SPATIAL MODELS OF MOLECULES IN CHEMICAL RESEARCH AND TUITION, I.

DESCRIPTION OF A NEW TRUE-ANGLE MODEL OF ATOMS

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I. Theoretical models of atoms and of molecules

Modern atomic theory has introduced many a seminal principle in chemical research since the kinetic theory of gases ascribed a well-defined spatial extension to molecules.

Initially, even the kinetic theory of gases was satisfied with a model that represented molecules as *mass points* with the momentum $m \cdot c$ in space. But quite soon (CLAUSIUS, 1857) spatial extension was attributed to these mass points. The oldest spatial model is due to MAXWELL (1860) who regarded molecules as *rigid elastic spheres*, i.e. as "elastic spheres of a definite radius". However, in 1877, this is classed as a "descriptive theory" by D. E. MEYER.

The attribute "rigid" means that the radius of such a sphere does not change on collision (i.e. that it is invariant to temperature). Thus a collision has a definite beginning and end (instantaneous collision) since the repulsive forces, or more precisely: those of elasticity, are infinite on collisions. Due to this, the introduction of the concept of *free paths* became possible.

On the basis of this concept, an *r geometrical radius* for the spherical model of a molecule could be calculated, this was designated as the van der Waals radius because this value could be also calculated from the van der Waals equation (1873).

The elaboration of this model was due mainly to CHAPMAN (1912). Thus, this model likens the molecules to smooth billiard balls, therefore molecules are often thought of as smooth, rigid, elastic spheres.

This model has since been subjected to many corrections. In 1893 already, SUTHERLAND attributes a *force of attraction* to these rigid spheres: "smooth rigid elastic spheres surrounded by fields of attractive force" or "rigid elastic attractive sphere". This model, owing to the introduction of the so-called Sutherland constant, also took account of the temperature dependence of molecular radii, when dealing with transport phenomena. (Apparently, the attractive force increased the rigid radius of the molecule.)

In the interpretation of the rotationary energy of molecules the idea of a regular, smooth sphericity of the model had to be abandoned and in this

way the picture of "rough elastic rigid spherical molecules" was evolved (CHAPMAN, 1912).

Alongside these geometrical "billiard ball" models are felt to be much too elementary; soon suggestions based on the idea of forces: molecules with a so-called *point centre of force*, were put forward. MAXWELL himself abandoned, in 1867, the geometrical model mentioned and it was mainly MAXWELL who elaborated a theory of gases on the basis of this new point centre of force model.

Later, BOLTZMANN suggested some corrections of this point centre of force hypothesis.

In essence, the force centre model eschews the somewhat naive picture of molecules extended in space. Accordingly, centres of force have no spatial extension; a molecule is not any longer of some definite geometrical shape of which rigid physical surfaces would mark the boundary where two molecules meet on collision. However, also two molecules imagined as centres of force cannot approach each other but up to a certain distance: up to the limit where a repulsive force, in inverse ratio at a power higher than 2 to the distance, checks the impulse of the "incident molecule". This "checking" or "collision distance", i.e. the distance of closest approach of two molecules at an encounter, takes the place of the radius of the sphere of a rigid geometrical model.

Obviously, the molecular radius defined in this way will be a function also of the velocity of the colliding molecules, i.e. of the temperature (decrease with increase of temperature).

These point centres of force are thus "non-rigid molecules" and, in contrast to the former billiard ball simile, rather that of tennis balls is evoked, and this means that there is no definite beginning and end in a collision of two molecules, and thus the concept of a free path also becomes a source of difficulties. (CHAPMAN does not use this concept in conjunction with non-rigid models of molecules.)

From the temperature dependence of the viscosity, and of the diffusion constant of gases the exponent for the distance $(P = k/r^n)$ that defines the field of the repulsive force of a molecule became calculable. According to the value of the exponent n, hard molecules (He, Ne, H_2), where $n = 15$, are distinguished from soft molecules (NH_3, Cl_2, HCl), where $n = 5$, the behaviour of the former is well enough accounted for by the first, rigid model, while that of the latter is correctly characterized only by the force centre model. Thus, the rigid model is a limit, at $n = \infty$, of the non-rigid force centre model.

First, only repulsive forces were sited into the centre of the molecule: "point-centre of repulsive force".

The so-called *Maxwellian molecules* were those special cases within the class in which the repulsive force was in inverse proportion to the fifth power of the distance. Integration of such complex functions could be only for this case carried out in MAXWELL's time. In view of the predominance of electrostatic forces, for *ionized gases* repulsive forces were approximated with the second power. by CHAPMAN.

