TEXT FLY WITHIN
THE BOOK ONLY

UNIVERSAL
LIBRARY

OU_158949

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No 541.5/M 34 P Accession No 22173

Author Mark. H.

Title Physical Chemistry..... System.

This book should be returned on or before the date last marked below.

HIGH POLYMERS
Volume II

HIGH POLYMERS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY, PHYSICS AND TECHNOLOGY OF HIGH POLYMERIC SUBSTANCES

Editorial Board

R. E. BURK, *Cleveland, Ohio;* H. MARK, *New York, N. Y.*

E. O. KRAEMER, *Philadelphia, Pa.;* G. S. WHITBY, *Teddington, Middx.*

Volume II

Physical Chemistry of High Polymeric Systems

By H. MARK

INTERSCIENCE PUBLISHERS, INC.

New York

PHYSICAL CHEMISTRY
OF
HIGH POLYMERIC SYSTEMS

By

H. MARK

Adjunct Professor of Organic Chemistry
Polytechnic Institute of Brooklyn,
New York

TRANSLATED FROM THE MANUSCRIPT BY K. SINCLAIR
REVISED BY J. EDMUND WOODS
Queens College, New York

With 99 illustrations

1940

INTERSCIENCE PUBLISHERS, INC.
New York

Copyright, 1940, by
INTERSCIENCE PUBLISHERS, INC., New York, N. Y.

INTERSCIENCE PUBLISHERS, INC.
215 Fourth Avenue, New York, N. Y.

Printed in U. S. A.
WAVERLY PRESS, BALTIMORE, MD.

CONTENTS

PREFACE ... ix

A. THE GEOMETRY OF MOLECULES ... 1

1. Structure Determination with X- and Cathode-Rays ... 2

(a) The Method of M.v. Laue ... 3

(b) The Method of W. H. and W. L. Bragg ... 5

(c) The Method of Debye-Scherrer and Hull ... 6

(d) The General Crystal Rotation Method of Polanyi, Schiebold and Weissenberg ... 7

(e) The X-Ray Goniometers of Böhm, Dawson, Sauter, Schiebold and Weissenberg ... 8

(f) Evaluation of the Diagrams ... 8

(g) Interferometric Measurement of Molecules in the Gaseous State 9

(h) Presentation and Discussion of the Principal Results ... 11

2. The Behavior of Molecules in the Electric Field ... 22

(a) Polarizability ... 24

(b) Applications and Results of Polarization Measurements ... 26

(c) Dipole Moments ... 29

(d) Application of Dipole Measurement in Determining Molecular Structure ... 31

3. Optical Behavior of Molecules ... 34

(a) The Kerr Effect ... 34

(b) The Degree of Depolarization ... 35

(c) Results of Optical Molecule Measurements ... 36

B. THE INTERNAL MOTIONS OF MOLECULES ... 39

1. Methods of Determining Internal Motions of Molecules ... 40

2. Results ... 43

(a) Moments of Inertia, Nuclear Distances and Dissociation Energies ... 43

(b) Natural Vibrations and Group Frequencies ... 45

(c) Internal Molecular Potential and Free Rotation ... 53

(d) The Double Bond and Cis- Trans-Isomerism ... 66

(e) Internal Molecular Dynamics and Statistics ... 69

Conclusion ... 78

C. PRIMARY AND SECONDARY VALENCES ... 81

1. Chemical Primary Valence ... 81

(a) The Heteropolar Linkage Between Oppositely Charged Ions ... 82

(b) The Homopolar Linkage Between Neutral Atoms ... 85

(c) The Metallic Linkage ... 89

2. The Secondary Valences ... 91

(a) The Orientation Effect of Rigid Dipoles ... 91

(b) The Induction Effect ... 92

(c) The Quantum Mechanical Interaction of Internal Electron Motions (Dispersion Effect) 93
(d) Co-Action of the Three Types of Secondary Valences 94
3. General Remarks on the Formation of Molecule Aggregates 98
(a) Aggregate Formation by Dipole Forces 98
(b) Aggregate Formation by Dispersion Forces 103
4. Molecular Associations and Intermolecular Forces . . . 106
(a) The Molecular Associations of Unsaturated Hydrocarbons . 106
(b) Molecular Association Between Carboxylic Acids . . . 110
(c) Calculation of the Molecular Cohesion 112
D. Crystal Structure, Lattice Forces and Chemical Structure of the Unit Cell 117
I. Classification of Crystals from the Aspect of Forces . 117
1. The Ionic Lattice 119
2. The Atomic Lattice (Diamond Type Lattice) 126
3. The Metallic Lattice 127
4. Secondary Valence Lattices . 129
(a) Secondary Valences and Density 129
(b) Different Types of Secondary Valence Lattices 132
(c) Molecular Lattices of Long Chain Substances 139
(d) Molecular Lattices and Symmetry of the Unit Cells 146
5. Lattices with Different Forces in Different Directions . . 147
(a) Lattices with Atomic and Ionic Linkages . 148
(b) Lattices with Atomic and Metallic Linkages 149
(c) Lattices with Homopolar Primary Valency Linkage and van der Waals Linkage . . . 150
II. Classification of Crystals from the Aspects of Symmetry . . . 151
1. General Remarks on the Symmetry of Crystal Lattices . . 151
2. Primary Valence Lattices 157
3. Primary Valence Networks 159
4. Primary Valence Chain Lattices . . 162
5. Structure of Silicates 169
6. Internal Mobility and Form of Molecules in Relation to Lattice Structure 171
E. Molecular Arrangement in Liquids and the Investigation of Very Minute Crystals 177
1. General Remarks on the Arrangement of Particles in a Liquid . . 177
2. Scattering of X-Rays in Liquids 179
(a) The Scattering of X-Rays by Monatomic Liquids 182
(b) The Arrangement of the Molecules in Liquid Water . . . 188
(c) Structure of Liquids Containing Elongated Molecules . . . 191
3. Determination of Size and Form of Very Small Crystals with X-Rays 194
4. Observations on Mesophases or Crystalline Liquids 199
(a) Experimental Results in the Investigation of Mesophases . 200
(b) The Molecular Arrangement in the Mesophases 202
F. The Behavior of Mixtures 207
1. General Remarks on the Investigation of High Polymeric Substances in Solution 207

2. Remarks on Processes in the Formation of Binary Mixtures 210
(a) Mixing of Two Gases 212
(b) Mixtures of Liquids 215
3. Lowering of Vapor Pressure in Binary Mixtures 219
4. Osmotic Phenomena 228
(a) The Origin of Osmotic Pressure 228
(b) Experimental Results of Osmotic Measurements 231
(c) Osmotic Behavior at Higher Concentrations 234
(d) Effect of Temperature on Osmotic Pressure 241
(e) A Few General Data on Solubility with Particular Regard to Chain Molecules 245
(f) The Distribution of Chain Molecules in the Dissolved State. . 252
(g) Theories Regarding Interaction Between Solvent and Solute . . 254
5. The Viscosity of Liquids and Solutions 258
(a) The Normal Viscosity of Pure Liquids 259
(b) Theories Regarding the Viscosity of Pure Liquids 265
(c) Anomalies in the Flow Properties of Pure Liquids 267
(d) Viscosity of Solutions 272
(e) The Origin of Viscosity in Suspensions 277
(f) Expressions relating to the Effect of Concentration upon Viscosity 293
G. Kinetic Phenomena in High Polymer Chemistry 297
1. The Phenomena of Diffusion 297
(a) The Free Diffusion of Dissolved Particles; General Principles . 297
(b) Measurement of Rate of Diffusion 299
(c) A Few Important Results 300
(d) The Application of High Centrifugal Fields; General Principles of Centrifugal Analysis 303
(e) A Few Important Results 307
2. The Mechanism of Formation and Degradation of Long-Chain Molecules 309
(a) Short Outline of the Mechanism of Polymerization Reactions ... 310
(b) The Kinetics of Polycondensation Reactions 322
(c) The Degradation of Long-Chain Molecules 327
Authors Index 335
Subject Index 341

PREFACE

During the last few years the chemistry of the high polymers has passed through an important phase of development and has become an independent, rapidly expanding branch of chemical science. Its increasing technical importance and the close relation to the biological sciences justifies a comprehensive treatment of the whole sphere of high polymer chemistry.

Ten years ago interest centered in the structural principle governing the high polymers, the forces of cohesion of the large molecules and the paths leading from the chemistry of the low molecular substances to the high polymers. Today these fundamentals may be regarded as solved in essentials and the research worker in this field is occupied with other questions.

What physical and chemical methods have proved necessary and effective in the preparation, purification, examination and elucidation of the high polymers? In what manner and under which conditions can the fundamental laws of physical chemistry be applied to the high polymers?

While for a long time individual workers in this field favored a given method of investigation and tended to stress the importance of their results, it is now essential to apply all the available methods simultaneously, and to attach particular weight to results which confirm and are complementary to one another. While previously in the field of high polymers it was possible to be satisfied with a few, more or less empirical relationships and rules, it appears necessary and possible today to visualize the extension of many of the more exact laws of physical chemistry—vapor pressure, osmosis, viscosity, diffusion, kinetics of reaction, etc.—and thus to incorporate the chemistry of the high polymers securely in the fundamentals of our science.

Apart, however, from these theoretical considerations, the rapidly increasing mass of data demands a comprehensive, systematic description of the substances available and studied. In this, emphasis mainly falls on the material properties of the individual representatives and on their mutual relationships. It is hardly possible at present to discuss fundamental questions of structure but the time has arrived to present the relation between structure and properties in all its details. Material facts

which can almost be termed excessive need to be sifted and arranged systematically.

In this volume (the second of the series) an attempt has been made to treat the first category of problems discussed above and to take the reader shortly through those parts of general and physical chemistry particularly necessary to a study of the high polymers.

This book was started and essentially completed when the writer was professor of Chemistry at the University of Vienna. During this time he enjoyed the valuable help of Professor K. H. Meyer and Dr. A. J. A. van der Wyk, of the University of Geneva and of Dr. E. Broda in Vienna. He wishes to express his sincerest thanks for their kind and suggestive assistance. Most of the proofreading and several additions were carried out while the writer was Manager of Research for the Canadian International Paper Company in Hawkesbury, Ontario. It is a very pleasant duty for the author to express in connection herewith his sincerest gratitude to Dr. C. B. Thorne, Technical Director and Mr. S. Wang, Manager of Laboratories of the Canadian International Paper Company. The translation was revised by Dr. J. Edmund Woods of Queens College, Queens, New York, to whom the writer is much indebted for a series of very helpful suggestions for improvement.

H. MARK.

New York, N. Y.
October, 1940.

A. THE GEOMETRY OF MOLECULES

Continued experience has shown that, in general, the smallest chemically active units of matter—atoms and ions—are not identical with those particles called molecules which we regard as the limit to which homogeneous matter may be reduced by mechanical subdivision or other physical means. It is characteristic of compound molecules that they contain a definite number of the constituent atoms and can be represented by empirical formulas such as

$$A_xB_yC_z \cdots \tag{1}$$

The nature of A, B, C, etc., as well as the relative values of x, y, z, etc., are determined by chemical analysis, while molecular weight determinations yield the absolute values of these subscripts.

Such a compound as (1) has a definite range of stability toward external parameters—pressure, temperature, fields of force, etc.—within which it can be investigated. Over and above the purely numerical values of x, y, z, however, each kind of molecule has a characteristic and definite arrangement of the atoms constituting it; in small molecules, such as NaCl, CH_4, PCl_3—apart from vibrations of the individual atoms which are trivial geometrically although highly important dynamically—the arrangement is obvious and is given by the coördinates of all atomic centers of mass relative to one of them, chosen as the origin. With larger molecules and especially, with organic molecules, there are, in addition to the atomic vibrations just mentioned, still other internal motions such as rotations, vibrations of entire radicals, etc., which indicate that the molecule can no longer be considered as having a fixed arrangement which is the same in each state of aggregation. Very frequently, however, even in such cases, a quite definite configuration of atoms prevails—at least, in the crystalline state—constituting a *nuclear frame-work*. We shall, therefore, turn our attention first to this state and describe methods for the measurement of crystal properties which have made very important progress during recent years.

Several methods are available for establishing the nuclear framework of a rigid molecule, i.e. for determining the interatomic distances and the angle between connecting links—the so-called *valence angle*. In general there is satisfactory and remarkable agreement between the values ob-

tained by very different means. Where discrepancies occur they generally mean that the different experimental techniques do not measure exactly the same magnitudes. Thus the different methods control and supplement one another in a very effective way.

The following methods are particularly important:

a) Investigation of molecules by interferometry, using x-rays or cathode rays.
b) Measurement of the permanent dipoles and polarizability.
c) Observation of the Kerr effect and of the degree of depolarization.
d) Measurement and evaluation of frequencies in the infra-red, band and Raman spectra.

In presenting this review, the individual methods will first be discussed with special emphasis on their range of application, subsequently passing on to a consideration of the results furnished by them (particularly in the domain of large molecules).

1. Structure Determination with X- and Cathode Rays

It is usual, except in special cases, to work with x-rays of 0.5 to about 3.0 Å wave lengths or with cathode rays of 10^3 to 10^5 volts. The latter coincide, according to the de Broglie relation, with a wave length range of about 0.4 to 0.04 Å. The molecules under investigation may be in the free state (gas or solution) or in the form of a homogenous condensed phase (liquid, crystal, mixed crystal).

The historical development of the experimental procedures began with the examination of molecules in the crystalline state, principally with the aid of x-rays. Here the early work following Max von Laue's fundamental discovery[1] should be cited, particularly that of W. H. and W. L. Bragg[2] and of P. Debye and P. Scherrer,[3] while in subsequent years and up to the present day a great number of eminent research workers have contributed to this field. After the proof by Davisson and Germer[4] and by G. P. Thomson[5] of the wave nature of electrons in rapid motion, this technique was also applied to the study of molecular structure in the crystalline state.[6]

[1] W. Friedrich, P. Knipping and M. v. Laue, *Sitz. ber. bayer. Akad. Wiss.*, **5**, 303 (1912).

[2] W. H. and W. L. Bragg, *Nature*, **90**, 410 (1912).

[3] P. Debye and P. Scherrer, *Physik. Z.*, **17**, 277 (1916); A. W. Hull, *Phys. Rev.*, **10**, 661 (1917).

[4] I. Davisson and L. H. Germer, *Phys. Rev.*, **30**, 772 (1927).

[5] G. P. Thomson, *Proc. Roy. Soc. London*, (A) **117**, 600 (1928).

[6] See e.g. B. G. J. Finch and H. Wieman, *Ergeb. exakt. Naturw.*, **16**, 353 (1937) and especially G. P. Thomson, *Electronic Diffraction*, London 1939.

In contrast, investigation of the gaseous state had been undertaken about ten years previously by Debye[7] and his co-workers with the aid of x-rays, and by Mark and Wierl[8] with electrons. Later, the method was used by other workers and it furnished very valuable experimental data.[9]

It will be useful to review very briefly the most important features of the different investigation methods employing x- and electron-rays.

a) M. v. Laue's Method

Penetration of a single stationary crystal by parallel polychromatic (i.e. "white") x-rays led to the discovery of x-ray interference by Friedrich, Knipping and v. Laue[10] in 1912; it gave the well known symmetrical, sharp point diagram which certainly constitutes one of the most beautiful experimental effects of modern physics. Its use for the purpose of determining molecular structure in the solid state is, however, comparatively difficult and ambiguous; for on working with "white" x-rays, nearly all the network planes are simultaneously reflecting in accordance with the Bragg equation (see below). The Laue method is therefore applicable by itself only in especially simple cases (graphite, diamond, NaCl, $CaCO_3$). Nevertheless, the Laue method, in combination with others to be discussed, has sometimes proved particularly useful when the intensities of reflection from lattice planes of very high index were to be measured and reliance placed upon the precise determination of atomic coördinates. Further, it has been possible to deduce from the cleavage of the interference points—the so-called *asterisms*—very important conclusions on the occurrence of lattice distortions and mosaic structure.[11] Similarly, Laue diagrams prove particularly suitable for gaining an initial insight into the symmetry relationships of a given crystal (see Table 1). It may be added that with modern x-ray tubes and good fluorescent screens, the Laue points can be observed directly on the fluorescent screen without difficulty; this glimpse is particularly impressive when, on the slightest movement of the irradiated crystal, bright points suddenly disappear and new interferences flash up

[7] P. Debye, *Ann. Physik*, **46**, 809 (1915); P. Debye and P. Scherrer, *Physik. Z.*, **19**, 474 (1918).

