijn SiF_4, GeF_4, ZrF_4. De overgang gaat heel geleidelijk; terwijl SiF_4 op het eerste gezicht nog „omhuld" schijnt, zal aan ZrF_4 waarschijnlijk een coördinatierooster moeten worden toegekend.

Complexvorming is een aanwijzing, dat wisselwerking van deze soort bestaat. Een dergelijke wisselwerking treedt bovendien altijd op in het geval van vlakke moleculen in een richting loodrecht op het vlak van het molecuul. Ook hier kunnen anionen van andere moleculen dicht tot het centrale ion naderen, wat aanleiding geeft tot extra wisselwerking. Voorbeelden hiervan zijn de borium halogeniden en de aetheenderivaten.

Het BF_3 vertoont waarschijnlijk beide soorten van wisselwerking. Het kan plausibel worden gemaakt, dat deze bijzondere wisselwerkingen geen London werkingen zijn.

We hebben de bovengenoemde verschijnselen ook nauwkeurig bestudeerd aan de hand van nulpuntsvolumina volgens Biltz. In het algemeen blijkt, dat bij sterke wisselwerkingen er een contractie in het kookpuntsvolume optreedt. Dipoolwerkingen en werkingen die afnemen met een hogere macht van de afstand, geven geen aanleiding tot merkbare contracties in het kookpuntvolume, echter wel in het nulpuntsvolume.

In Hoofdstuk II zijn bovengenoemde beschouwingen toegepast op de gemengde en ongemengde halogeniden van C, Si, Ti, Zr, Hf, Th, Ge, Sn, B en Al.

Tenslotte zij nog vermeld, dat men, ondanks het feit, dat niet voldaan wordt aan de formule

$$T_s = k\frac{(V - V_A)^2}{V}$$

kan aantonen, dat de additiviteit der kookpunten ten naaste bij blijft bestaan.

Een discussie van de gevonden refractiewaarde leert ons, dat de refractie van de anionen niet altijd behoeft af te nemen bij groter worden van de straal van het kation (Omkeereffect I). Dit effect treedt alleen op bij voldoend grote anionen en het komt daarop neer, dat de vergrote polariseerbaarheid van de laatste het veld van het centrale ion ter plaatse van het anion sterk tegenwerkt.

Bij groter worden van alle anionen treedt bij vastgehouden kation nooit een omkeereffect (Omkeereffect II A) op. Wel treedt iets dergelijks op, wanneer we één anion en het kation vasthouden en de drie overige anionen groter maken. Dan kan de refractie van het beschouwde anion een minimum doorloopen (Omkeereffect II B). Een „schijnbaar" omkeereffect II A treedt op wanneer we gaan vergelijken de $\frac{\alpha}{\alpha_0}$-waarden van verschillende anionen bij vastgehouden kation, waarin α_0 de refractie is van het „vrije" ion. Dat dit optreedt is het gevolg van het feit, dat de refractieveranderingen niet alleen afhangen van de bindingsenergie (c.q. het veld), maar ook, zoals begrijpelijk is, van de absorbtiefrequenties van de beschouwde ionen.

Ten slotte wordt gediscusseerd, welke betrekkingen er bestaan tussen de karakteristieke grootheden bij tetraedervormige moleculen. Kennen wij A(E) als functie van E, dan blijkt het, dat wij b.v. de kooktemperatuur en de brekingsindex van een willekeurige van deze verbindingen kunnen berekenen bij kennis van de stralen en Kopp'se volumina der ionen en de refractie van het kation.

We hebben verder verschillende dipoolloze en dipoolhoudende gemengd gehalogeneerde methaanderivaten nauwkeurig op brekingsindex, dichtheid en refractie onderzocht. In hoofdstuk III zijn de daartoe gebruikte toestellen beschreven, terwijl in hoofdstuk IV de bereiding, de zuivering en de meting van de onderzochte stoffen wordt beschreven. In de tabel aan het slot van hoofdstuk IV vindt men alle uitkomsten verenigd.

In hoofdstuk V wordt nu uiteengezet, hoe men de gevonden refracties bevredigend kan berekenen met behulp van bepaalde standaardwaarden voor de waterstof- en de halogeen-ionen en zogenaamde „wisselwerkingstermen" die de wederzijdse beinvloeding van 2 ionen in het methaanderivaat aangeven. Een theoretische methode wordt ontwikkeld, om deze wisselwerkingstermen in twee stukken te splitsen, waarbij ieder stuk toegevoegd moet worden gedacht aan een van de twee beschouwde ionen.

Op deze wijze wordt het mogelijk de ware „ionenrefractie" in een bepaalde verbinding, althans bij benadering, te berekenen. Deze ionenrefracties zijn niet constant voor een bepaald ion, wel is natuurlijk hun som gelijk aan de totale refractie van het molecuul.

De gevonden waarden stellen ons nu in staat om verschillende physische en chemische eigenschappen van organische moleculen te voorspellen. In de eerste plaats kunnen we laten zien, waar wij afwijkingen moeten verwachten van de additief berekende kookpunten volgens van Arkel en de Boer in het geval van de methaanderivaten.