Around 1920, the molecular model according to LENNARD-JONES was proposed. This model attributed *forces* both of attraction and repulsion to the centre of a molecule (point centre of attractive and repulsive force); studies on models with combinations of distances at various powers were carried out for attraction and repulsion.

On the basis of these two main types of models, and several sub-types, the calculation from measured data of transport phenomena of the so-called van der Waals, or collision, radii became possible. The numerical value of molecular radii changed according to the model used when measured data were interpreted. Thus, values of both geometric and collisional van der Waals radii of molecules are even today rather uncertain.

In a similar manner the van der Waals radii of single atoms in a crystal (r_{cryst}), or in ionized form (r_{ion}) can be calculated. Of course, the models described on the basis of the kinetic theory of gases cannot shed any light on the geometrical location of atoms within a molecule composed of them. However, modern infrared spectroscopy, X-ray diffraction, and n.m.r. measurements have furnished quite accurate values of the distances between the centres of the atoms that form a molecule of the so-called "bond length" (0.01Å) and of the so-called bond angle ($\pm 0.5°$). Bond lengths ($2\,R$) and bond angle values do not depend on some uncertain model but are real atomic dimensions. The accuracy of these is far better than that of van der Waals radii r, not to say anything of the temperature dependence of the latter.

Thus, on the basis of the foregoing, we have very accurate information about the positions of atomic centres within molecules, whereas about the external extension of molecules (van der Waals radii) only approximate knowledge is available.

II. Molecule models made visual

The average molecular radius (r = van der Waals radius) of the chemical physicists, and the bond length (a) of spectroscopists, did not tell much to the organic chemists till MAGAT [1] did not link them up to the qualitative model that had haunted preparative chemistry for ages, to the concept of *steric hindrance* (sterische Hinderung). The well-defined, but in terms of spatial geometry only qualitatively formulated concept of steric hindrance was, by MAGAT, put equal to the geometrical dimensions already quantitatively measurable with the aid of the kinetic theory of gases, to the so-called "ex-

tensiveness" ("Raumbeanspruchung") of molecules. According to his line of thought, the molecular collisional distances or ranges of influence ($d_M = 2 r_M$) measured up to then were only average distances that are equal to the van der Waals radii of atoms only in the case of monatomic noble gases.

To be able to calculate this atomic radius r_A for other, diatomic molecules, i.e. in order to split the average molecular diameter, to reduce it
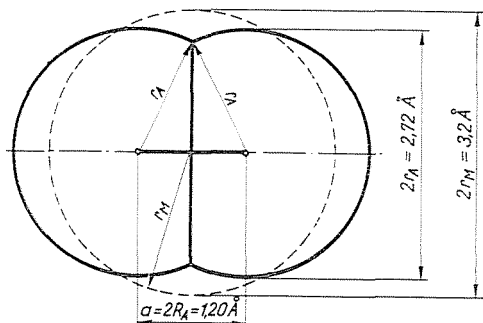

Fig. 1. MAGAT's atom-calotte model of a molecule

to atomic radii proper, MAGAT had to assume that molecules e.g. of O_2, H_2 formed of like atoms originate from atoms assumed to be spheres with a radius r_A, in such a way that a spherical calotte of appropriate dimensions (Kappenhöhe, height of calotte) is cut off a sphere and the calottes thus emerging will join up to form a molecule (cf. Fig. 1)

The spherical sector, the so-called valence sector, is thus a plane normal to a bond length.

The height of the calottes cut off must allow the centres of the atoms joined in the way described to be accurately $2R_A = a$ distance apart, i.e. in the case of molecules formed of like atoms he defined the half bond length as the bond radius R_A of an atom.

The basis of further calculations is the assumption that the extension of the two-atoms calotte thus constructed is equal to the fictitious collisional sphere of the molecule *(additivity of atom volumina)*

$$2\left[\frac{4\pi}{3} r_A^3 - \frac{\pi}{3} (r_A - R_A)^2 \cdot (2r_A + R_A)\right] = \frac{4\pi}{3} r_M^3 \qquad (1)$$

or

$$2r_A^3 - \frac{1}{2} (r_A - R_A)^2 \cdot (2r_A + R_A) = r_M^3 \qquad (1a)$$

When $d_M = 2r_M$, and $R_A = 2a$ are known, this equation can be solved for r_A, the atomic radius. A similar calculation is possible in the case of a molecule,