[8] H. Mark and R. Wierl, *Naturwiss.*, **18**, 205 (1930).

[9] See e.g. the bibliography by J. T. Randall, *X-ray and Electron Diffraction*, p. 101, London 1934, and the recent publications of L. Pauling and his collaborators cited under 22 and 23.

[10] W. Friedrich, P. Knipping and M. v. Laue, *Sitz. ber. bayer. Akad. Wiss.*, **5**, 303 (1912) and for historical development also *Naturwiss.*, **20**, 527 (1932) and *Current Science*; Special Number on "Laue Diagrams"; January 1937.

[11] F. Halla and H. Mark, *Röntgenographische Untersuchung von Kristallen.* Leipzig 1937, p. 203 *et seq.*

TABLE 1[1]

SUMMARY OF THE APPLICABILITY OF INTERFERENCE METHODS

	1. Laue method	2. Rotating crystal method W. H. and W. L. Bragg		3. Powder method Debye-Scherrer, Hull		4. Goniometer method Weissenberg, Schiebold, Dawson
		Photometric	Ionometric	Photometric	Ionometric	
Convenient crystal size	0.1–0.01 cm.	0.1–0.01 cm.	Greater than 0.1 cm.; natural or polished surfaces	Small	<0.1 cm.	0.1–0.01 cm.
Convenient crystal symmetry	Any	Any	Any; but difficult for non-orthogonal crystals	Only from rhombic system upwards		Any
Number of reflections observed	Very large (some hundreds)	Large; up to 200	Optional; but tedious and difficult for many surfaces	Under 40	Very few	Optional; readily distinguishable
Indications	Simple and certain	Tedious but certain	For many surfaces difficult but certain	Certain only for planes of low index		Absolutely reliable
For determination of geometric lattice parameters	Impracticable	Maximum accuracy	Accurate	Fairly accurate for a few surfaces, uncertain for higher indexed planes		Very good
Symmetry determination	Best method	Not efficient	By intensity estimation	Impossible		Good method
Space group determination	Subject to error	Suitable	Reliable only with a sufficient number of planes	Impossible		Best method
Accuracy of intensity measurement	Inadequate; too many corrections required	Better than Laue	Standard method; but extinction correction necessary	Best photographic method	Very accurate; few corrections but of limited applicability	Fairly good

[1] From Halla-Mark, *Röntgenographische Untersuchung von Kristallen*, Leipzig 1937; Tab. 9, p. 30.

on other places. It is also possible to identify the interference spots from the relation

$$\lambda_{min} = \frac{h \cdot c}{e \cdot V}$$

by their disappearance when the tube potential falls below a certain value. (V = tube potential in absolute units, h = Planck's constant, c = velocity of light, e = electrical unit charge.)

b) The Method of W. H. and W. L. Bragg

If an attempt is made to reflect approximately parallel and monochromatic x-rays from a plane surface of any single crystal, it will be found that, contrary to the phenomenon of normal reflection from a mirror, no appreciable intensity of reflected radiation is obtained unless the condition expressed by Bragg's law of reflection is rigorously fulfilled. This condition is determined by the spatial arrangement of the system. Bragg's law states that a strong reinforcement of the incident ray occurs only if

$$n \cdot \lambda = 2\, d\, \sin \varphi \qquad (2)$$

where λ is the wave length of the impinging radiation, d is the distance between the adjacent lattice planes involved in the reflection and φ is the angle between the incident rays and the reflecting planes; n is an integer, usually small, which denotes the order of the reflection. It is not known from a single observation but is revealed by comparing several reflections obtained at different glancing angles, one of which will give a value of $n = 1$. Inasmuch as the ordinary law of reflection,

Angle of incidence = angle of reflection

applies in this case in addition to Bragg's law, the angle θ between the reflected rays and the incident rays prolonged is equal to 2φ. This angle θ is known as the angle of deviation; φ is called the *glancing angle*, although this designation has not quite the same meaning as is ordinarily attached to the term.

The Bragg experiment is also very impressive when performed with a fluorescent screen,[12] if a crystalline plate of NaCl, sugar, calcite, etc. is placed at any desired angle in a parallel, monochromatic x-ray beam, no reflection can be detected on a fluorescent screen placed on the side remote from the x-ray tube. If, however, the crystal is rotated slowly in the beam and the screen is observed, a spot of light suddenly appears upon

[12] Compare W. H. and W. L. Bragg, *X-rays and Crystal Structure*; 4th edition; London 1924 and *Crystalline State*, London 1934.

the screen whenever the surface of the crystal makes a particular angle with the incident beam. This is due to reinforcement through interference. The spot disappears just as rapidly when the crystal is turned a little further. Reflection of the x-ray beam occurs only if the angle of incidence φ has exactly the value given by equation (2). In the present case this condition is necessarily fulfilled if λ and d remain constant and φ is continually changed by rotating the crystal until it reaches the critical value required by (2) (reflection position).[12a]

This method allows of measurements of *one* of the magnitudes characteristic of the given lattice plane, namely d, the distance between the planes, and has proved very useful in investigating simple crystals, particularly in the earlier stages of structure elucidation. In more complicated crystals, especially in organic crystals, it is usually necessary to combine this technique with others to obtain reliable evidence (see Table 1).

c) *The Method of Debye-Scherrer and Hull*

Continual variation of the angle of incidence φ and the corresponding satisfaction of condition (2) may be attained in a different way.[13] If, instead of a single crystal, a powder consisting of very many small crystals is placed in the path of an x-ray beam, it will happen in general that, because of the random orientation of the little crystals, a characteristic lattice plane will always be available for any incident angle whatsoever; a multiplicity of φ values is furnished in this case by the proximity of many tiny particles.

By reason of the random arrangement of the small crystals, reflection occurs at every suitably placed plane in the crystalline mass and a band of interference lines is obtained simultaneously, each belonging to a particular lattice plane. This makes it possible, as in the earlier methods, to determine experimentally the lattice distance between these planes. The diffraction patterns appear as concentric circles on a flat photographic plate, and as more complicated curves on the cylindrical film usually employed. Such "*powder*" or "Debye-Scherrer-Hull-*diagrams*" can also easily be observed directly in the fluorescent screen. They are important whenever it is impossible to grow sufficiently large single crystals of the material under investigation, e.g. in metallography and in colloid chemistry.

It may be added that the Laue-diagram affords the third possibility,

[12a] It may be mentioned that G. D. Preston, *Nature* **142**, 569 (1938), has recently discovered x-ray reflections of a different type, which are due to the interaction of the x-rays with the heat waves, which travel through the lattice in all directions.

[13] P. Debye and P. Scherrer, *Physik. Z.*, **18**, 291 (1917); A. W. Hull, *Phys. Rev.*, **10**, 661 (1917).

and one that is easily realizable experimentally, of fulfilling the Bragg condition, i.e. by keeping d and φ constant and using an x-ray beam comprising a continuous distribution of wave lengths. Accordingly, with the aid of the variables in equation (2) the three methods thus far described afford a means of determining one of the characteristic parameters of a lattice plane, namely, the *inter-planar distance.* It has been mentioned previously that this can lead to complete elucidation of the structure of simple crystals but in complicated cases it is necessary to know also the position in space of any lattice plane; this knowledge can be gained by one of the following methods.

d) The General Crystal Rotation Method of Polanyi, Schiebold and Weissenberg

This method represents an extension of the Bragg procedure in so far as it serves to record photographically, not only the reflections from one or more lattice planes lying parallel to the axis of rotation, but also the reflections from as many other planes as possible, which are oblique to the axis of rotation. This is accomplished by surrounding the specimen with a cylindrical strip of film. In such a way it is possible to establish a second parameter of the reflecting planes. This is best achieved by using the so called layer-line relation first derived by Polanyi,[14] which states that on such rotary diagrams the individual reflections arrange themselves in parallel "layer lines" and the reciprocals of the distances separating them furnish directly the *period of identity* for the axis of rotation. This period of identity denotes the distance in a given direction around the lattice from one lattice point to the next identical one. The separation of the layer lines is connected with the identity period I by the expression

$$I = \frac{n \cdot \lambda}{\sin \mu} \tag{3}$$

in which μ is the angle between the equator of the diagram and the layer line concerned (as seen from the specimen) λ the wave-length and n the series of the layer line.

The use of such layer line diagrams has frequently proved highly useful in determining complicated structures.

With regard to reflection from planes which are not parallel to the axis of rotation, there is an important effect observable on irradiating a disoriented crystal powder. If, for example, the small crystals in the irradi-

[14] M. Polanyi, *Naturwiss.*, **9**, 337 (1921); *Z. Physik*, **7**, 149 (1921); H. Mark and K. Weissenberg, *Z. Physik*, **16**, 1 (1923); **17**, 301 (1923).

ated preparation are not oriented in a completely random manner but, instead, certain positions in space are favored, the interference rings mentioned above are replaced by striated and segmented patterns which throw light upon the predominant arrangement in the preparation. Since such patterns were first observed by Herzog and Jancke,[15] and by Scherrer[16] in ramie fibres, they have been named fibre diagrams by Polanyi,[17] who first explained their origin. They have played an important part in the elucidation of the structure of high polymers and will be discussed in greater detail in another volume of this series.

e) The X-Ray Goniometers of Böhm, Dawson, Sauter, Schiebold and Weissenberg

Three independent parameters are required for characterizing a lattice in space (e.g. the interplanar distance and two angles in space); therefore the need has arisen in course of time and in the face of increasingly difficult problems to obtain three mutually independent sets of experimental data for every lattice plane in order to deduce the three indices from them by the aid of easily derivable equations. The so-called x-ray goniometers serve this purpose. The desired effect is achieved by moving both the crystal and the recording film. The motion of the film and its relation to the reflection position of the crystal fixes just the degree of freedom lacking for the positive identification of a lattice plane. According to the nature of the problem, the choice of goniometers lies between the various instruments designed for this purpose by different investigators, e.g. Dawson, Böhm-Weissenberg and Schiebold-Sauter.

f) Evaluation of the Diagrams

By ordinary use of the above described methods, it is nearly always possible to work out experimentally a long list of lattice plane distances and reflection intensities which form the basis for further evaluation of the diagrams. This list contains implicit data of particular interest to the chemist—*atomic distances, valence angles,* etc.—but the information is not in a form which is directly usable. Instead, the data must be converted by a more or less complex calculation, which is more trustworthy the greater the number of lattice planes listed and the more accurately the interplanar distances and, especially, the intensities have been measured.

[15] See, for example, R. O. Herzog and W. Jancke, *Z. physik. Chem.*, (A) **139**, 235 (1920).

[16] P. Scherrer, *Göttinger Nachr.*, **1918**, 98.

[17] M. Polanyi, *Naturwiss.*, **9**, 288 (1921).

It would lead too far to go into the nature of such a calculation here but it may be said that the treatment is partly geometrical and partly physical.

In the first, geometrical part, the crystal system, the *crystal class*, the *translation group* and the *space group* of the crystal under investigation are determined by systematic application of crystal structure theory in conjunction with tables. In addition the volume of the *elementary cell*, i.e. the smallest unit from which the whole crystal can be built up merely by parallel displacement, is established by calculation of its axes and angles.

In the second part the values just obtained are used in locating the centers of mass of the constituent atoms. In this second stage the intensities of the observed reinforcements are *analyzed harmonically* on the basis of certain well founded assumptions as to the scattering power of individual atoms. Usually this is possible in complicated molecules only by the use of successive approximations; obviously, by continued refinement of the calculation a false assumption can be corrected and an accurate one built up (stepwise) to almost complete certainty (method of trial and error).

If, finally, the spatial arrangement of all atoms in the elementary cell is known, the intra-molecular distances and the angle between the directions of valence are established.

Information on performing the calculations and the special precautions to be observed may be obtained from the fairly numerous appropriate text and handbooks; Table 1 summarizes the individual methods and their applicability. More detailed advice can be found in the comprehensive books of W. H. and W. L. Bragg and in the well known monographs of R. W. G. Wyckoff and G. L. Clark.[18]

g) Interferometric Measurement of Molecules in the Gaseous State

The interference pattern of a crystal arises from myriad (about 10^{19}) atoms or ions arranged regularly in space, and in it are mirrored the numerous distances which separate the crystallographically equivalent points in a crystal from one another. In gases, on the other hand, according to Debye and Ehrenfest,[19] only the few intra-molecular distances are responsible in the interference pattern, because the distances between separate molecules have no fixed values. This gain in simplicity is of

[18] W. H. and W. L. Bragg, *X-rays and Crystal Structure*, London 1924 and 1934; R. W. G. Wyckoff, *The Structure of Crystals*, 2nd ed., New York 1931, *Suppl.* 1935; G. L. Clark, *Applied X-rays*, New York 1940.

[19] P. Debye, *Ann. Physik*, **46**, 809 (1915); P. Ehrenfest, *Proc. Amst. Acad.*, **23**, 1132 (1915).

course at the expense of loss in sharpness of the diagrams, because the number of the particles giving rise to interference is incomparably smaller.

Debye[20] has developed a theory for evaluating gas exposures which, for given atomic coördinates, represents the intensity of the scattered beam as a function of the angle of diffraction. It is obviously not possible in general to deduce a definite molecular model from one experimental diagram without further assumptions (harmonic analysis). Frequently the evaluation of the diffraction pattern must be based on a tentatively assumed plausible model, the interferences given by it calculated and the model compared with the diagram actually obtained.

The evaluation is particularly simple and clear if in the conjectural molecular model only a single effective (independent) distance connects the different atoms. This is the case, for example, in CCl_4 where, according to well founded assumptions of structural organic chemistry, the C-atom lies at the central point and the Cl-atoms at the apices of a regular tetrahedron. Here and in other similar instances the intensity distribution admits of a definite conclusion regarding the atomic distances and the angle between the individual valences.

Interferometric investigation of gases with x-rays is difficult experimentally because the intensity of the scattered radiation is small and relatively long exposure periods are accordingly required. This led to the use first by Mark and Wierl[21] of cathode rays of medium velocity which give very useful diagrams in a few seconds due to the greater reciprocal action between electrons and matter; evaluation of these has to be done by a somewhat different and not so completely reliable formula from that used for x-rays. Later very accurate experiments on numerous simple molecules in the gaseous state have been performed with cathode rays by L. Pauling and his collaborators,[22] which have afforded useful confirmation of results on crystals obtained with x-rays. Recently P. Debye, Jr. has introduced an important experimental improvement of cathode-ray patterns from gases by applying a rotating sector in front of the photographic film, which reduces the continuous background and makes the patterns liable for a photoregistration.

[20] See, for example J. T. Randall, *The diffraction of x-rays and electrons*, London 1934, p. 62; G. P. Thomson, *Electronic Diffraction*, London 1939.

[21] H. Mark and R. Wierl, *Naturwiss.*, **18**, 205 (1930).

[22] E.g. L. Pauling, H. D. Springhall and K. J. Palmer, *J. Am. Chem. Soc.*, **61**, 927 (1939); furthermore T. Y. Beach and D. P. Stevenson, *J. Am. Chem. Soc.*, **61**, 2643 (1939); D. P. Stevenson and H. O. Burnham, *J. Am. Chem. Soc.*, **61**, 2922 (1939); D. P. Thomson and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 3173 (1939).

h) Presentation and Discussion of the Principal Results

The results of interferometric determination of molecular structures present themselves in different ways and can be evaluated scientifically along different lines.

It may be convenient to take first the most general result and report it numerically. This is that, in the molecules of organic substances at any rate, there is for any given chemical primary valence a *definite distance* between the atoms linked by this valence and this is true quite independently of any substituents carried by the two combined atoms. As a first approximation—as *quantum mechanics* shows—the homopolar binding forces between two given atoms are determined essentially by their charge clouds and by the power of mutual interchange of portions of these charge clouds. The *interatomic distances* corresponding to the linkage are known today in great number and with remarkable accuracy. Detailed tables are to be found in appropriate monographs,[23] in Landolt and Börnstein's and the International Critical Tables[24] and in several comprehensive articles in this field.[25]

We will first present the numerical data for some important organic linkages (Table 2). In order to confirm their reliability, values are occasionally added which have been obtained by methods other than the interferometer method. The possibilities of application of these methods will be discussed in detail in the next section. The figures of Table 2 extend back to 1930; some more recent values are given in Table 3.