Vooral in de laatste tijd zijn er diverse van deze verbindingen bereid waarin het kookpunt ongeveer 7° of meer afwijkt van de additief berekende waarden. We zijn nu in staat alle afwijkingen $> 3^\circ$, zowel in positieve als in negatieve zin, behoorlijk te voorspellen.

Verder kunnen wij, nu we een inzicht hebben gekregen in de refractie van ieder ion van een methaanderivaat afzonderlijk, voorspellen, welke de regelmatigheden zijn, die optreden wanneer wij met elkaar vergelijken de dipoolmomenten, niet alleen van de methaanderivaten, maar ook van de aethaan-, propaan- en butaanderivaten, die een of meer halogeenatomen aan eenzelfde C-atoom dragen.

Ook de regelmatigheden bij de overgang van primaire naar secundaire en vervolgens naar tertiaire verbindingen, kunnen op bevredigende wijze verklaard worden. In het algemeen kan men zeggen, dat het dipoolmoment van de gehalogeneerde alkanen in hoofdzaak bepaald wordt door het aantal en de mate van binding van de waterstofatomen, die gebonden zijn aan het halogeendragende C-atoom.

Ten slotte blijkt het, dat wij met behulp van de verkregen refractiewaarden, qualitatief de resultaten kan voorspellen, welke door Polanyi en medewerkers verkregen zijn betreffende de reactiviteit van halogeen- en waterstofatomen in methaanderivaten.

In hoofdstuk VI hebben wij de refractie onderzocht van mengsels van CBr_4 resp. van CHI_3 met verschillende organische stoffen. Tevens blijkt hierbij, zoals trouwens in de literatuur al vermeld is, dat het dipoolmoment een nauwelijks merkbare invloed heeft op de refractie.

STELLINGEN.

I.

De mening van Nitta en Suenaga, als zouden de symmetrie-eigenschappen van het thiophosphorylbromide kristal die zijn van de ruimtegroep T_h^6, is in strijd met het experiment.

I. Nitta en K. Suenaga, Sc. Pap. I. P. C. R. (Tokyo), 31, 121 (1937).

II.

De bewijzen, die Holleman aanvoert voor de structuur van het azijnzuurmolecule, zijn niet afdoende.

A. F. Holleman, Leerboek der Organische Chemie I, blz. 119, Groningen 1937.

III.

Een ruimere toepassing van geconcentreerd phosphorzuur als condensatiemiddel in de praeparatieve organische chemie verdient zeer de aanbeveling.

A. E. Tchitchibabine, Bull. soc. chim. [5], 2, 497 (1935).

IV.

Het heeft geen zin moleculaire refracties in drie decimalen op te geven.

V.

De regels van **Latimer** en **Porter** en van **Svirbely** en **Warner** betreffende de richtende werking van bepaalde groepen bij substitutie in de benzeenkern bieden geen voordelen boven de oudere regels van **Crum Brown** en **Gibson**, **Hübner** en **Nölting**, **Vorländer** en **Armstrong**.

W. M. **Latimer** en C. W. **Porter**, J. Am. Chem. Soc. **52**, 206 (1931).
W. J. **Svirbely** en J. C. **Warner**, J. Am. Chem. Soc. **57**, 655 (1935).

VI.

De mening van **Candler**, als zouden **van Arkel** en **de Boer** alle verbindingen als heteropolair willen opvatten en alle „karakteristiek homoïopolaire eigenschappen" willen verklaren door afscherming van het centrale ion, is onjuist.

A. C. **Candler**, Atomic Spectra I, blz. 167, Cambridge 1937.

VII.

De juistheid van de opvatting van **Fajans** en **Joos**, als zou de refractie van kationen toenemen bij de vorming van moleculen, is niet experimenteel bewezen. Bovendien is deze toename ook theoretisch niet te verwachten.

K. **Fajans** en G. **Joos**, Z. Physik 23, 1 (1924) en latere verhandelingen.

VIII.

Het is mogelijk, om een opstelling voor een spiegelgalvanometer te bedenken, waarbij met behoud van de gebruikte toestellen de afleesnauwkeurigheid groter is dan bij de meest gebruikelijke opstelling.

IX.

De titratie van ferrosulfaat met kaliumdichromaat in zure oplossing met behulp van o-phenanthroline als indicator verdient verre de voorkeur boven die, waarbij men ferrosulfaat bepaalt door toevoeging van overmaat kaliumdichromaat en vervolgens van overmaat kaliumjodide en terugtitratie met natriumthiosulfaat.

G. H. Walden, L. P. Hammett en R. P. Chapman, J. Am. Chem. Soc. **53**, 3908 (1931); **55**, 2649 (1933).

X.

De verschillen tussen de dipoolmomenten van de verbindingen, welke men verkrijgt door in alkanen één of meer waterstofatomen, gebonden aan eenzelfde koolstofatoom, door halogeenatomen te vervangen, worden hoofdzakelijk bepaald door het aantal en de mate van binding van de overblijvende waterstofatomen, die gebonden zijn aan dat koolstofatoom.

XI.

De eenvoudige koolstofverbindingen zijn, meer dan enige andere categorie van verbindingen, geschikt als materiaal voor de toetsing der physisch-chemische theorieën, zodat een nauwe samenwerking tussen de beoefenaren der physische en der organische chemie de wetenschap ten goede komt.