e.g. CO built from two different atoms:

$$r_1^3 - \frac{1}{4}(r_1 - R_1)^2(2r_1 + R_1) + r_2^3 - \frac{1}{4}(r_2 - R_2)^2 \cdot (2r_2 + R_2) = r_{M_{12}}^3 \quad (2a)$$
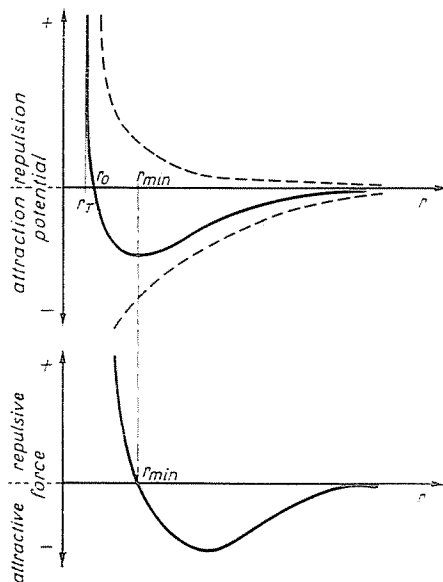

Fig. 2. Potential-function for short distances of a force-centre. according to WOHL [15]

For a solution of these equations, also the *independence of the collision radii* r must be assumed, i.e. that the value of van der Waals radii is independent of the partner, that in every molecule the atom maintains its proper collision radius it possessed in the simple molecule of the element. In this case if the atomic radii r_1 and R_1 of one of the partners are known from data r_{M_1} and a_1 of the molecule of the element, then also the value $R_2 = a_{12} - R_1$ is known and the r_2 action radius of the other partner can be calculated according to Eq. (2a) from its $r_{M_{12}}$ value.

Since, according to the molecule model derived from the kinetic theory of gases the diameters of molecules depend on the temperature, the radii of atoms calculated in the way described will also be dependent on the temperature. This temperature dependence can be illustrated by the graph showing molecular distance and energy (cf. Fig. 2).

1. In a collision infinitely slow, two molecules can approach to a distance r_0 where energy of repulsion and attraction are in equilibrium. This infinitely slow collision is realized around $0°K$.

2. At any higher temperature T, the molecules collide with an impulse $Mc_{(T)}$, therefore they can approach each other to a distance $r_T < r_0$. Usually

r_T-values are referred to at $T = 300°K$ ($27°C$). This can be calculated from internal friction of gases at temperature T.

3. In static state (in crystals with atomic lattice, or in the so-called zero-point volume of a liquid at $0°K$) the equilibrium of *forces* of attraction and of repulsion, i.e. the minimum energy, determines the average distance between molecules; this is designated as r_{min}. This is the static radius, in contradistinction to the dynamic radii r_0 and r_T.

Thus $r_T < r_0 < r_{min} \simeq r_{cryst}$, and if the force of attraction is in the inverse ratio to the power $m = 6$ of distance, and the force of repulsion is in the inverse ratio of the power $n = 12$ of distance, then, according to STUART [6, p. 55]

$$r_{min} = 1.1225 \cdot r_0 \tag{3}$$

Based on data measured:

$$r_T^* \simeq r_{min}^* - (0.15 \div 0.25)\,\text{Å} \tag{4}$$

(r^*: van der Waals radii in polar bonding; see later)

From STUART [2] with

$$O, N \text{ and } F, r_T = 0.91 \cdot r_{min} \tag{5}$$

The difference between the three r values is the less the more rich the atom in electrons is, i.e. the "softer" it is. Based upon directives stated by MAGAT, STUART [2, 2c] developed further the idea of how to visualize the molecules: The thesis about the independence of the action radius of atoms did not prove correct; MACK [16] had found that, in organic compounds, the bond radius r^* of a single atom is not the same as r in a molecule of the element. E.g. the H-bond in H_2 has $r_{min} = 1.5$ Å, in methane $r_{min} = 1.00$ Å, in ethane 1.16 Å, and in many organic compounds 1.29 Å. This is partly explained by the different charge distribution of the bonding electrons between the two partners, and partly by the fact that the bonding partner of H also exerts a measurable influence on the molecule colliding with the H. Today this is expressed by the electrophilic effect of the C atom as against the H atom.

Following MAGAT's idea, even today the van der Waals radii of bonded atoms (Wirkungsradien gebundener Atome) are presented in this way, only that their values are not calculated from simple molecules of the element but from lattice constants of the crystals of organic compounds, $r_{min}^* = r_{cryst}^*$.