By reason of this general constancy of the primary valence bonds, quite sharp limitations are placed upon the basic assumptions of stereochemistry which are fully confirmed by modern research. These limitations restrict the possibility of synthesizing organic molecules and exclude many of those formulae previously used for purposes of convenience in designing structural formulae on paper. Our present knowledge authorizes and compels us to recognize and apply the constancy of the valence distances as an experimentally well-founded law in proposing any structural formula. It will be shown later by a few examples how important the consistent employment of this important principle has become in individual cases.

[23] E.g. by H. A. Stuart, *Molekülstruktur*, Berlin 1934; H. Sponer, *Molekülspektren*, Berlin 1936; Tabellenband; L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935); further, D. C. Carpenter and L. O. Brockway, *J. Am. Chem. Soc.*, **58**, 1270 (1936); L. Pauling and D. C. Carpenter, *J. Am. Chem. Soc.*, **58**, 1274 (1936); J. M. Robertson, *Chem. Rev.*, **16**, 417 (1935).

[24] Landolt and Börnstein, *Phys.-chem. Tab.*, 3. Erg.-Bd., 1.Teil, p. 104 et seq.; *International Critical Tables;* Vol. I, p. 338; Vol. V, p. 409.

[25] E.g. H. Mark and F. Schossberger, *Ergeb. exakt. Naturw.*, **16**, 183 (1937).

In a second approximation we must, of course, expect exceptions to the law of constant valence distances, particularly if two united atoms carry substituents which on their part have special requirements with regard to charge shell. A review of the available experimental material actually shows that one and the same linkage in different molecules can under certain conditions exhibit values which differ from one another to a degree beyond the experimental error. An example of this shown by the figure on page 14 where the difference in the values obtained experimentally are certainly well outside the experimental error; some experi-

TABLE 2

A FEW IMPORTANT ATOMIC DISTANCES IN ORGANIC MOLECULES. EARLIER DATA

Linkage	Substance	Distance in Å	Method used	Year of determination
C—C, aliph.	Ethane	1.56	Band spectrum	1932
	Cyclohexane	1.53	Electron diffraction	1930
C—C, arom.	Benzene, liquid	1.36	X-ray diffraction	1931
	Benzene, vapor	1.39	Electron diffraction	1931
C=C	Ethylene	1.30	Band spectrum	1932
C≡C	Acetylene	1.19	Band spectrum	1932
C—H	Methane	1 08	Band spectrum	1932
	Ethylene	1.04	Infra red spectrum	1934
C—F	Methyl fluoride	1.43	Ultra violet spectrum	1934
C—Cl	Methyl chloride	1.86	X-ray diffraction	1931
C—Br	CBr_4	1.93	"	1937
C—I	CI_4	2.12	"	1937
C—O	Methyl alcohol	1.46	Infra red spectrum	1933
C=O	Formaldehyde	1.19	Ultra violet spectrum	1934
C—N	HCN	1.15—1.17	Band spectrum	1932
C≡N	Cyanogen	1.18	Electron diffraction	1932
H—O	Water vapor	1.02	Band spectrum	1934
H—N	Ammonia	1.02—1.06	Ultra violet spectrum	1934

mental material on this point is given in Table 4; it may, of course, be still too scanty to permit of final quantitative conclusions regarding the influence of substituents on valence distances. In spite of this, it must be emphasized that an extremely interesting way is opened for studying experimentally the mutual influence of substituents in the central atom on the nature and strength of a bond, since it is a general rule—particularly in keeping with wave mechanical conceptions—that atomic distance and bond strength are closely related to one another.

The recent experimental results of the influence of substituents on the

carbon-carbon bond is summarized in Figure 1. Lennard-Jones[26] has emphasized the fact that although the single, double and triple bonds are outstanding types of linkage, intermediate cases have to be admitted. In such cases the actual bond possesses to a certain extent the characteristics of single and double bonds and its atomic distance as well as its energy

TABLE 3

SOME RECENT VALUES ON ATOMIC DISTANCES IN ORGANIC MOLECULES

Linkage	Substance	Distance in Å	Reference
C—C aliph.	Nonacosane	1.553	A. Müller, *Proc. Roy. Soc., London*, **120A**, 437 (1928)
C—C arom.	Hexamethyl-benzene	1.42	K. Lonsdale, *Proc. Roy. Soc., London*, **133A**, 536 (1931)
C—C aliph.-arom.	Hexamethyl-benzene	1.48	"
C=C	Benzoquinone	1.32	J. M. Robertson, *Chem. Rev.*, **16**, 417 (1935)
C—N	Cyanurtriazide	1.38	J. E. Knaggs, *Nature*, **135**, 268 (1935)
C=N (ring)	"	1.31	"
N=N	"	1.26	cf. L. Pauling and J. H. Sturdivant, *Proc. Nat. Ac. Sc. U. S.*, **23**, 615 (1937)
N≡N	"	1.11	"
C—O	Oxalic acid dihydrate	1.25	W. H. Zachariasen, *Z. Krist.*, **89**, 442 (1934)
C=O	Urea	1.25	R. W. G. Wyckoff, *Z. Krist*, **81**, 102 (1932)

behavior lie between those of the two pure types. Lennard-Jones has introduced the idea of "order of a bond" as a means of denoting its position between the single, double and triple linkages. In Figure 1 the distances

[26] J. E. Lennard-Jones, *Trans. Faraday Soc.*, **35**, 811 (1939). See also L. Pauling, *The Nature of the Chemical Bond*, Ithaca 1940.

between two carbon atoms are plotted as ordinates against the order of the bond as abscissae. One sees that the distance of 1.55 Å is characteristic of the pure single bond, 1.34 Å of the pure double bond and 1.19 Å of the pure triple bond. They correspond to the actual distances in ethane, ethylene and acetylene, respectively. If such bonds existed alone in nature, the representation of all organic compounds would be accumulated along the ordinates erected at the points 1, 2, and 3 of the horizontal axis.

In reality this is not the case. As Figure 1 shows very clearly, there are many intermediate distances, corresponding to mixed types of carbon-carbon bonds, which exhibit very interesting properties as regards their degree of unsaturation and reactivity.

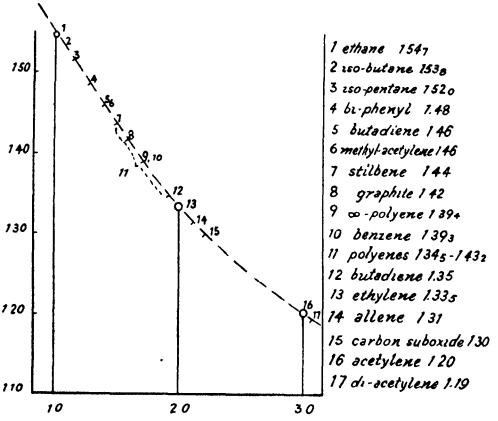


Fig. 1. Relationship between the character of substituents and carbon-carbon bond.

It may be emphasized that the quantum-mechanical theory of homopolar valence gives a very detailed picture of this situation and in some cases makes possible a quantitative description of the bond.[27]

But apart from this effect of higher order, the extent of which amounts to a few percent, we may consider the law of the constancy of valence distances as applicable to the topics following and, in particular, to the discussion of highly polymerized substances.

A second general rule that can be deduced from the existing material is the constancy of the valence angle.

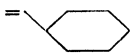
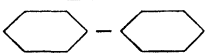
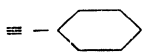
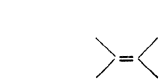
This, indeed, has been one of the main pillars of classical carbon stereo-

[27] Cf. the article of L. Pauling in H. Gilman, *Organic Chemistry*, N. Y. 1938, Vol. II, Chap. 22, page 1850.

chemistry and has proved sound when tested quantitatively with the aid of the newer methods. Table 5 summarizes a few important cases; Table 6 shows nuclear distances and valence angles obtained by H. A. Stuart[28] for molecules of the type AX_2, and Table 7 from another paper by H. A. Stuart gives corresponding data for pyramidal molecules of the type AX_3. As can be seen from the estimated experimental errors, the constancy of

TABLE 4

INFLUENCE OF SUBSTITUENTS ON VALENCE BOND DISTANCES

Bond	Substance	Structure	Distance in Å
C—C[1]	ethane		1.547
	propane		1.541
	isobutane		1.538
	cyclopropane		1.526
	cyclopentane		1.520
C—C[2]	butadiene		1.46
	cyclopentadiene		1.46
	styrene		1.44
	p-diphenylbenzene		1.46
	diphenyl		1.48
	tolane		1.40
	diacetylene		1.36
	cyanogen		1.37
	dimethylacetylene		1.38
C—Cl[3]	vinyl chloride		1.69
	1,1-dichloroethylene		1.69
	trichloroethylene		1.71
	tetrachloroethylene		1.73

[1] L. Pauling, *J. Am. Chem. Soc.*, **59**, 1223 (1937).

[2] L. Pauling, H. O. Springhall and K. J. Palmer, *J. Am. Chem. Soc.*, **61**, 927 (1939).

[3] L. O. Brockway, J. Y. Beach and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2693 (1935).

the valence angle holds only in rough approximation, and the effect of different substituents on it is quite appreciable. For example, wave-mechanical considerations of Hückel,[29] Pauling[30] and Slater[31] indicate a

[28] H. A. Stuart, *Z. physik. Chem.*, (B) **36**, 155 (1937). Compare also recent experimental work of A. Lüttringhaus and K. Buchholz, *Ber.*, **73**, 134, 145 (1940).

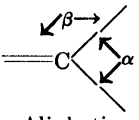
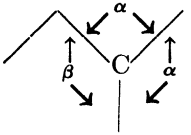
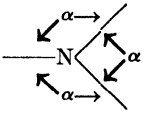
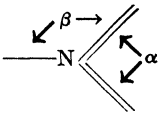
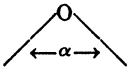
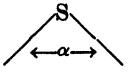
[29] E. Hückel, *Z. Physik*, **60**, 423 (1930); **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).

[30] L. Pauling, *Phys. Rev.*, **36**, 430 (1930); **40**, 891 (1932).

[31] J. C. Slater, *Phys. Rev.*, **37**, 682 (1931); **38**, 1109 (1931).

TABLE 5

A Few Important Valence Angles

Atom	Valence angle	Measured in	Methods
C aliphatic	Tetrahedron angle 110°	Many organic aliphatic compounds	X-ray and electron interference Dipole moment
 Aliphatic double bond	$\beta \sim 130°$ $\alpha \sim 110°$ } plane	Thiourea	X-ray interference
	$\beta \sim 120°$ $\alpha \sim 120°$ } plane	Formaldehyde	Band spectra
	$\beta \sim 125°$ $\alpha \sim 110°$ } plane	$COCl_2$, $COBr_2$, CH_3COCl	Band spectra
≡C— Triple bond	180°	Acetylene Hydrocyanic acid	Band spectra
 Aromatic-aliphatic linkage	$\alpha \sim 120°$ $\beta \sim 120°$	Benzene derivatives	Dipole moment
	α = 112°—116° spatial α = 120° plane	NH_3 $B_3N_3H_6$	Band spectra Electron interference
—N=	180°	Isonitriles	Dipole moment
	α = 130° β = 115° } plane	$NaNO_2$	X-ray interferences
	α = 120° β = 110° } spatial	Nitrobenzene	X-ray interferences
	$\alpha \sim 104°$—106° $\alpha \sim 122°$ $\alpha \sim 128°$ $\alpha \sim 105°$ $\alpha \sim 111°$	Water Ozone Diphenyloxide OF_2 Dimethylether	Band spectra Band spectra Dipole moment Electron interferences Electron interferences
	$\alpha \sim 113°$ $\alpha \sim 108°$	Diphenylsulphide S_8	Dipole moment X-ray interferences

value of 90° for the valence angle in oxygen, sulphur and nitrogen atoms, because precisely at this angle between the directions of maximum bond strength the total bond energy is a minimum. Quantum-mechanically this configuration shows a certain stability, so that we must conclude from the presence of greater angles the existence of repulsive forces between the two substituent atoms. Table 6 shows that these repellent forces are already acting in the water molecule and increase the normal valence

TABLE 6

NUCLEAR DISTANCES AND VALENCE ANGLES OF PLANE MOLECULES OF TYPE AX_2

Substance	Distance between substituents		Valence angle observed	Deformation	$2r_{min}$ Å
	Observed Å	Calculated for 90° Å			
H_2O	1.57	1.35	104° 40′	14° 40′	2.2
F_2O	2.22	1.98	105°	15°	3.1
Cl_2O	2.8	2.4	111°	21°	3.7
$(CH_3)_2O$	2.38	2.04	111°	21°	3.4–3.9
H_2S	1.95	1.91	92° 20′	2° 20′	2.2
S_8	3.37	3.0	105°	15°	3.6

TABLE 7

NUCLEAR DISTANCES AND VALENCE ANGLES OF A FEW PYRAMIDAL MOLECULES OF THE TYPE AX_3

Substance	Distance X—X		Valence angle observed	Deformation	$2r_{min}$ Å
	Observed Å	Calculated for 90° Å			
NH_3	1.61	1.43	106°	16°	2.2
PCl_3	3.13–3.18	2.83–2.9	100°–104°	10°–14°	3.7
$AsCl_3$	3.4	3.12	102°	12°	3.7

angle of 90° to a value of 104° 40′. Actually, the two hydrogen atoms would be distant only 1.35 Å from one another at a normal valence angle of 90°; the normal distance between two combined hydrogen atoms exerting no forces upon each other amounts however to about 2.2 Å. The oxygen atom must, therefore, bring the two hydrogen atoms nearer by 0.85 Å, if the normal valence angle is to be restored. This compression of the charge clouds of the hydrogen atoms represents, however, such a considerable performance of work that the valence bond O—H does not

suffice. An intermediate state is reached which strikes a balance between the quantum-mechanical stability of the spatial valence field of the oxygen atom on the one hand and the repulsion of the two combined hydrogen atoms on the other; the valence angle is deformed. The distance H... H is diminished from 2.2 to 1.57 and the angle of 90° increased to 104° 40′.

The accuracy of this interpretation is confirmed by a glance at conditions in the hydrogen sulfide molecule. By reason of the greater diameter of the sulfur atom, the distance between the substituent H atoms is already 1.91 Å at normal valence angle, so that only a very small deformation of 2° 20′ is necessary for a state of equilibrium to be established in the molecule with a distance of 1.95 Å between the two hydrogen atoms. The other data in Table 6 are to be interpreted in the same way and together they afford a very clear and instructive picture of the interaction between primary valence attraction and secondary valence repulsion within the molecule.

Table 7 shows similar relations for pyramidal molecules, where the normal valence angle can be deformed by repulsive forces between the substituent atoms up to values of 16°.

It appears to be of interest concerning the energy required for the *deformation of the valence angle* to arrive at an expression for a given spreading or deformation angle in calories per mol. Table 10 gives a few relevant data, taken again from H. A. Stuart, which indicate that in deformations of the order of 10°, energy values of the order of 1000–2000 cal. per mol are involved. On the other hand, the work required to extend a primary valence bond in the direction of its greatest strength is estimated at 10^4–10^5 cal. per mol, for an extension of 0.1–0.3 Å. It is evident that appreciable changes in valence distance seldom have to be considered in organic molecules. Should they occur, they will be only of the order of hundredth Å. In contrast, variations in valence angle of the order of 10–15° are to be expected and are frequently observed. The primary valences are thus much less variable in respect to distance than in respect to angle. The first indication of the existence of such a relationship is afforded by the *Bayer tension theory*; today by the aid of available experimental data we can extend our view to some considerable extent to the quantitative side.

Tables 8 and 9 contain further relevant data; in Table 8 the distances between the Cl atoms of CCl_4, $CHCl_3$ and CH_2Cl_2 are recorded. It is evident that here also a valence angle deformation has taken place with decreasing number of substituent halogen atoms. It is very instructive that this effect can be observed just as well by x-rays as by electrons.

Table 9 shows the relation between valence angle deformation and *heat of combustion.* It points to the existence of relationships between the geometrical structure of the molecule and its energy capacity.

Table 11 records a few data on the effective radii of combined atoms in contact with identical atoms. The term $2r_{min}$ denotes the closest distance of approach for two identical atoms within a molecule capable of internal motion. For example, although the two atoms in a hydrogen molecule are separated by a distance of 0.75 Å, the hydrogen atoms which are combined with carbon, oxygen or nitrogen in an organic molecule cannot come closer to each other than about 2 Å, as the table shows.