According to PAULING's rule [4, p. 263]

$$r_{min}^* \simeq r_{cryst}^* = R + 0.8\,\text{Å} \tag{6}$$

Further, according to PAULING (p. 258) "... the van der Waals radius of chlorine should be about equal to its ionic radius, inasmuch as the bonded

atom presents the same face to the outside world in directions away from its bond as the ion :$\overset{..}{\underset{..}{Cl}}$:$^-$ does in all directions" i.e.

$$r^*_{min} = r^*_{ion} = \text{ion radius} \tag{7}$$

However, BRIEGLEB [5] has shown that van der Waals radii of an atom in a polar bond (r^*) are greater than those of an atom in a non-polar bond (r) (cf. Fig. 3).
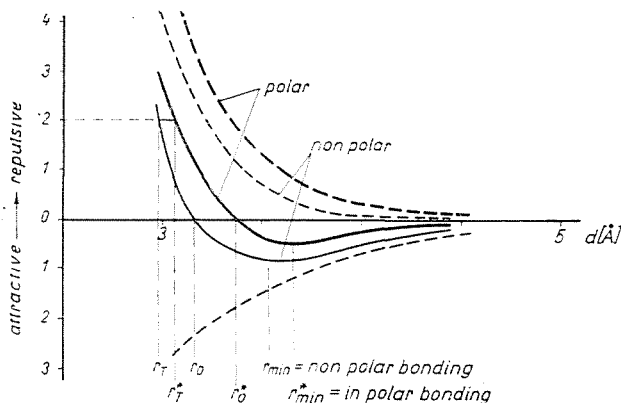

Fig. 3. Potential-field of atoms in polar bonding, according to BRIEGLEB [5]

It is especially among the halogens that he found differences between r and r^* values; thus in this case the halogens act as electron attractants (cf. Table I).

Table I

		F	Cl	Br	I
1.	From (Hal)$_2$ molecules				
11.	Zero-point volume gives r_{min}	—	1.76	1.85	1.96
12.	Viscosity gives r_{300}	—	1.51	1.64	1.71
2.	From compounds with polar bonds				
21.	Lattice constant gives r^*_{min}	1.35	1.80	1.95	2.15
22.	Calculation gives[1] r^*_{300}	1.30[2]	1.55	1.75	1.90

[1] From formula $\dfrac{r^*_{min} - r^*_T}{r^*_{min}} = \dfrac{r_{min} - r_T}{r_{min}}$ $\tag{8}$

[2] Extrapolated figure

Similarly, a more extended electron cloud was found in the plane normal to the double bond of atoms in organic compounds. Of course, the r^* radii thus defined of bonded atoms refer to organic collisions with a like atom of like bonding, but the supposition is allowed that interaction with other atoms is not far different from this, except in the case of H which, however, in hydrocarbons, collides mostly with a H anyhow (STUART [2]).

<p align="center">*</p>

On the basis of R bond radii and action radii r_T at room temperature, STUART devised adequate atom calotte models from wood, glass, and celluloid,
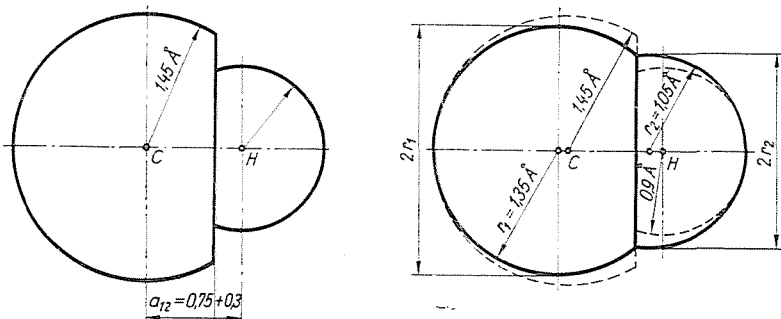

Fig. 4. Shift of centres according to STUART
(The figure of the original article is misconstructed)

not only accurate in their dimensions but also very pleasing to the eye. It was also STUART who proposed the so-called method of centre shift (cf. Fig. 4) for the esthetically more suitable construction of calottes.

When calculating atom-radii, STUART used two assumptions besides the correlation (5):

$$\left(\frac{r_A}{r_B}\right)_{\text{atom}} \cong \left(\frac{d_A}{d_B}\right)_{\text{molecule}} \tag{9}$$

r_A, and r_B, are radii of two different "bonded atoms";
d_A, and d_B are average diameters of the molecules in the element of the same and

$$\frac{r_{\text{oxygen}}}{r_{\text{sulphur}}} = \frac{r_{\text{fluorine}}}{r_{\text{chlorine}}} \tag{10}$$

Using the calculations of STUART, the german firm of LEYBOLD's put sets of the so-called STUART—LEYBOLD calottes, scale $1 : 2 \cdot 10^8$, then $1 : 1.5 \cdot 10^8$, on the market, in the form of tinted wooden pieces, executed according to the principle of centre-shift [11].

In a very thorough treatment in his monograph [3] on molecular structures, BRIEGLEB uses, in 1937, the STUART—LEYBOLD models for illustration, but subjects them to some criticism, in 1950 [5], in so far as he

1. on the basis of recent measurements, modifies in part the data concerning the radii;

2. on a theoretical basis, proposes a pear-shaped construction of larger molecules, instead of the centrum-shift, where the bond section of the smaller atom demands this. Thereby obstructions which do not in fact operate against rotations are eliminated from the models (cf. Fig. 5);

3. since in the molecule lattice of benzene derivatives the distance of planes parallel to the ring is $d_{min} = 3.7$ Å, and since $r_T \simeq 0.9 \cdot r_{min}$, proposes that $r_T = 1.6$ Å should be chosen for the van der Waals radius normal to π-bonds in the π-bonding generally of all the atoms.
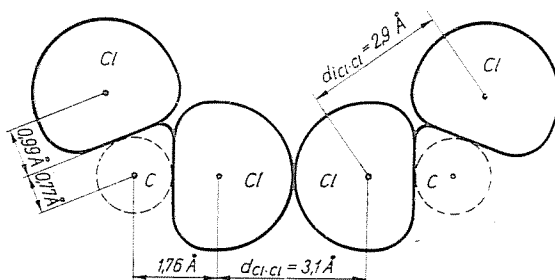

Fig. 5. Pear-shaped construction of the electron cloud of atoms in covalent bonding, according to Briegleb [5]: Model: CCl_4

The newer models of Leybold's, on sale today, are constructed according to these suggestions, and are designated as the Stuart—Briegleb calotte models [11a].

Stuart's monograph (1952), modern even today, refers only to this novel Stuart—Briegleb model [6].

In the early fifties, Catalin Ltd., in Great Britain, produced the original Stuart models, in a phenolic resin, at a scale of 1 cm to 1 Å [12].

Also in the early fifties, the British firm Courtauld broke with the Magat—Stuart—Briegleb tradition [13]. According to their criticism [7, 8, 9], among the van der Waals radii of action the measured $r^*_{min} \simeq r^*_{cryst}$ data are those to be accepted with the most confidence. The models of Leybold's are based on $r^*_T = r^*_{300}$ data, though values of r^*_T are calculated, in a not quite reliable manner, from r^*_{min} values. Courtauld also used the rule $r^*_{min} = R +$ $+ 0.8$ Å, of Pauling [4]. For a criticism of both, cf. [6, p. 96].

A new set of models made of wood according to r^*_{min} data, scale 1 Å $=$ $= 0.8$ inch, was put on the market by Courtauld in the early fifties. Scientific requirements are so much better served by this model, for due to special patented bonding elements the interatomic distances can be varied (the van der Waals radius of the π-bond is calculated with 1.7 Å [13]). Lately this set is made from polystyrene [13a].

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Table II

van der Waals radii

	Magat 1932 [1]			Mack 1932 [16, 17]				Stuart 1934—37 [2, 2a, 2b]		
	r_T	r_0	r_{min}	r_T	r_{min}^*	r_T^*	r_{min}^*	r_T^*	r_0^*	r_{min}^*
C	1.44	1.64	—	—	—	—	1.54	1.45 (1.40)	—	—
C—π-bond	—	—	—	—	—	—	1.7	1.45 (1.40)	—	—
H	0.96	1.26	—	—	1.5	0.5—0.63	1.0—1.29	0.9 (1.05)	1.0	1.1
H-bond	—	—	—	—	—	—	—	—	—	—
— O —	—	—	—	—	—	—	—	1.22	1.36	1.5
O—π-bond	1.25	1.37	1.51	—	—	—	—	1.22	1.36	1.5
— N ⟨	—	—	—	1.22	—	—	1.5	1.35	1.47	1.6
N : π bond	1.35	1.51	—	—	—	—	—	1.35	1.47	1.6
F	1.21	1.43	—	—	—	—	—	1.25	1.4	1.55
Cl	1.51	1.65	1.78	—	—	1.32—1.44	—	1.58 (1.50)	1.7	1.85
Br	1.64	1.80	1.85	—	—	—	—	1.7	1.8	2.05
J	1.80	1.90	1.95	—	—	—	—	1.82 (1.80)	1.95	2.2
S	—	—	—	—	—	—	—	1.54	1.6	1.8
S—π bond	—	—	—	—	—	—	—	—	—	—
P	—	—	—	—	—	—	—	—	—	—
Si	—	—	—	—	—	—	—	—	—	—