TABLE 8

DEFORMATION OF THE TETRAHEDRON ANGLE BY SUBSTITUENTS

Molecule	Distance Cl—Cl in Å	
	X-ray interferences	Electron interferences
CCl_4	2.99 ± 0.03	2.98 ± 0.03
$CHCl_3$	3.11 ± 0.05	3.04 ± 0.06
CH_2Cl_2	3.21 ± 0.11	3.16 ± 0.08

TABLE 9

VALENCE ANGLE DEFORMATION AND HEAT OF COMBUSTION IN CYCLIC COMPOUNDS

Number of C-atoms in the ring	3	4	5	6	7
Molar heat of combustion for $(CH_2)_x$ gaseous in Cal.	505.5	662.5	797	950	1103
Heat of combustion per CH_2-group in Cal.	168.5	165.5	159	158	158
Deviation from normal value in Cal. .	10.5	7.5	1	0	0
Deformation of the valence angle	49° 28′	19° 28′	1° 28′	0°	0°

Closer approach is prevented by the repulsive forces then arising out of quantum-mechanical resonance effects. The column headed r_T in the table contains those minimum distances which prevail at room temperature in consequence of thermal agitation. They are somewhat smaller than those considered heretofore because the repulsive forces are overcome to a slight extent by the inherent kinetic energy of the separate parts of the molecule.

We can summarize as follows: the parts of a large molecule attract one another just as do complete molecules in a real gas, a liquid or a crystal. Among organic substances the distances at which such forces (corresponding to van der Waals forces) act is between 3.5 and 4.5 Å. Regarding

their origin, their magnitudes and their importance in highly polymerized substances more will be said in the section on the structure of solid and liquid phases. When an attempt is made, however, to force the parts of a large molecule, or even whole molecules, very close together, steadily

TABLE 10

VALENCE DEFORMATION IN ENERGY UNITS

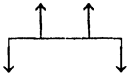
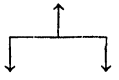
Compound	Energy for valence angle deformation in cal/Mol		Nuclear distance in 10^{-8} cm
	By 5°	By 10°	
HCN 	197	788	H—C = 1.08
C_2H_2 	193	772	H—C = 1.08
CO_2 	432	1730	C=O = 1.15
CS_2 	291	1160	C=S = 1.5

TABLE 11

EFFECTIVE RADII OF LINKED PAIRS OF IDENTICAL ATOMS

Nature of atom	Effective radii in Å	
	r_{min}	r_T
Hydrogen	1.1	0.9
Nitrogen	1.6	1.3_5
Oxygen	1.5	1.2_5
Sulfur	1.8	1.5_4
Fluorine	1.5_5	1.2_5
Chlorine	1.8_5	1.5_8
Bromine	2.0_5	1.7
Iodine	2.2	1.8_2

increasing forces of repulsion have to be overcome, their ultimate effect being to limit approach to those minimum distances set forth in Table 11. It is evident that accurate knowledge of this relation is of great importance in all considerations of large molecules with internal mobility, particularly in studies on the behavior of chain molecules.

These data on primary valence distances, valence angles and effective radii complete the evidence from which *general* assertions about molecular geometry can be deduced with the aid of interference measurements.

Before passing on to the next experimental methods, it will be shown by two special examples how far an investigation of structure, employing all the modern techniques, can give an insight into the minute structure of a molecule.

1. It has been possible to elucidate the structure of *p*-dinitrobenzene[32] to the minutest detail by accurate geometric measurement of the elementary cell and by an exact determination of numerous interference intensities. Fig. 2 shows plan and elevation views of the molecule with all numerical data inserted. The research showed that the atoms of dinitrobenzene are not found in one plane, but that two irregularities occur, small indeed, but demonstrable with certainty by the precise experimental technique employed. The distance between the para-carbon atoms of the benzene ring and the nitrogen atoms of the nitro group was 1.5 Å which is appreciably greater than the distance N—C found elsewhere. We have here an excellent example of the case mentioned before that special conditions in the molecule (in this case the nitrogen atom carries two oxygen atoms while the carbon atom belongs to a benzene ring) may influence the linkage distances. The two oxygen atoms of the nitro group are not equidistant from the nitrogen atom. The difference between 1.25 and 1.10 Å is greater than the limit of error of the method used, a fact which points to a difference in the way in which two oxygen atoms are linked to the nitrogen. Such a difference is also shown by quantum-mechanical analysis of the NO_2 group. Further, the benzene ring is itself deformed by the two nitro groups. It is no longer a regular hexagon; the shortest ring edge lies parallel to the bond N = O. Conceivably there is interaction between the aromatic C—C bond and the bond N = O. That forces exist between electron shells representing these linkages is suggested by the observation of H. O. Jenkins,[33] who deduced from an accurate measurement of the

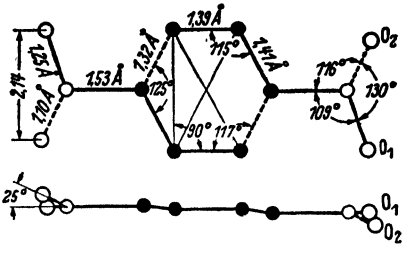


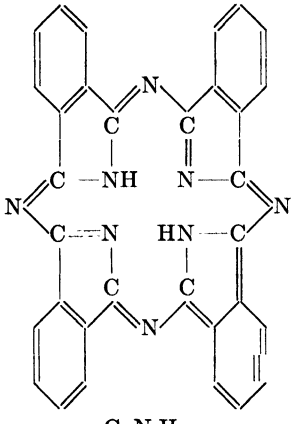
Fig. 2. Plan and elevation of the *p*-dinitrobenzene molecule, with atomic distances and valence angles.

[32] R. W. James, C. King and H. Harrocks, *Proc. Roy. Soc. London*, (A) **153**, 225 (1935).

[33] H. O. Jenkins, *Nature*, **134**, 217 (1934).

dipole moment that there is no freedom of rotation round the CN-bond. In the equilibrium position represented in Fig. 1 only vibrations are active. It is also well known that between nitro groups and aromatic rings there exist distinct attractive forces, which lead to molecular compounds of remarkable stability (cf. p. 106).

2. The structure of phthalocyanine may be cited as the second example, the elucidation of which is due to experiments by J. M. Robertson.[34] The molecule has a plane, square pattern; the usual organic structural formula, represented by Fig. 3 can be regarded as a very good approximation to the actual situation. Fig. 3a on page 23 shows a contour map of the electron density in nickel phthalocyanine as obtained by evaluating intensities by the Fourier method. The four benzene rings are clearly seen at the corners of the molecule and also the iso-indole ring and the central nickel atom. The distance of the iso-indole nitrogen from the nickel atom is 1.83 Å; one can imagine it as made up of the radius of the neutral nickel atom (1.24 Å) and the radius of a double-bonded nitrogen atom (0.61 Å). The other dimensions of the molecule agree very closely with the known normal distances of the main valence linkages. We have a striking example of how it is possible by the aid of x-ray analysis to elucidate quantitatively a complicated molecule down to the last detail. A necessary proviso is, of course, the presence of well defined, not too small individual crystals, a condition which can be satisfied only in exceptional cases for high polymers. Up to the present only a few proteins have been obtained in sufficiently large crystals to allow of the application of this method.



$C_{32}N_8H_{18}$

Fig. 3. Structural formula of the phthalocyanine residue.

2. The Behavior of Molecules in the Electric Field

If molecules are introduced into a uniform electric field, two effects are observable which yield important information on the internal structure of the particles.

a) When mobile charged constituents—negative charge clouds—are present in the molecules, they are displaced or deformed by the field.

[34] J. M. Robertson, *Proc. Roy. Soc. London*, (A) **146**, 473 (1934); *Rep. on Progress in Physics*, **4**, 332 (1938).

In the first place there are the electron shells of the atoms which undergo a deformation in the electric field. The result of this deformation is that under the influence of the field the centers of positive and negative charge no longer coincide in space, so that an otherwise neutral and isotropic particle exhibits in the electric field two distinct charges, which can exert

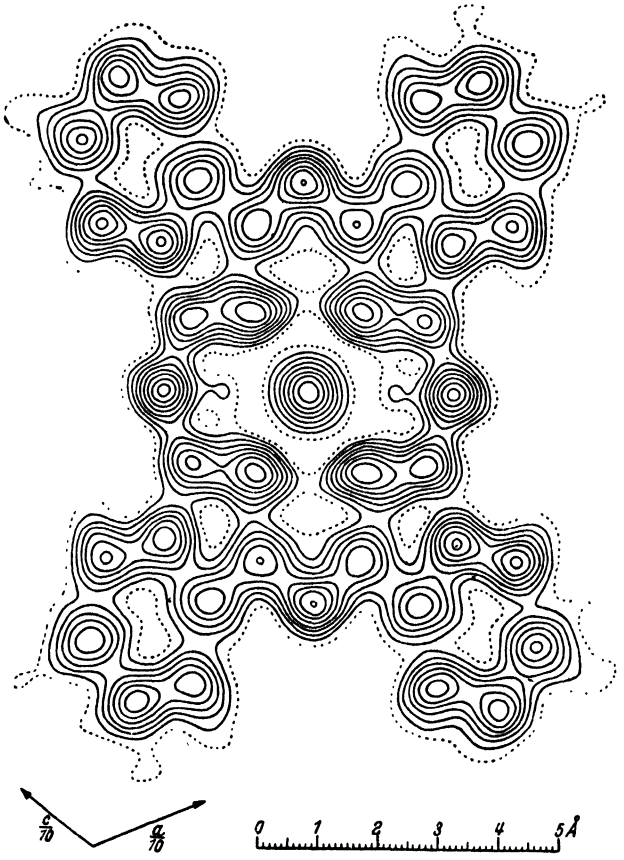


Fig. 3a. Distribution of electron density in nickel phthalocyanine parallel to the plane of the molecule; compare this diagram with Fig. 3.

external effects; the two charges are equal and opposite so that the molecule as a whole remains neutral. Since these two poles are produced only by the external field, the phenomenon is termed electrical *polarization* and the atoms are said to possess *induced* or *influenced* dipole moments. The stronger the field and the more mobile the charges, the greater is the polarization effect.

b) There are molecules in which the centers of mass of the positive and negative charge are not coincident by reason of internal structure, which themselves possess an electric moment independent of the existence of an electric field, i.e. they have an electric dipole. Such particles orient themselves in a uniform electric field, attempting, in fact, to align themselves with the dipole axis parallel to the direction of the field. The final result of this directional effect again depends upon the strength of the field, the magnitude of the permanent dipole moment and the temperature. The irregular thermal motion always disturbs the arrangement of the dipole axes caused by the field, so that macroscopically a stationary state is observed resulting from the action of the mutually opposing forces. Dipole moments are, of course, also polarized additionally by an electric field. However, the induced moments are generally much smaller than the permanent ones.

Since both phenomena afford important information on molecular structure we will consider them in greater detail later on.

a) Polarizability

If the charge shell is capable of deformation equally in all directions, the induced moment μ_i can be taken as approximately proportional to the field strength E producing it:

$$\mu_i = \alpha \cdot E. \tag{4}$$

If the charges are isotropically deformable the proportionality factor α is a characteristic material constant independent of direction; it is termed the polarizability of the substance and has volume dimensions. To determine polarizability experimentally, we start with the dielectric constant ϵ of the substance to be investigated; α is related under certain generally valid suppositions to ϵ by the Clausius-Mosotti equation

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} N\alpha \tag{5}$$

In this:

ρ = density of the substance.
M = molecular weight.
N = number of molecules per mol (Loschmidt number).
α = polarizability (for static fields).
ϵ = dielectric constant of the substance.

In deriving this equation it must be remembered in addition to (4) that the polarized molecules exert forces *on one another*; the whole polarization effect arises therefore from the *external* field acting and the *internal* field

resulting from its influence; (5) holds only for isotropic phases—gases, solutions, liquids, regular crystals—but not for anisotropic liquids or for other types of crystal. $\frac{4\pi}{3} \cdot N \cdot \alpha$ is termed the molecular polarization P.

In particles possessing no permanent dipole moment, equation (5), by application of the Maxwell relation between refractive index and dielectric constant, becomes the Lorentz-Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} \cdot N \cdot \alpha = R, \tag{6}$$

which combines polarizability with refractive index; the right hand side of equation (6) is termed molar refraction and is denoted by R. For ideal gases under normal conditions M/ρ can be taken as 22.4×10^3 cm^3; since the refractive index is nearly unity, the term $(n^2 + 2)$ can be replaced by the value 3, whereupon the simplified equation valid for ideal gases is obtained

$$\alpha = 2.94 \times 10^{-21}(n^2 - 1). \tag{7}$$

It is known that the molar refraction R may be deduced additively from the atomic refractions by considering that double bonds, triple bonds, ring linkages etc. come into existence by increments. The additive condition is fulfilled even better if, following Fajans and Knorr,[35] characteristic linkage refractions are ascribed not to individual atoms but to individual linkages—e.g. the C—H or C = C linkage. The superiority of the Fajans-Knorr method of calculation is founded on the fact that the components of the electron shell in the molecule which are specially subject to deformation are no longer to be correlated with given atoms, but are dependent rather upon the nature of the bond between the atoms; actually according to the new concept, non-polar valence is produced by those electron shells which are common to several atoms of a molecule. The discussion of refractions showing exceptions to additivity has long been a valuable aid in elucidating the structure of organic substances; such exception invariably suggests the presence of special conditions. Apart from exceptions which must be dealt with by corrections, however, molecular refraction is independent of the state of combination and still more so of the degree of aggregation of the participating atoms.

We have hitherto denoted the polarizability of the molecule by a single term; actually, however, the polarizability in non-isotropic molecules differs in different directions. Molecules having axial symmetry possess

[35] K. Fajans and F. Knorr, *Ber.*, **59**, 256 (1926).

two polarizabilities, asymmetrical molecules three. Obviously, in measuring polarization by refractive index, this anisotropy is not perceptible because the molecules of the substance concerned are normally in random arrangement and there is no total effect. Anisotropy of polarizability is the first observed when individual particles are fixed in definite directions. This is true of the irregular crystals and of gases exposed to an electric field (Kerr-effect). Table 12 shows a series of atomic refractions (AR) taken from Landolt-Börnstein's Handbook which can be used in calculating molar refractions.

Molecular refractions deduced from the refractive index (optical method) are not always entirely consistent with molecular polarizations from dielectric constants (static method); the reason is that only the light electrons can follow the high frequency vibrations ($\nu \sim 10^{15}$ per sec.) of visible

TABLE 12

ATOMIC REFRACTIONS FOR λ = 6583 Å

Type of atom	AR in cm³/mol
C singly linked	2.413
H	1.092
O in the carbonyl group	2.189
O in ethers	1.639
O in the hydroxyl group	1.522
C doubly linked	4.099
C trebly linked	4.741
Cl	5.933
I	13.757

light and accordingly molecular refraction indicates only the (optical) electron polarization. The slower the vibrations become, however, the sooner can heavier particles, e.g. ions or charged groups of atoms, follow them and so contribute (in the limiting case electrostatically) to polarization—so-called atomic polarization. The frequency of the atomic vibrations ($\nu \sim 10^{12}$ per sec.) lies in the infra red. Since atomic polarization is obtained as a small difference between two large numbers—molecular polarization and refraction—its value is known only inexactly in most cases. For practical purposes, it is frequently merely estimated and has heretofore been little used on structure problems.

b) Applications and Results of Polarization Measurements

Molar refraction has long been an important aid for determining constitution in organic chemistry. Since there seems to be a growing

tendency towards its use in the sphere of high polymeric compounds, which may be developed in the near future to allow of safe conclusions when sufficient data are available, the most important relationship between molar refraction and constitution will next be briefly summarized.

In the optical sense, an increase in molar refraction always means a relaxation of the negative charge clouds of the atoms constituting the molecule. If, for example, it is proved that there is no change in molar refraction on ring closure of an open aliphatic chain, we may assume that there is also no relaxation of the charge clouds which represent the separate principal valence bonds in the chain and in the ring. On the other hand, where considerable ring tension is observed, increases in molar refraction are known to occur, as, for example, in tetramethylene and in trimethylene. This obviously implies that the forcibly compacted electron clouds of the homopolar valence bonds are mutually relaxed and perhaps this is likewise true for the neighboring nuclear charges. In the trimethylene ring this effect extends so far that its molar polarization approaches that of the aliphatic double bond.