MAGAT [1] calculated, via r_{min} values, the r_0 values listed from zero-volumina of H_2, O_2, N_2 and CO, published by WOHL [15]. Since in the original communication [1] of MAGAT some numerical errors occur, we have re-calculated the whole on the basis of the data, and principles proposed by MAGAT, and on the basis of data published by WOHL [15], completed with values of r_T (derived from gas-kinetic diameters) and with r_{min} values where zero-volume data were available.

MACK [16, 17]. H-values; $r_{min} = 1.5$ (crystalline H_2); $r_{min}^* = 1.0$ (CH_4); 1.165 (C_2H_6); 1.29 (crystal lattice of several organic compounds); $r_T^* = 0.5$ (CH_4), and 0.63 (benzene); r_{min}^* values of N, and C. from hexamethylenetetramine; r_T of N from N_2; r_T^* of Cl from viscosity of CCl_4-vapour.

STUART [2, 2a, 2b] estimates r_T^* values for bonded atoms from r_0^*, and r_{min}^* data published in the literature. Values in brackets are corrected atom-radii found by "centrum-shift".

THEILACKER [18] determined the minimum of the cloud of electrons of bonded atoms (r_i-radii) from coordination-numbers and from intermolecular atom distances of crystals. The explanation of the intramolecular van der Waals radii ($r_i = d_i/2$) see by BRIEGLEB [5] (cf. Fig. 5) and 8. ("innermolekularer Abstand").

of bonded atoms

Theilacker 1948 [18]	Briegleb 1950 (1952—55) [5], [5b]				Stuart 1952 [6, pp. 97, 99]			Pauling 1939—60 [4]
r_i	r_T	r_{min}	r_T^*	r_{min}^*	r_T^*	r_0^*	r_{min}^*	r_{min}^*
1.23	—	—	1.3	—	1.35	—	—	—
—	—	—	1.6	1.85	—	—	1.70	1.70
0.8	—	—	0.95	1.01 (1.2)	0.9	—	—	1.2
—	—	—	0.5	—	—	—	—	—
1.13	—	—	1.23	1.4	1.2	1.3	1.4	1.40
—	—	—	1.6	—	—	—	—	—
1.17	—	—	1.4	1.6 (1.55)	1.35	1.4	1.5—1.6	1.5
—	—	—	1.6	—	—	—	—	—
1.12	—	—	1.30	1.35 (1.5)	1.25	1.3	—	1.35
1.45	1.51	1.76	1.55	1.80	1.55	1.65	1.85	1.80
1.62	1.64	1.85	1.75	1.95	1.70	1.80	1.9	1.95
1.84	(1.71)	1.96	1.90	2.15 (2.05)	1.80	1.9	2.0—2.1	2.15
1.55	—	—	—	— (1.7)	1.4	1.55	1.65	1.85
—	—	—	—	— (1.85)	1.55	1.7	—	1.9
—	—	—	—	— (2.0)	1.7	—	—	—

r = atoms in elemental, or simple molecules
r^* = radii of atoms in organic (polar) covalent bonds

BRIEGLEB [5] determined r values for halogens from viscosity data of Cl_2 (r_T) or from zero-point volumina (r_{min}). He estimated r^* values for atoms bonded in organic compounds from lattice constants (r_{min}^*), and r_T^* values from the former. Since, at room temperature, in the molecular lattice of aromatic compounds the distance between rings $d_{cryst}^* = 3.7$ Å, hence the van der Waals radius of the carbon atom in the benzene ring $r_{mi}^* = 1.85$, Waals radius normal to the π-bond for every atom (O, N). The values in brackets are later (in 1955) modified values of BRIEGLEB [5b], which had been published previously (in 1952) in the book of STUART [6, p. 99].

STUART [6]. His 1952 data are slightly modified values of his 1934 data.

PAULING [4] calculates on the basis of $r_{min}^* = r_{ion}^*$, except for N, P, As and Sb, where $r_{min}^* = r_{ion}^* - 0.2$ Å. The thickness of a benzene ring he sets equal to the distance between crystal layers in graphite (p. 262).

On the basis of similar data, r^*_{min}, a limited number of sets was made, around 1940, by the California Institute of Technology, designated as the COREY—PAULING model; an amended type of this, the so-called CPK (COREY—PAULING—KOLTUN) Atomic Models, scale 1 Å = 1.25 cm, was put on the market in 1966 [14].

In 1958, based on the latest and most probable values of the r^*_T STUART radii, also in Hungary a set of atom calottes, scale $1 : 10^8$, the EUGON set,* was prepared in plastics [10].
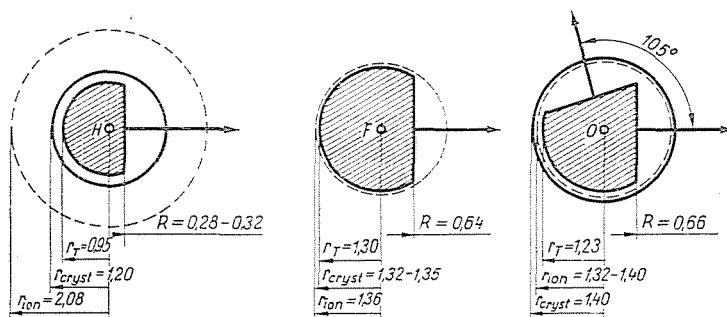

Fig. 6. Dimensions of bonded atoms on calotte models. R = radius of a covalent bond; r_{ion} = ion radius (H⁻, F⁻, O⁻⁻): r_T = van der Waals radius in compounds. T = 300° K; r_{cryst} = van der Waals radius in crystals

According to the foregoing, atoms H, F, and O in organic bonding, may be visualized as shown in Fig. 6. For comparison's sake, the relevant ionic dimensions are also drawn in this Figure. It can be seen also here that for non-metal elements the action radius r_{min} is about equal to the radius r_{ion} of the negative ion.

Thus, for the dimensions of atom-calottes, the bond length (distance between centres of atoms, $a = 2R$) is an accurately known spectroscopical datum published in the literature, consequently data on bond radii agree well enough (within 0.01 to 0.02 Å) in the different sets available. The same holds true for bond angles. However, the situation is different for van der Waals radii. As mentioned before, one of the causes of this is that these values are still rather doubtful (cf. Table II). The other is the debatable choice between r^*_T, r^*_0, and r^*_{min} values for the basis of a design of calotte models.

Up to now, two "schools" have emerged.

1. Treading in the footsteps of STUART [6], r_T^* data for $T = 300°K$, calculable from gas kinetics, were accepted as the basis of design, assuming that operations with organic compounds are mainly carried out at room temperature.

It might be maintained contrary to this view that whereas for molecules of elements, say for H_2, or O_2, and for those of simple compounds, say for CO, the r_T data of gas kinetics derive from direct measurements of viscosities, the r_T^* data for "atoms in bonds" are rather less accurate approximations and are calculated every time from r_0^* or r_{min}^* data only referable to direct measurements. It might be noted, however, that the inaccuracy of those approximations is not greater than the deviation in the original r_0^* and r_{min}^* values.

2. Following the suggestion of PAULING [4], just because of the doubts mentioned, values of van der Waals radii r_{min}^* supported by directly measured data were lately chosen as the basis in the design of calotte models (cf.TableIII).

These dimensions — according to PAULING's approximations — are equal, at the same time, to the radii of the negative ions of the non-metallic elements (cf. earlier parts). Of course, the latter, i.e. calotte models designed on the basis of r_{min}^* values, may indicate steric hindrance where STUART type models designed on the basis of r_T^* values still do not indicate it.

Leaving the duality manifest in a choice (r_T^* or r_{min}^*) of van der Waals radii out of consideration, a modern set of calotte models should thus meet the following requirements.

1. All the dimensions of the models should correspond to real atomic dimensions, and the scale factor should be a round number. The accuracy of manufacture should reach the level of the accuracy of spectroscopic measurements.

2. The device selected for the construction of bonds should adequately simulate the real situations, i.e. rotation should be possible where a σ-bond is indicated, and the bond should be rigid when it indicates π-bonding (models should be capable of illustrating stereo-isomerism).