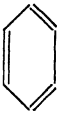
The aliphatic double bond, as well as the bonds C=O and N=O show considerable intensifications; this is easily understood inasmuch as the rather dispersed, four-electron charge cloud of a double linkage is naturally excited to vibration by an incident light wave more easily than the considerably more rigid single bond comprising only two electrons. Conjugated double bonds show an enhanced effect, which agrees very well with the result of experiments due mainly to R. Kuhn and his coworkers.[36] These experiments showed that with accumulation of conjugated double bonds, relaxation of the electron clouds finally proceeds so far that the compounds absorb light in the visible region and in consequence appear colored. Moreover, the quantum-mechanical discussion of conditions obtaining in the polyene compounds makes a mutual relaxing effect of double bonds intelligible.

On the other hand, in aromatic compounds, particularly in benzene, a decrease is apparent in the molar refraction. This depression is specific to the aromatic character and is consistent with the fact that, on account of the ring arrangement of the three double bonds within the nuclear framework, a definite distribution of negative charge density occurs. The same consequence was deduced from quantum-mechanical considerations by the far-reaching studies of Hückel, Pauling and Slater.[37] It

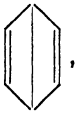
[36] For recent work see R. Kuhn, *Ber.*, **71**, 442, and 783 (1938) and especially R. Kuhn, *Angew. Chem.*, **50**, 703 (1937).

[37] See the two books of H. Hellmann, *Quantenchemie*, Vienna 1936, and L. Pauling

signifies a stability associated with the system of three normally conjugated double bonds. This accords with the view that the benzene ring, as regards its chemical behavior, should not be represented either by the simple Kekulé formula or by those proposed by Dewar, Claus or Ladenburg;[38] the truth is most nearly approached if the benzene molecule is conceived as essentially an assemblage of the two spatially possible Kekulé structures K_1 and K_2

$K_1 =$  , $K_2 =$ 

of equal energy value and the three possible Dewar structures (also of equal energy value).

$D_1 =$  , $D_2 =$  , $D_3 =$  ,

K_1 and K_2 are present in the same proportion, while D_1, D_2 and D_3 are likewise equal in amount. In this collection of the five forms the Kekulé properties emerge as unquestionably stronger than the Dewar. This conception is also supported by all other methods of attack—x-ray interference, electron interference and Raman effect. The further discovery that cumulative double bonds give smaller excentrics of refraction and dispersion accords with the quantum mechanical idea of the nature of the double bond.[39]

Finally, attention may be drawn to some interesting experiments on the variation in optical behavior of isomeric compounds. Generally it is found that highly branched aliphatic molecules, as well as molecules whose form permits dense packing, exhibit higher molecular refractions. As examples may be cited *trans*-α-β-dibromoethylene (MR_D = 26.16) and the *cis* isomer (MR_D = 25.64) as well as *p*-dibromobenzene (MR_D =

---

and E. B. Wilson, *Introduction to Quantum Mechanics*, New York 1935; compare also the article of L. Pauling in H. Gilman, *Organic Chemistry*, New York 1939, vol. II, p. 1850.

[38] See also the comprehensive treatise by E. Hückel, *Z. Elektrochem.*, **72**, 657 (1936) and a series of very interesting publications of R. S. Mulliken, *J. Chem. Phys.*, **7**, 339, 353, 356, 364 (1939).

[39] More details are given in the two mentioned books of Hellman and Pauling, in the comprehensive paper of E. Hückel and furthermore K. W. F. Kohlrausch, *Phys. Z.*, **37**, 58 (1936); J. H. Hibben, *Chem. Rev.*, **18**, 7 (1936); L. Simons, *J. Applied Phys.*, **9**, 781 (1938).

42.78) and *o*-dibromobenzene (MR_D = 41.81). The internal molecular interaction between the positive nuclear charges and the electron shells of the different atoms produces obviously similarly a fixation of the spatially dispersed negative electricity, as is now recognized in the theory of solutions of electrolytes.

The generally additive character of molar refraction and heat of combustion causes the quotient of the two magnitudes to be a constant under normal conditions, amounting in paraffins to 33.2 and in olefines to 32.3.

W. Herz[40] has established similar data for other substances and has deduced information regarding the density of packing in the most varied compounds.

In the domain of high polymeric substances refraction data are available principally for cellulose and its derivatives, but these have been determined almost entirely on solid or swollen fibres and will be referred to later in discussing the crystalline and liquid phases. In solutions of high polymeric substances the refractive index can be used to great advantage for following polymerization reactions; these will be discussed further in the chapter on the kinetics of these processes. Constitutional deductions regarding the structure of carbon chains—on length, end groups, branchings, ring closures, etc.—have hitherto not been drawn from optical experiments. The present state of knowledge seems inadequate for this, because all the equations available are empirical and permit definite assertions only for pure substances and small molecules and may therefore be applied to polymeric mixtures only with the greatest caution.

c) Dipole Moments

Molecules with permanent moments are termed polar molecules or dipole molecules. The permanent moments are usually considerably larger than the induced moments.

For dipole molecules the following expression holds

$$P = P_E + P_A + P_O = MR_\infty + P_O \tag{8}$$

P = total polarization
P_E = electron polarizability
P_A = atom polarizability
P_O = permanent moment
MR_∞ = molecular refraction extrapolated to long waves.

In a uniform electric field, dipole-free molecules orient themselves with the axis of greatest polarizability aligned with the field (induction effect);

[40] Cf. W. Hertz and E. Levy, *Z. Elektrochem.*, **39**, 26 (1933).

the dipole molecules orient themselves with the axis of moments in the direction of the field (direction effect). In order to separate the two effects in the same molecule, it is assumed, following Debye,[41] that the induction effect is independent of temperature, since electron displacement requires only the briefest period of time; the direction effect, however, depends on temperature because the oriented dipoles are always thrown into disorder again by thermal agitation.

According to Debye, the Clausius-Mosotti equation for dipole molecules can be expanded to

$$\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{\rho} = \frac{4\pi}{3} N \left(\alpha_\infty + \frac{\mu^2}{3kT} \right) \tag{9}$$

μ = permanent moment
k = Boltzmann constant
T = absolute temperature
ϵ = dielectric constant.

Since ϵ for dipole molecules is a linear function of the reciprocal (absolute) temperature of the form

$$f(\epsilon) = a + \frac{b}{T},$$

in which

$$a = \frac{4\pi}{3} N \alpha_\infty$$

and

$$b = \frac{4\pi}{3} N \frac{\mu^2}{3k}$$

the two magnitudes a and b can be separately determined by measurement at several temperatures. If we insert numerical values of π, N and k, we obtain

$$\mu = 0.0127 \cdot 10^{-18} \cdot \sqrt{b} \text{ electrostatic units} \tag{10}$$

The unit of 10^{-18} e.s.u. is termed one Debye.

The Debye theory holds strictly only for gases because they alone satisfy the condition of completely random distribution of molecules assumed by

[41] See for example P. Debye, *Polar Molecules*, New York 1929; also G. Briegleb, *Zwischenmolekulare Kräfte und Molekülstruktur*, Stuttgart 1937, p. 30; compare also, *A Symposium on the Dielectric Properties of Matter; Chem. Rev.*, **19**, 163–363 (1936); especially N. V. Sidgwick, *ibid.*, p. 183 and J. G. Kirkwood, *Chem. Rev.*, **24**, 233 (1939).

the theory on account of the large average distances between molecules. In the liquid phase—as recent experiments have confirmed—orientation effects are present even in the absence of an external field due to the reciprocal action of the molecular dipoles; viewed macroscopically, these compensate one another and cause no polarity of the system as a whole but from the point of view of the molecule they imply a significant deviation from the equal condition that all directions in space shall be represented at any instant. Restriction to gases is very troublesome in experimental practice because of the small effects obtainable; the measurements are difficult and actually only substances with high vapor pressure can be used. Consequently we often determine the moments of molecules in the dissolved state and choose dipole-free solvents of small polarizability and low concentrations of solutes, in order to reduce the reciprocal action of the dipoles on one another and on the solvent. It is best if the values of μ

TABLE 13

DIPOLE MOMENTS FOR A FEW IMPORTANT ATOM GROUPINGS

Bond	Moment $\mu \times 10^{18}$	Bond	Moment $\mu \times 10^{18}$
N—O	0.1	O—H (Phenol)	1.56
C—H	0.4	O—H (H_2O)	1.58
O—CH_3	1.23	N—H (NH_3)	1.66
C—I	1.35	C=O	2.8
C—Br	1.52	N=O	3.22
C—Cl	1.54	NO_2	3.9
NH_2	1.54	C≡N	3.94

obtained at different concentrations are extrapolated to infinite dilution. The moment obtained from the polarizability of the solvent is determined by control measurements and subtracted. Comparison of the moments obtained in different solvents is useful in this connection. By these means quite satisfactory agreement is obtained with values obtained for gases.

d) Application of Dipole Measurement in Determining Molecular Structure

In classifying the great bulk of experimental material, it is convenient, as a first approximation, to ascribe to individual linkages (groups of atoms) constant characteristic dipole moments—so-called group moments. Recent data reported by H. A. Stuart for a few important group moments are summarized in Table 13. Obviously their magnitude is not entirely independent of the atoms or radicals surrounding them, so that, as in primary valence distance, allowance must be made for the influence of surroundings on the group moments.

The moment of the whole molecule may be obtained by vectorial addition of the group moments, taking into account magnitude, direction and sign. The result is that molecules which contain several polar groups may be non-polar as a whole, if there is internal compensation between the various polar components. Thus, we know from experience that methane and carbon tetrachloride, for example, are actually non-polar, whereas Table 13 indicates that both the C—H bond and the C—Cl bond possess a moment.

Due to this circumstance, measurement of the total moment frequently affords a convenient way of deducing valence angles in a molecule. For instance, *p*-hydroquinone dimethyl ether has a measurable moment which, through valence inclination, occurs at both oxygen atoms (see Fig. 4). Table 14 shows by a few *p*-substituted benzene derivatives that in oxygen a valence angle of about 110° is indicated, a value which is in good agreement with that derived from x-ray data (Table 4) and from spectrographic data. The dipole method accordingly supplements and expands the evidence respecting nuclear lattices hitherto discussed, and it is clearly evident that comparatively complex molecules can be investigated fairly safely with its aid.

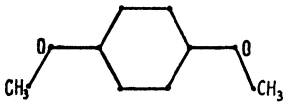


Fig. 4. Valence angle at the oxygen atom in hydroquinone dimethyl ether.

It should be strongly emphasized here that in working on a definite structural problem, even though it relates to small and simple molecules, success can be assured only if more than one of the methods available are employed. This is, naturally, even more necessary when investigating larger molecules, particularly in studying high polymeric substances, to employ concurrently every possible method in order to obtain a picture of the particular substance based as far as possible on experimental evidence. The different methods available will be reviewed later in respect to their individual suitability for elucidating given structural problems (see pp. 78 and 79).

The dipole method has proved particularly useful, apart from valence angle determination, in investigating *cis-trans*-isomerism, because it allows of a simple and satisfactory differentiation between the various modifications. As shown in Table 15, the moments of the *trans*-dihalogenated ethylenes are practically always nil, while the *cis*-compounds are definitely polar. Similar conditions hold for other isomerisms of analogous nature.

The dipole method has afforded valuable evidence also on the structure of simple aromatic parent substances. Benzene, diphenyl, naphthalene and higher condensed ring systems are recognized as plane structures.

Symmetrically substituted methane derivatives prove non-polar and therefore tetrahedral; compounds of quadrivalent tin and quadrivalent titanium exhibit the same symmetry.

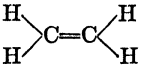
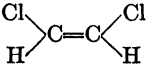
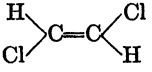
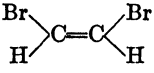
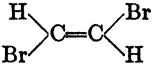
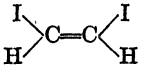
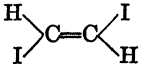
TABLE 14

A FEW DIPOLE MOMENTS OF p-SUBSTITUTED BENZENE DERIVATIVES ACCORDING TO H. A. STUART

Substance	$\mu \times 10^{18}$	$\mu \times 10^{18}$ calculated; angle at the O-atom = 110°	$\mu \times 10^{18}$ calculated without regard to angle
p-CH_3—C_6H_4—OH	1.50	1.60	2.10
p-CH_3—C_6H_4—OCH_3	1.10	1.13	1.60
p-NO_2—C_6H_4—OCH_3	4.80	4.35	2.60
p-Cl—C_6H_4—OH	2.65	2.47	0.15

TABLE 15

DIPOLE MOMENTS OF *cis*- AND *trans*-DIHALOGENATED ETHYLENES

Substance	Formula	$\mu \times 10^{18}$ observed	Boiling point in °C
Ethylene		0	—
cis-Dichloroethylene		1.8	59
trans-Dichloroethylene		0	48
cis-Dibromoethylene		1.35	112
trans-Dibromoethylene		0	108
cis-Diiodoethylene		0.75	188
trans-Diiodoethylene		0	190.5

Thus, the dipole method has a considerable share in the deduction of those principles which have to be employed today in designing structural models of high polymeric substances. Still more important, however, in

regard to large molecules with internal mobility, is the possibility of learning from dipole measurements something about the free rotatory power. This will be discussed, however—according to the arrangement of the present chapter—only in Section B on the vibrations and rotations in the interior of the molecules (see p. 64 et seq.).[42]

3. Optical Behavior of Molecules

Analysis of the light scattered by a free molecule has recently led to the development of a very effective means of drawing far-reaching conclusions regarding the symmetry and arrangement of the atoms in the molecule. Again, valence inclination is the main problem treated in this way but the free motion of parts of the molecule can also be so treated. Two effects are available for obtaining experimental evidence, the Kerr effect and the depolarization of the scattered beam.

a) The Kerr Effect

If a gas, a solution or a pure liquid is introduced between the plates of a charged condenser, the molecules strive, as already pointed out, to orientate themselves with the axis of their maximum polarizability or, if a permanent moment exists, with the axis of this moment, parallel to the direction of the field. Should the thermal agitation be such, however, that this orientation is effected only to a very small extent, the previously isotropic medium exhibits anisotropy which can be detected as double refraction on the passage of polarized light. This electric double refraction imposed by the presence of the external field is called the Kerr effect. The phenomenon is measured by the path difference $\Delta\lambda$, between the beam polarized in the direction of the field and that polarized perpendicular to the field. It is given by the equation

$$\Delta\lambda = K\frac{l \cdot E^2}{\lambda} \tag{11}$$

in which l is the extent of substance traversed in centimeters, E is the intensity of the field in volts per cm and λ is the wavelength also in centimeters. The constant K is characteristic for the substance investigated at given concentration (pressure) and temperature and is known as the Kerr constant. The physical theory of the Kerr effect we owe essentially to Lord Rayleigh, Born and Langevin. The principal experimental re-

[42] Recently W. T. Busse and R. M. Fuoss have contributed very important applications of the dipole method by the investigation of polyvinylchloride and similar substances at different temperatures, frequencies and with different amounts of plasticizers. Cincinnati meeting of the ACS, April 1940.

searches into its applicability to problems of molecular structure are due to H. A. Stuart,[43] K. L. Wolf and their collaborators.

The Kerr constant is evaluated theoretically by means of a formula derived by Born and Langevin, which relates primarily to systems with vanishing intermolecular reciprocal action—ideal gases or dilute solutions; the form is

$$K = 3\pi N(\Theta_1 + \Theta_2) = K_1 + K_2 \tag{12}$$

N is the Loschmidt number while Θ_1 and Θ_2 are complex functions of the dipole moments and polarizabilities belonging to the molecule. The Kerr constant itself can be split into two terms of which one (K_1) merely expresses the anisotropy of the optical and electrical polarizability and is named the anisotropy term K_1, while the other represents the effect of possibly existing electric moments. This is called the dipole term K_2. The two terms differ from each other in their dependence upon temperature; the Kerr effect of dipole-free molecules is proportional to $1/T$, that of dipole molecules is proportional to $1/T^2$.

It is mainly through this difference in temperature relationship that it is possible by sufficiently exact measurement to separate the two factors. Generally speaking, the dipole term is very much greater than the anisotropy term, so that it is convenient to determine the latter separately from measurements of the degree of depolarization of scattered radiation (see later). If we know both Kerr constants and are able to make plausible assumptions regarding the symmetry of the molecule, we can occasionally deduce from them quite extensive conclusions regarding the shape of the molecules investigated. Since this is usually possible only in conjunction with the degree of depolarization, the main points about this latter will be briefly stated before discussing the results.

b) The Degree of Depolarization

If light is scattered by isotropic molecules, it is to be expected from the transverse nature of the waves that the scattered light emitted normally to the primary beam will be linearly polarized. If, however, the experiment is carried out on gases, liquids or solutions, there is found in most cases a depolarization of the scattered radiation. This is due to the fact that the molecules causing scattering are not isotropic with respect to their polarizability. The classical theory of light scattering as developed by Lord Rayleigh,[44] Gans[45] and Born[46] allows a relationship to be established

[43] H. A. Stuart, *Ergeb. exakt. Naturw.*, **10**, 159 (1931).
[44] Lord Rayleigh, *Sci. Pap.*, Vol. VI, p. 540.
[45] R. Gans, *Ann. Physik*, **37**, 881 (1912); **62**, 331 (1920); **65**, 97 (1921).
[46] M. Born, *Ann. Physik*, **55**, 177 (1918).

between the extent of depolarization of the scattered light—the so-called degree of depolarization—and the anisotropy of the polarizability. Through this relation, the degree of depolarization is connected with the polarizability of the molecule in three directions perpendicular to one another (main polarizabilities).

For definite results it is useful to work with molecules having axial symmetry because they have only two main polarization directions—parallel and vertical to the axis. These two may, however, be calculated satisfactorily on the one hand from the average polarizability α determined from the refractive index (see p. 25) and from the degree of depolarization Δ so that two equations are available for the two unknowns.

TABLE 16

DEGREE OF DEPOLARIZATION OF ISOMERIC ALCOHOLS (H. A. Stuart)

Substance	Formula	$100 \times \Delta$
Butyl alcohol	$H_3C \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	1.7
Isobutyl alcohol	$(H_3C)_2CH \cdot CH_2OH$	0.8
Tertiary butyl alcohol	$(H_3C)_3C \cdot OH$	0.7
Amyl alcohol	$H_3C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2OH$	1.3
Isoamyl alcohol	$(H_3C)_2CH \cdot CH_2 \cdot CH_2OH$	1.1

c) *Results of Optical Molecule Measurement*

The two methods briefly outlined above furnish direct evidence regarding the symmetry of molecules from which we can arrive at conceptions of the nuclear framework and its internal mobility. Results concerning nuclear framework only will be reported here, while molecular oscillations and rotations will be discussed in the next chapter.

According to the laws of classical optics, depolarization of scattered radiation should disappear if the molecules are completely independent of one another and are themselves spherically symmetrical. Experimentally this is not strictly true, yet it holds with a fair degree of approximation. The inert gases and highly symmetrical compounds exhibit extraordinarily small Δ values, which to some extent fall within the limit of experimental

error. In part, however, they are attributable to reciprocal action between the molecules and in part to causes not yet clearly understood, as in the case of the fluorides and chlorides of carbon and silicon. The farther the particular molecule departs from the spherical shape, the greater is its degree of depolarization, an experimental fact borne out by the data in Table 16. Multiple linkages too show increased Δ values, a circumstance possibly connected with their greater polarizability.

Much greater insight into nuclear framework may be gained by making use of the Kerr effect. It is often possible to tell the polarization ellipsoid of the molecule by axis ratios and position relative to the nuclear frame-

TABLE 17

POLARIZATION ELLIPSOIDS OF MOLECULES

(H. A. Stuart)

Substance	Formula	$3a \times 10^{25} = (b_1 + b_2 + b_3) \times 10^{25}$	$b_1 \times 10^{25}$	$b_2 \times 10^{25}$	$b_3 \times 10^{25}$	Position of the optical axes and of the electric moments, structure of the molecule
Acetylene . .	C_2H_2	99.9	51.2	24.3	24.3	b_1 axis of symmetry straight molecule
Methane*	CH_4	78.3	26.1	26.1	26.1	regular tetrahedron
Carbon-tetrachloride. . .	CCl_4	315	105	105	105	regular tetrahedron
Methyl chloride.	CH_3Cl	137	54.2	41.4	41.4	b_1 axis of symmetry
Ethyl chloride . .	C_2H_5Cl	192	66.0	50.1	75.9	angular molecule according to position of axes
Propyl chloride	C_3H_7Cl	246	—	—	—	
Benzene . .	C_6H_6	309.6	123.1	63.5	123.1	b_2 axis of symmetry
Toluene . .	$C_6H_5CH_3$	367.8	136.6	78.4	156.4	plane molecule; $b_2 \perp$ to plane of molecule
Pyridine. .	C_5H_5N	285	118.8	57.8	108.4	

* Calculated for complete spherical symmetry, the Kerr constant has not yet been measured.

work and to calculate the polarizabilities b_1, b_2 and b_3 in three mutually perpendicular directions. As a result, interesting and far-reaching evidence on the structure of molecules may often be adduced, again in conjunction with other methods.

Table 17 gives, by way of example, polarizabilities for different molecules in different directions. It is evident that acetylene is particularly easily polarizable parallel to the triple bond, that methane and CCl_4 appear entirely symmetrical in excellent agreement with their actual behavior, that CH_3Cl possess an axis of symmetry, but that higher aliphatic chlorides are asymmetrical and so on. There is very clear evidence concerning

valence angularity, that straight molecules are uniaxial while angular molecules behave as bi-axial.

An investigation of the simplest ether demonstrated very clearly the valence angle of oxygen and indicated a value of 110°, which is in complete agreement with the value obtained by previously mentioned methods. For ethyl ether, criteria could even be derived regarding the free rotatory power which however will be discussed in detail in the next chapter. A systematic investigation of aliphatic ketones supplied similar evidence consistent with previous knowledge regarding the nuclear framework, and similarly with ethyl nitrite.

The methods of the Kerr effect and the depolarization of scattered light have not so far been applied to the realm of high polymers, but it is conceivable that by their aid it will be possible to obtain data for relatively complex molecules on the symmetry and form of the particles and on the position of substituents. It should, of course, be emphasized that both methods are particularly sensitive to molecular interaction and they should therefore be applied as far as possible to the gaseous state or to that of dilute solution.

B. THE INTERNAL MOTIONS OF MOLECULES

It has been emphasized in Section A that the nuclear framework of molecules must not be conceived as a rigid structure formed of fixed immobile particles. Rather, the individual atoms execute various motions under the influence of the forces holding the whole molecule together and under the influence of temperature; knowledge of these motions is just as important to an understanding of the molecular structure as is knowledge of the nuclear framework itself. For the study of these *internal motions* throws light on the field of force to which the molecule owes its existence and by which its physical and chemical properties are determined.

The internal motions of a molecule may be divided conveniently and easily into two distinct types: into oscillations and rotations.[1]

In precise investigation of atomic oscillations in the molecule, it appears that two different types are again distinguishable: valence oscillations and deformations or break oscillations. The former consist of the periodic motion of the atoms in the direction of the main valences linking them; the oscillation therefore causes an intermittent variable extension and contraction of any bond distance, a few data for which are shown in Table 2. In the break oscillations, however, the deformations of the atom are executed perpendicular to the bond direction and effect a periodic increase and diminution of the valence angle; numerical data are also given for these in Table 4.

Both oscillations suggest that the rigid nuclear framework of the molecule can actually be regarded only as a temporary mean position. At any particular instant it is distorted according to the magnitude and direction of the existing elongations of the atoms.

The rotation of individual parts of the molecule plays a role which is especially prominent in larger molecules. This is particularly true in organic molecules, where, in consequence of the possibility of free rotatory power around the simple primary valence bonds, the components of a molecule may be moved toward one another without causing appreciable

[1] However it must be pointed out, that in some cases oscillations go over into rotations and vice versa. Hence a sharp differentiation of these two types of movements is not possible.

change in the total energy of the molecule. These rotations or oscillations at constant or nearly constant total energy are the result of thermal collisions which the particles suffer from their environment and they will be more violent the higher the temperature. Owing to the reciprocal influence which exists between distant atoms in a molecule, the rotation is in most cases not entirely free but a certain energy pertains to any given configuration. If the energy differences between different spatial arrangements of atoms are large as compared with the average thermal kinetic energy, this will not be sufficient to induce rotations, but the mobile parts of the molecule will merely execute oscillations about the positions of minimum energy: rotation then degenerates into a complicated deformation oscillation. If, however, as frequently happens (see page 69), the various configurations, particularly in organic molecules, differ from one another only by amounts of the same order of magnitude as the mean thermal energy, then each arrangement is assumed equally often and the rotatory power about certain valence directions appears to be free.

In rotations, therefore, the internal molecular field of force determines the motions which occur, and its study occasionally leads to interesting glimpses into the dynamics of the molecule.

After these general remarks on the importance of oscillations and rotations, it is now time to describe briefly the experimental methods available for investigating the internal motions of a molecule. In this connection, the results will be discussed in detail in relation to our present knowledge of valence fields, and, in conclusion, particular attention will again be paid to long chain molecules and high polymeric substances.

1. Methods of Determining Internal Motions of Molecules

Following the interpretation of atomic spectra, one of the principal services of the quantum theory has been to give a complete explanation of the highly complex molecular spectra. While the relatively simple line spectra of the atoms have given impetus to the development of the quantum theory, molecular spectra have only lately been taken in hand and could only be satisfactorily employed in conjunction with wave mechanics for determining the internal structure and the force fields of the molecule.

The frequencies of an atomic spectrum may all be represented as differences in energy states of the atom, so that each of these states is characterized by a definite arrangement of the electrons in the atom, i.e. by a definite distribution of the negative charge density. A line is emitted if the atom passes from one state to another; its frequency is cal-

culated from the liberated energy difference ΔE by the aid of the fundamental equation

$$\nu = \frac{\Delta E}{h}.$$

In the molecule, the energy of a given state is determined not only by the distribution of the electrons but also by the particular state of the atomic nuclei building up the molecule. In addition to the energy of electron transition, there are energies involved in changing the states of oscillation and of rotation. This explains why the spectrum of a molecule consists of very many more lines than that of an atom. A mere glance shows that this is so, if one compares an atomic spectrum with a molecular spectrum; the former can properly be described as a line spectrum, the latter as a band spectrum.

Experimental examination of band spectra has made extraordinary strides in recent years and a mass of experimental material has accumulated, which can be utilized profitably in regard to molecular structure only by the enlightening ideas of quantum mechanics.

Generally, the frequency of any line of a molecular spectrum is due to the co-action of three energy contributions. First, in the emission of a line, the electron state of the whole molecule must be altered just as in the emission of a line of an atomic spectrum, liberating the energy ΔE_1. In addition, however, the state of oscillation of two atomic nuclei of the molecule can also change by one or more oscillation quanta, thus liberating additional energy ΔE_2; this must be added to that of the electron transition, with a positive or negative sign according to whether the molecule is passing from a higher state of oscillation to a lower, or *vice versa*. There is the final possibility of change in the state of rotation of the whole molecule or of one of its components, giving rise to a rotational energy ΔE_3, which must again be added with the appropriate sign to the two earlier values. Thus, we should expect that the frequency of any individual line of a band spectrum may be expressed by an equation of the form

$$\nu = \frac{1}{h}(\Delta E_1 + \Delta E_2 + \Delta E_3)$$

The energy changes in the electron transitions are of the order of magnitude of 10^{-11}–10^{-12} erg per atom, the corresponding frequencies ($\nu \approx 10^{15}$ sec^{-1}) i.e. in the ultraviolet or visible region; the energy differences for changes in oscillation state amount to 10^{-13}–10^{-14} erg per molecule, the frequencies

corresponding to them ($\nu \approx 10^{14}$ sec^{-1}) in the near infra-red. The change in energy of a molecule on assuming different states of rotation is, however, only of the order of 10^{-15}–10^{-16} erg per molecule; the pure rotation frequencies therefore occur in the wave length region of $\nu \approx 10^{12}$–10^{13} sec^{-1} (far infra-red).

If it is desired to observe molecules in the unexcited state, which is really assumed only on absorption, attention must be directed to oscillation and rotation frequencies and work must be done in the infra-red region. Actually, the accurate study of infra-red absorption spectra of simple molecules in the gaseous state has contributed information which has proved very informative and important in the interpretation of molecule spectra, and in the knowledge of molecular structure.

If electron transition occurs as well, it is possible to make observations also in the emission spectrum. Owing to the larger energy quota liberated, the spectra shift into the visible or the ultra-violet. The investigation is much simplified from the experimental point of view, because spectroscopically this region is much more easily accessible than the infra-red, but interpretation of the spectra is more involved and there is the added difficulty that the molecule is always in a state of excitation. The result is that in complicated molecules—particularly organic—emission spectra cannot be analyzed because the particles are usually destroyed at once by the inevitable high temperature.

The year 1926 brought the very important effect discovered by C. V. Raman[2] and predicted a few years earlier by A. Smekal[3] on the basis of the quantum theory. Raman found that the oscillation and rotation spectra of molecules reveal themselves by the light which they scatter laterally. Whereas classical optics requires that light scattered laterally by a molecule must have the same frequency as the primary radiation, the experiment shows that other frequencies—displaced lines or Raman lines—appear in addition to the initial frequency. The differences in frequency between normal and displaced lines correspond exactly to the oscillation and rotation frequencies of the molecule and afford a relatively convenient means of measuring these magnitudes in the visible or ultra-violet regions instead of the much more difficult task of observing in the near or far infra-red. Upon looking at a Raman-spectrum of phenol or other organic substances, one can realize the possibility of measuring the shifted lines with considerable sharpness and certainty.

Absorption spectra in the infra-red, emission spectra in the visible and ultra-violet and Raman-spectra together provide the most important

[2] C. V. Raman and K. S. Krishnan, *Nature*, **121**, 501 (1928).

[3] A. Smekal, *Naturwiss.*, **11**, 873 (1923).

experimental foundation for the analysis of the oscillation and rotation states of a molecule. In addition, specific heat and its dependence upon temperature also throw much light on oscillations and rotations of molecules. In recent years a very important development has taken place indicating the possibility of evaluating heat capacity measurements on organic molecules by introducing deuterium instead of hydrogen at certain positions in the molecules. This procedure has been applied particularly to elucidate the internal mobility of the ethylene and ethane molecules.[4] In conclusion, it has been mentioned previously that interferometric measurement of molecules in the gaseous state, investigation of the total moments of larger molecules and evaluation of the degree of depolarization can yield information on the internal mobility of a larger structure, particularly with regard to the more or less free rotatory power of molecular components about one another.

It has been shown in discussing nuclear framework, that several methods independent of one another and based on very different physical principles can give concordant results. It has thus been possible to approach one and the same problem from different angles and to secure good control of the individual results. This possibility is of the utmost value to the accuracy of the quantitative data.

It is the same with internal molecular movements. Again there are several experimental methods available based upon different physical principles and the greatest possible use should be made of them to secure accuracy of the results by independent proof.