3. Since data (R, bond angle, and even r^*) of constituent atoms vary according to types of bonding, it is necessary that sets include many calotte-variants for one element in order to allow the building up of as many compounds as possible. Of course, in cases when only a small difference exists between two types of bonding it is a question of economics whether the making of such variants for not too divergent cases are justified, or a compromise at the expense of accuracy is called for. E.g. in sets of different manufacture only one calotte form serves for various olefinic-, carbonyl-, and amide-carbons which differ but to a few degrees in their bond angles (COURTAULD, and CATALIN have only the carbonyl-carbon to do the work, LEYBOLD and EUGON, only the olefinic carbon, CPK has two: an "ethylenic double bond" and an "amide" carbon calotte form. In contrast, the single (σ) bond length is 0.772 for olefinic

Table III

Commercially available sets of atom calottes

van der Waals radius	Firm of Leybold's		Catalin 1954? [12]	Eugon 1967 [10]	Courtauld 1952 [13]	CPK 1966 [14]
	Stuart model 1934 [5]	Stuart — Briegleb model 1950 [11]				
	r_T^* Å, values at room temperature				$r_{min}^* \simeq r_{cryst}^*$, from crystal lattice data	
C	1.375	1.30	1.27	1.30	—	
C—π-bond	1.325	1.60	1.27	1.30	1.60—1.70	1.50
						1.60
						1.70
H	0.9	1.03	0.95	0.95	1.0	1.0
H-bond	—	?	—	0.5	0.5—1.0	"adjustable"
—O—	1.2	1.27	1.16	1.23	1.4	1.35
O =	1.22	1.60	1.16	1.23	1.4	1.35
— N<	1.2	1.30(1.33)	1.20	1.311	1.5	1.45
N—π-bond	1.35	1.60	1.20	1.40	1.6—1.7	1.50—1.70
F	1.25	1.30	1.22	1.30	1.35	1.35
Cl	1.50	1.54	1.44	1.55	1.80	1.80
Br	1.70	1.74	1.57	1.75	1.95	1.95
J	1.80	1.84	1.73	1.90	2.15	2.15
S<	1.47	1.47	1.49	1.47	1.85	1.70
S—π bond	1.55	—	1.49	1.47	1.85	—
P	—	—	1.50	1.52	1.9	?
Si	—	1.66	1.57	1.69	2.0	—

LEYBOLD—STUART *model* (scale $1 : 2 \cdot 10^8$. later $1.5 : 10^8$) with centre-shift.
LEYBOLD—STUART—BRIEGLEB *model* ($1 : 1.5 \cdot 10^8$); bond planes chamfered. For thiophene-S:
    $r_T^* = 1.33$ Å!? Amino-N: 1.33 Å, the others: 1.30 Å
CATALIN ($1 : 10^8$)
EUGON ($1 : 10^8$) Based upon data (1950) of BRIEGLEB; detailed explanations see in Chapter III.
COURTAULD (1 Å $= 0.8$ inch, i.e. about $1 : 2 \cdot 10^8$) Carbonyl-S $r_{min}^* = 1.6$ Å, the other π-bond
    carbons: $r_{min}^* = 1.7$ Å
CPK ($1 : 1.25 \cdot 10^8$) Amide-C: $r_{min}^* = 1.5$ Å, ethylene-C $= 1.6$ Å, other π-bond $= 1.7$ Å.

carbon, and 0.752 for single-bond in conjugated double bond chains, therefore no set takes account of this difference).

    4. In providing for requirements 2 and 3, care should be taken that the realization of these principles should not allow models to be constructed of compounds that do not occur in nature and cannot be synthesized either.

    5. A separate problem is given by the making of calottes for modelling ring systems. Of course, special carbon calottes for 6-membered saturated, or unsaturated, rings must be made available. However, for 5-membered

rings, e.g. furane, cyclo-pentadiene, pyrrole, thiophene series, for each hetero-atom a different "5-member unsaturated carbon" calotte should be designed, because the internal bond angle of this carbon rather differs (range from 108° to 112.5°) from compound to compound, within the series of compounds mentioned.

In the design of the EUGON set, we attempted a solution of this problem by a single special 5-member unsaturated carbon calotte form (see later on).

6. An obvious requirement is that calotte sets be pleasing esthetically and easy to handle. That is why calottes for the several elements are coloured according to a pattern internationally adopted.

(To be continued)

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