2. Results

a) Moments of Inertia, Nuclear Distances and Dissociation Energies

Among the experimental results prominence may be given to the determination of moments of inertia and dissociation energies from the investigation of molecular spectra, since these afford yet another important contribution to the geometry and energetics of the nuclear framework. In discussing Table 2 it was suggested that atomic distances in simple

[4] E.g. J. R. Partington, *Proc. Roy. Soc.*, (A) **100**, 27 (1922); A. Eucken and F. Luede, *Z. physik. Chem.*, (B) **5**, 413 (1929); A. Eucken and A. Parts, *Z. physik. Chem.*, (B) **20**, 161 (1933); A. Eucken and K. Weigert, *Z. physik. Chem.*, (B) **23**, 265 (1933); A. Eucken and A. Bertram, *Z. physik. Chem.*, (B) **31**, 361 (1936); J. B. Howard, *J. Chem. Phys.*, **5**, 442 (1937); K. Schäfer, *Z. physik. Chem.*, (B) **40**, 357 (1938); G. B. Kistiakowsky and F. Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *J. Chem. Phys.*, **6**, 407 (1938); G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **7**, 281 (1939); G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *J. Chem. Phys.*, **7**, 289 (1939); F. Stitt, *J. Chem. Phys.*, **7**, 297 (1939).

molecules can be ascertained also from band spectra. The method proceeds from the discussion of the rotation lines and is useful for determining the moment of inertia I. For diatomic molecules this is connected with the masses m_1 and m_2 of the atoms and with their nuclear distance d by the equation

$$I = \frac{m_1 \cdot m_2}{m_1 + m_2} \cdot d^2 \tag{13}$$

If the masses are known, the nuclear distance can be calculated. A few nuclear distances ascertained in this way are tabulated in Table 18. Generally, complete evaluation of rotation fine structure of a molecular

TABLE 18

NUCLEAR DISTANCES AND DISSOCIATION ENERGIES

Molecule	Nuclear distance in Å	Dissociation energy		Molecule	Nuclear distance in Å	Dissociation energy	
		v	cal.			v	cal.
H_2^+ ...	1.070	2.62	60,260	CH...	1.12	3 5	80,500
H_2	0.749	4.454	102,442	NH	1.08	4.2	96,600
HD. .	0.748	—	—	OH ..	0.964	4.4	101,200
Li_2	2.670	1.14	26,220	HF	0.864	—	—
Na_2.....	3.07	0.76	17,480	HCl .	1.272	4.40	101,200
N_2	1.094	7.35	169,050	HBr	1.410	—	—
P_2	1.88	5.008	115,184	HI..... . . .	1.617	- -	—
O_2.....	1.204	5.09	117,070	CO .	1.13	9.6	220,800
S_2..... ..	1.603	4.45	102,350	NO ..	1.146	5 3	121,900
F_2.....	1.3	—	—	SO	1.489	5.053	116,219
Cl_2.....	1.983	2.468	56,764	CS. ..	1.532	<7.7	<177,100
Br_2.....	2.28	1.961	45,103	CN ..	1.169	6.7	154,100
I_2.....	2.660	1.535	35,305	LiH ..	1.6	2.47	56,810

spectrum is achieved only in di- and tri-atomic molecules. The agreement between band spectroscopic and interferometric atomic distances has already been emphasized.

It may be observed here that inferences may be drawn from the rotation fine structure of molecular spectra, using equation (13), regarding the presence and proportions of isotopes, a circumstance that led to the discovery of the isotopes of nitrogen and oxygen.[5]

In addition to this geometrical evidence, the band spectra allow further conclusions regarding the dissociation energy of di-atomic molecules. We proceed from the oscillation spectrum which, for large oscillation

[5] See W. F. Giauque and H. L. Johnston, *Nature*, **123**, 318, 831 (1929); also S. M. Naudé, *Phys. Rev.*, **34**, 1499 (1929); **36**, 333 (1930).

differences, is known to lose its intensity gradually and finally to disappear. At the point at which the oscillating spectrum vanishes, the molecule is obviously no longer capable of oscillation. If an amount of energy is added to it which corresponds to the distance of the vanishing point from the original position—the so-called convergence position—the molecule will be dissociated. Thus the dissociation energies of simple molecules can be deduced by ascertaining directly or by calculation the convergence position of band spectra.

Table 18 gives a few relevant data to which are added in Table 19 some data determined thermally for purposes of comparison. It is evident that the two entirely different methods gave concordant results. Attention may be called to the point that the nuclear distances and dissociation energies of structures such as H_2^+, HD, Li_2, CH, NH, OH, etc. can be investigated in this way; these cannot in the ordinary chemical sense be

TABLE 19

SOME THERMALLY MEASURED HEATS OF DISSOCIATION

Molecule	D in cal.	Molecule	D in cal.	Molecule	D in cal.
H_2	95,000	Na_2	16,800	Br_2	46,200
Li_2	23,400	Cl_2	57,000	I_2	35,670

claimed to be in any way stable molecules. The possibilities mentioned are less applicable to organic substances because they give satisfactory results only on very simple molecules.

b) Natural Vibrations and Group Frequencies

The aim of molecular spectrum analysis is to reduce the vibrations observed in the infra-red, visible and ultra-violet band spectrum as well as in the Raman spectrum to a definite model locating exactly the individual atomic centers of mass on the one hand, and specifying quantitatively the forces between the constituent atoms on the other. The former object is relatively easy to attain from data on inter-nuclear distances and valence angles, while the latter is a difficult problem as yet unsolved. In interpreting band spectra, we have assumed that, among all the atoms of a molecule, including even those not directly united, forces interact which depend only upon the distances separating the atoms.

This *central force system*, which has been used, for example, by D. M. Dennison[6] and in which the potential energy of the molecule retains a

[6] D. M. Dennison, *Phys. Rev.*, **41**, 304 (1932); *Proc. Roy. Soc. London*, **148**, 250 (1935).

relatively simple form, is not, however, in keeping with experimental results.

Accordingly, N. S. Bjerrum[7] has proposed an alternative theory. As a first approximation, in describing the internal molecular field of force, he assumes that forces dependent upon distance exist only between directly united atoms; in addition he introduces elastic forces which resist changes in the valence angle. The chemical forces are, therefore, defined by two elastic constants, in this concept of valence force. One of them corresponds to a tension in the main valence direction, the other to a deflection of the bond perpendicular thereto. It is clear that this theory is particularly well suited to the internal field of *organic* molecules; actually it has proved valid even for complex molecules, giving results which show reasonably good agreement with the experimental evidence.

Generally, greater forces are required to stretch a primary valence lengthwise than to deflect it from its normal direction. Preliminary information has already been reported in Table 10 and in the text on page 18 regarding the energy relationships; the natural vibrations allow the presentation of more definite evidence.

K. W. F. Kohlrausch[8] and R. Mecke,[9] who have sought to establish a clear relationship between the natural vibrations of a molecule and the valence forces, start out from the simplest case of a diatomic structure which undergoes harmonic oscillations of frequency ν. In this case the mean force f required to pull the molecules apart—termed by Kohlrausch the *spring force*—is connected[10] with the reduced mass μ and the frequency by the relation

$$f = 24.0 \times 10^{-8}\sqrt{\mu\nu^3}$$

Another measure for the elasticity of a linkage under tensile stress has been introduced by R. Mecke in the so-called *bond constant* k; this indicates the amount of work required to double the distance between the atomic nuclei in the molecule, assuming the validity of Hooke's law over the whole region. The bond constant is defined by the equation

$$k = 2\pi^2\mu\nu^2 r_0^2$$

r_0 = nuclear separation in the position of rest.

---

[7] N. Bjerrum, see especially in K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* Berlin 1938, p. 62 et seq.; J. H. Hibben, *Chem. Rev.*, **18**, 1–232 (1936); J. H. Hibben *The Raman Effect*, New York 1939.

[8] K. W. F. Kohlrausch, loc. cit. pp. 53 et seq.

[9] See e.g. R. Mecke, *Z. Physik*, **104**, 291 (1936).

[10] See e.g. K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt.* Berlin 1933; J. H Hibben, *Chem. Rev.*, **18**, 1 (1936).

The two terms f and k, serving as characteristic constants for the nuclear distance in the position of rest or for the dissociation energy of the molecule concerned, afford very considerable insight into the play of forces.

Table 20 shows, for example, that the single, double and triple linkage between C, N and O, the work of separation of which has already been given in Table 18, have f values which are almost exactly in the ratio 1:2:3; the same is true of their k values. Table 21 provides a very convincing example of the fact that the constants characteristic of different

TABLE 20

CHARACTERISTIC CONSTANTS OF THE DIFFERENT CARBON, NITROGEN AND OXYGEN LINKAGES (MEAN VALUES)

Type of linkage	Frequency ν in cm^{-1}	Distance r in Å	Bond constant k	Average force to pull apart $f \times 10^4$
X≡X	2200 ± 120	1.1 -1.1	79 ± 6	6.25
X=X	1650 ± 140	1.2 -1.35	54 ± 6	4.18
X—X	1025 ± 180	1.35-1.52	27 ± 7	2.17

TABLE 21

CONSTANTS OF THE X≡X-, X=X- AND X—X-LINKAGE

Linkage	Frequency ν in cm^{-1}	Nuclear distance in Å	Bond constant k	Average force to pull apart $f \times 10^4$
N≡N	2360	1.10	85	7.14
C≡O	2162	1.15	77	6.28
O=O	1577	1.20	53	4.14
$H_2C{=}CH_2$	1623	1.30	54	3.88
F—F	1140	1.27	37	—
Cl—Cl	560	1.98	40	1.32
Br—Br	327	2.28	40	—
I—I	214	2.66	38	—
I—Cl	383	2.31	39	—

types of linkage lie within very narrow limits, even though the vibrational frequencies are fairly far apart and the nuclear distances very different from one another. Obviously the fields of force, which, in different molecules, produce the double bond sometimes between C and C, at other times between C and O or C and N, are very nearly allied to one another and the potential curves which represent the energy as a function of distance are similar to each other.

Figure 5 shows the potential curve of the O = O linkage plotted from the vibration spectrum. The abscissa measures the distance between the

two atomic centers of gravity and the ordinate the (negative) energy of the molecule (in cm^{-1}); large forces of separation or high bond constants denote that the radius of curvature of the potential curve is small in the neighborhood of the equilibrium position, so that the potential trough has steep walls; this causes a high frequency vibration. Figure 6 gives in one diagram potential curves for the single, double and triple linkage; in this the various nuclear distances, work of separation and bond constants can be conveniently compared.

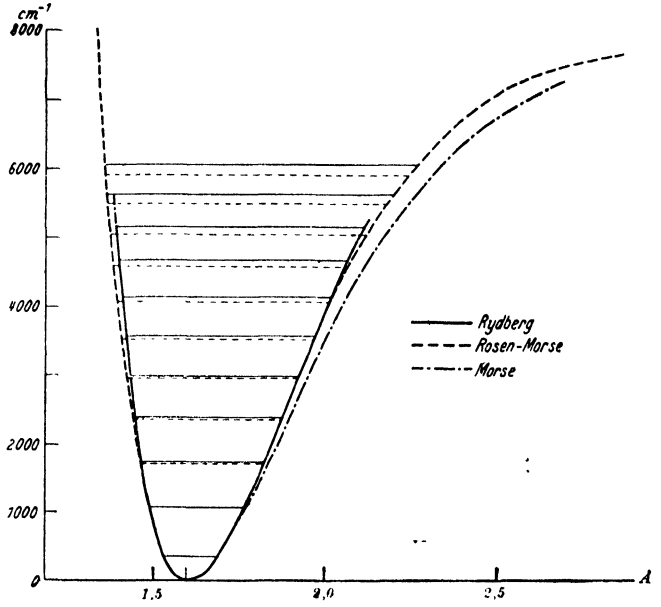


Fig. 5. Potential curve for the O_2, molecule. Energy in cm^{-1}.

If the di-atomic vibrational structure considered up to now is incorporated in a larger molecule, its vibrational frequencies and consequently its characteristic constants will be changed by the interactions newly brought into play. Initially, it is quite impossible to foretell the extent of the change and whether, within a large molecule, the physical identity of any individual linkage will be entirely lost. Experiment shows however that this is not the case. Although substituents attached to the mutually vibrating atoms exert a definite effect on frequency, this varies within moderate limits and is generally not very important even in a complex molecule, particularly in systematic investigation of homologous and analogous series. This fact, which is of special consequence in the applica-

tion of vibration analysis to organic chemistry is brought out by Table 22 which shows the influence of different substituents on the CH-frequency.

The same holds for other linkages so that it is legitimate to speak of group frequencies, whose appearance in the spectrum indicates the presence of a definite atomic group in the molecule. Table 23 gives a series of such group frequencies; the influence of the various substituents is again readily seen.

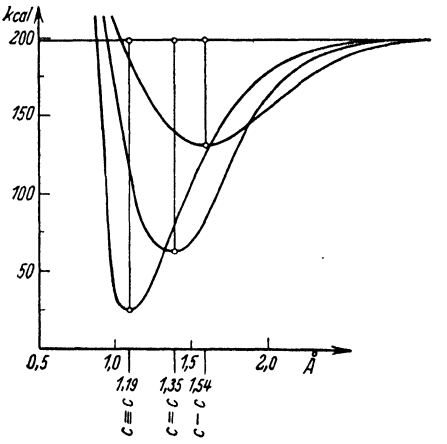


Fig. 6. Potential curve for the C—C / C=C / C≡C Bond Energy in Cal.

The possibility of applying this relationship to high polymeric substances is exemplified by recent work of Signer and Weiler[11] and of Mizushima, Morino and Inoue[12] who followed the polymerization of styrene with the aid of the Raman spectrum. Monostyrene has a very beautiful and easily measured Raman spectrum in which the frequency of about

TABLE 22

INFLUENCE OF CONSTITUTION ON THE C—H-FREQUENCY

Molecule	Frequency	Molecule	Frequency
$H\cdot CO\cdot CCl_3$	2867	$H\cdot CCl_3$	3018
$H\cdot CO\cdot NH_2$	2882	$H\cdot CBr_3$	3021
$H\cdot CO\cdot H$	2945	$H\cdot C_6H_5$	3050
$H\cdot CO\cdot OH$	2951	$ClHC{=}CHCl$	3078
$Cl_2HC\cdot CHCl_2$	2984	$Cl_2C{=}CHCl$	3082
$Cl_3C\cdot CHCl_2$	2985	$H\cdot C{\equiv}C\cdot N$	3213
$Br_2HC\cdot CHBr_2$	2986	$H\cdot C{\equiv}C\cdot H$	3320

1630 cm^{-1} due to the aliphatic double bond is very clearly observable beside that of the aromatic bond of about 1600 cm^{-1}. The ratio of the intensities is about 2:1. If now the substance is polymerized, this ratio is displaced gradually in favor of the aromatic frequency 1600 cm^{-1}, until

[11] R. Signer and H. Weiler, *Helv. chim. Acta*, **16**, 115 (1932).

[12] S. Mizushima, Y. Morino and R. Inoue, *Bull. Chem. Soc. Jap.*, **12**, 136 (1937).

ultimately in high polymers nothing further is to be seen of 1630 cm^{-1}. The Japanese authors named have found an intensity ratio 1:5 for a

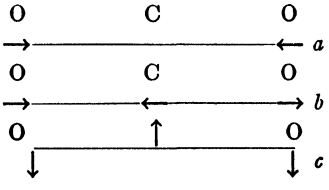
TABLE 23

GROUP FREQUENCIES. R = C_nH_{2n+1}; Ar = C_6H_5

Group	Frequency in cm^{-1}	Molecule	Group	Frequency in cm^{-1}	Molecule
C—I	~480	$R_3C \cdot I$	C=O	1650-1800	Various
C—I	~490	$R_2HC \cdot I$	N=O	~1640	$R \cdot O \cdot NO$
C—I	~500	$R \cdot H_2 \cdot C \cdot I$	C=C	1621	$H_2C=CH_2$
C—I	522	$H_3C \cdot I$	C=C	~1642	$R \cdot HC=CH_2$
C—Br	~510	$R_3C \cdot Br$	C=C	~1658	$R \cdot HC=CH \cdot R$ *cis*
C—Br	~530	$R_2HC \cdot Br$			
C—Br	~560	$RH_2C \cdot Br$	C=C	~1674	$R \cdot HC=CH \cdot R$ *trans*
C—Br	594	$H_3C \cdot Br$			
C—Cl	~570	$R_3C \cdot Cl$	C=C	1676	$R_2C=CR_2$
C—Cl	~610	$R_2HC \cdot Cl$	C≡C	1973	$HC \equiv CH$
C—Cl	~650	$RH_2C \cdot Cl$	C≡C	~2118	$RC \equiv CH$
C—Cl	710	$H_3C \cdot Cl$	C≡C	~2235	$R \cdot C \equiv CR$
C—C	750-1100	Open chains	C≡N	~2245	$R \cdot C \equiv N$
C—C	992	$H_3C \cdot CH_3$	C—H	2700-3000	$R \cdot CH_3$
C—C	802	Cyclohexane	C—H	3000-3100	$C=CH_2$
C—C	886	Cyclopentane	C—H	3113	$H \cdot CN$
C—C	~960	Cyclobutane	C—H	~3310	$R \cdot C \equiv CH$
C—C	1184	Cyclopropane	N—H	3310-3370	$R \cdot NH_2$
C—OH	1032	$H_3C \cdot OH$	N—H	~3330	R_2NH
C—NH_2	1037	$H_3C \cdot NH_2$	N—H	~3335	C=NH
C=N	1560-1660	Various	O—H	~3400	$R \cdot OH$

TABLE 24

FUNDAMENTAL VIBRATIONS OF THE CO_2 MOLECULE



Wave length in cm times 10^{-4}	Frequency in cm^{-1}	Character of the vibration
7.65	1322	*a*. Symmetrical
4.267	2363	*b*. Asymmetrical
14.78	667.9	*c*. Asymmetrical

product in a moderate state of polymerization and have calculated from it an average polymerization degree of 10 (Mol. wt. 1040). Cryoscopic

determination indicated 1150. They deduced from their experiments also the presence of molecular grouping in benzene-solution. Determination of the average degree of polymerization of very highly polymerized substances is, of course, not easy by this means, but it may be possible to measure very low intensities by a special experimental arrangement. Similar experiments have been carried out by Monnier, Susz and Briner[13] who followed the polymerization of acrylic ester with the aid of the Raman effect and by R. H. Kienle[14] and his coworkers, who applied the infra-red absorption spectrum and succeeded in getting a very good insight into the condensation of glycerol and dicarbonic acids.

We will now turn our attention to *break or kink vibrations* which are produced by a rapid succession of increases and decreases in the valence angle. It is to be expected from the evidence of Table 5 that much smaller

TABLE 25

FREQUENCIES, ELASTICITIES AND NUCLEAR DISTANCES OF DIATOMIC MOLECULES

Molecule	Frequency	$f \times 10^{-5}$	r in Å	Molecule	Frequency	$f \times 10^{-5}$	r in Å
H·H	4405	5.68	0.75	H·I	(2323)	3.14	1.62
H·D	3817	5.68	0.75	Cl·Cl	565	3.32	1.98
D·D	3117	5.68	0.75	O : O	1579	11.7	1.22
H·F	4141	9.55	0.92	N : O	1907	15.9	1.15
H·Cl	2989	5.06	1.27	C ⋮ O	2181	19.1	1.15
H·Br	2650	4.06	1.41	N ⋮ O	2359	22.8	1.09

forces are operating here and hence lower frequencies will be observed This is in fact the case.

Table 24 represents the vibration spectrum of CO_2; it consists of two valence vibrations and one break vibration; the frequency of the latter is considerably lower than that of the two former; the same holds for the deformation vibrations of water. The lower frequencies point to smaller values for the force of deformation compared with the force of separation. This is shown in Tables 25, 26 and 27, in which data for a series of diatomic, of branched triatomic or polyatomic molecules are tabulated; in every instance, the force of deformation d is considerably smaller than the valence force f. The nuclear distance and the valence angle in the rest position are also inserted. A few data for pyramidal molecules are given in Table 28, and for tetrahedral in Table 29.

[13] D. Monnier, P. A. Susz and E. Briner, *Helv. Chim. Acta*, **21**, 1349 (1938).

[14] R. H. Kienle, P. A. v. d. Meulen and F. E. Petke, in press.

The deformation constants are also influenced by substituents and in larger molecules they lose their simple and precise meaning. Passing

TABLE 26

VALENCE FORCES, f, DEFORMATION FORCES, d, VALENCE ANGLE α AND NUCLEAR DISTANCES r OF FORKED TRIATOMIC MOLECULES

Molecule	f	d	α	r in Å
O=S=O	9.56	1.60	~120°	1.46
H—O—H	7.55	1.37	105°	0.96
D—O—D	7.75	1.38	105°	—
H—S—H	3.91	0.90	92°	1.35

TABLE 27

VALENCE FORCES, DEFORMATION FORCES, VALENCE ANGLE AND NUCLEAR DISTANCES OF TRIATOMIC SYMMETRICAL CHAINS

Molecule 1 2 3	f	d	a	r_{12} in Å
$H_3C \cdot O \cdot CH_3$	4.53	0.68	116°	1.43
$H_3C \cdot NH \cdot CH_3$	4.24	0.64	114°	1.48
$Cl \cdot CH_2 \cdot Cl$	2.61	1.09	108°	1.8
$Br \cdot CH_2 \cdot Br$	2.13	0.82	113°	2.0
$I \cdot CH_2 \cdot I$	1.76	0.55	114°	2.2

TABLE 28

VALENCE FORCES, DEFORMATION FORCES, VALENCE ANGLE AND NUCLEAR DISTANCES FOR PYRAMIDAL MOLECULES XY_3

Molecule	f	d	a	r in Å
NH_3	7.09	1.36	108°	1.01
PH_3	3.36	0.75	100°	—
AsH_3	2.80	0.53	96°	—
PF_3	4.56	2.14	100°	1.64
AsF_3	3.90	0.80	97°	1.80
PCl_3	2.11	0.62	102°	2.14
$AsCl_3$	2.01	0.46	96°	2.24
$SbCl_3$	1.75	0.34	94°	2.30
$BiCl_3$	1.17	0.20	93°	2.46
PBr_3	1.62	0.54	104°	2.31

finally to longer, open, hydrocarbon chains—again important in respect to high polymers—the vibration spectrum changes very greatly at first but

later rather less. Fig. 7 illustrates this fact. The deformation frequencies of the C—C linkage lie in the region of 400 cm^{-1} for the lower members, the valence frequencies between 700 and 1100 cm^{-1}; between 1100 and 1500 cm^{-1} we find the break frequencies of the C—H bond and above this (due to the small mass of the H-atom) the valence vibrations of this bond. Enlargement of the molecule causes a significant lowering of the break frequency of the chain, so that the length of the chain may be estimated directly from its position. The number of the lines appearing is difficult to reconcile with the existence of a plane zig-zag chain and suggests that the molecule possesses partially free rotatory power which produces all kinds of configurations of the chain.

Thus we pass gradually from the sharp high frequency vibrations of the primary valence bonds by way of the break vibrations into the region

TABLE 29

VALENCE FORCES, DEFORMATION FORCES AND NUCLEAR DISTANCES FOR TETRAHEDRAL MOLECULES

	f	d	r in Å
CH_4 ...	4.75	0.814	1.1
CCl_4 .	1.89	0.348	1.76
$SiCl_4$.. ..	2.72	0.206	2.1
$TiCl_4$.....	2.48	0.110	2.3
$SnCl_4$	2.35	0.110	2.3

of internal molecular motions corresponding to the transition from slow vibrations to moderately hindered rotations. We will discuss this matter again later in the light of information derived from specific heats, electron diffraction and measurement of the electric moment.

c) *Internal Molecular Potential and Free Rotation*

Since the time of Van 't Hoff, the principle of free rotation around the single C–C bond has been a cornerstone of stereochemistry in organic molecules; it must be invoked to understand why it is impossible to prepare a large number of isomers which could exist were it not valid, and by its aid to harmonize theory with experience. It is very remarkable that, in this respect, as well as in those of constant valence distance and deformability of valence angle, organic chemistry has evolved the correct answers merely through intuitive grasp of general relationships. In consequence, its more modern development consists largely of adding quantitative data and putting finishing touches to the picture already drawn

in outline. The problem has been very thoroughly solved in recent years, as the following sections will show, so that today we have access to a

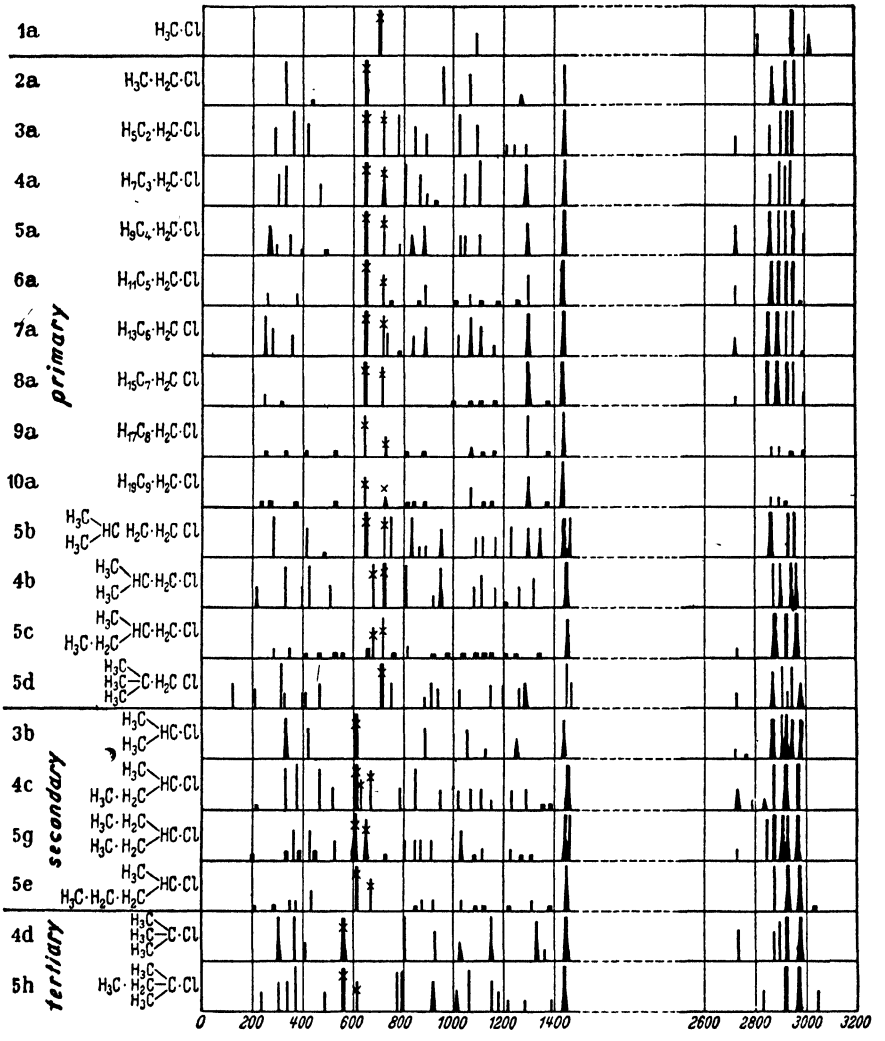


Fig. 7. Raman spectra of homologous compounds of the aliphatic chlorinated hydrocarbon series (frequencies in cm^{-1}). One observes that comparing spectra of 2a to 10a the lines belonging to the valence frequencies are fixed in the same place, while the break frequency lines (around 400) are shifted.

considerable quantity of data affording accurate ideas on the motions of

It will be convenient to discuss first the conditions obtaining in the simplest appropriate compound—ethane—passing on to more complex conditions and finally to the behavior of high polymeric substances in so far as this is possible.

The first purely empirical assumption of organic chemistry regarding free rotatory power around the simple C—C, C—O, or C—N bond has received full confirmation by the quantum mechanical theory of homopolar primary valence. Analyses of this bond carried out in conjunction with London and Heitler,[15] by Pauling,[16] Slater[17] and especially by E. Hückel[18] show that both the valence electrons causing cohesion of the atoms form a charge cloud, which exhibits rotational symmetry with reference to the line joining the atomic nuclei. Nothing prevents free rotation of the two atoms of the C—C linkage round this axis, any position

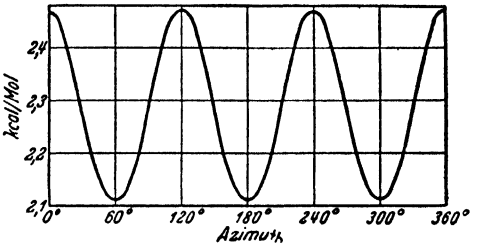


Fig. 8. Internal molecular potential of ethane; energy in Cal. per mol as function of the azimuth φ; calculated by H. Eyring

taken up by them in the course of rotation being equal in energy value to any other.

Conditions change if the three valences of the two atoms hitherto assumed free are saturated by substituents—perhaps by H atoms— because these can exert forces of attraction and repulsion on one another, whose potential depends upon the angle of inclination, φ, which the two methyl groups make with each other. Molecular mechanics does not allow of an exact calculation but only of a more or less rough estimate of this potential. Eyring[19] has summarized the results of his studies in a diagram reproduced in Fig. 8, in which the total internal potential of the ethane molecule is expressed as a function of the azimuth φ of the methyl groups capable

[15] F. London and W. Heitler, *Z. Physik*, **44**, 455 (1927).

[16] L. Pauling, *Phys. Rev.*, **40**, 891 (1932).

[17] J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

[18] E. Hückel, *Z. Physik*, **60**, 423 (1930); **70**, 204 (1931); **75**, 628 (1932). See also particularly R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932) and furthermore R. S. Mulliken, *J. Chem. Phys.*, **7**, 14, 20, 121, 339, 353, 356, 364 (1939).

[19] H. Eyring, *J. Am. Chem. Soc.*, **54**, 3191 (1932).

of rotation about one another. In the zero position represented diagrammatically in Fig. 9a, the two H atoms of each of the methyl groups lie directly over each other and induce a potential maximum. If φ is now increased, i.e. the two groups are rotated about each other, the potential falls and a minimum is reached at $\varphi = 60°$, corresponding to a state of stable equilibrium. The H atoms of the two methyl groups are now staggered with reference to each other and the molecule seen in the direction of the axis exhibits the form of Fig. 9b. On further rotation a peak of potential recurs, then a trough and so on. Thus there are three stable positions at which, due to molecular symmetry, the minima are equal in value and have the same form.

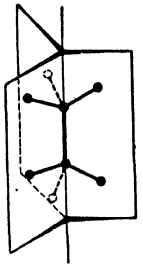


Fig. 9a



Fig. 9b

Fig. 9a. For $\varphi = 0$ the H atoms of both methyl groups lie directly over one another in the three planes drawn.

Fig. 9b. Ethane molecule for $\varphi = 60°$ seen parallel to the C—C bond; the methyl groups are rotated about one another and the H atoms are no longer directly above one another, but staggered.

If the energy difference between the maxima and minima of the potential curve is large compared with the energy of thermal motion, three stable isomers exist which can be transformed only very slowly into one another, if at all, and which in the present case would naturally be indistinguishable because of the identity of the H atoms in the methyl groups. We cannot, therefore, speak of free rotatory power in this instance, although the actual structure of the C—C bond allows of it; there are the van der Waals forces between the substituents which would not permit this natural movement. A glance at the figure shows, however, that the troughs are only about 300 cal. per mol deep. The average kinetic energy of one degree of freedom, $\frac{1}{2}$ RT, per mol, amounts to just the same at room temperature, so that it is quite sufficient to overcome the small energy thresholds opposed to the free rotary power by the internal molecular potential and to enforce the rotary power. The main effect will be that the velocity of rotation is not uniform but that the methyl groups will rotate around each other with periodically variable velocity. No kind of isomerism phenomenon can occur.

It seemed, at first, as if these purely theoretical findings would be confirmed experimentally by some researches of Eucken and his collaborators[20]

[20] A. Eucken and A. Parts, *Z. physik. Chem.*, (B) **20**, 184 (1933); A. Eucken and K. Weigert, *Z. physik. Chem.*, (B) **23**, 276 (1933); E. Bartholomé and J. Karweit, *Z. physik. Chem.*, (B) **39**, 1 (1938); J. Karweit and K. Schäfer, *Z. physik. Chem.*, (B) **40**, 357, 382 (1938).

in which a potential difference of 315 cal/mol between energy peak and energy trough has been deduced from the curve of specific heats at very low temperatures. Even the lowest vibrational state of the ethane molecule required by the zero point energy fills up the trough half way at $\varphi = 60°$, 120° and 240°; the next state lies high above the apices of the separating energy thresholds. Since, at room temperature, about 50% of all molecules assume the lowest state, while the other 50% are in higher states, it is evident that half the molecules can always rotate freely; consequently, by reason of the rapid energy interchange between the individual particles, a vibration about one of the equilibrium positions postulated in Fig. 9a can be only of extremely short duration (ca 10^{-10} sec.) and is immediately dissipated by rotation.

In recent years, however, a new experimental attack has been introduced into the study of the ethane molecule by G. B. Kistiakowsky and his coworkers.[21] This is the use of deuterium instead of hydrogen. If one investigates the spectra and the heat capacities of C_2H_6 and C_2D_6 and compares the results, a much better insight into the conditions can be reached. In a series of very careful experiments it could be shown that the general features of the potential curve given in figure 8 are correct, but that the energy difference between the maximum and minimum value amounts to about 2750 cal. per mol instead of 300.

The shape of the potential curve can be represented by

$$E = \tfrac{1}{2} E_0 (1 - \cos 3\varphi)$$

E_0 being of the order of magnitude of 3×10^3 cal. per mol.

As far as can be concluded up to date from the vibrational spectrum of C_2H_6 and C_2D_6 the most probable configuration is that of a staggered molecule as shown in Fig. 9b. The energy barrier, which hinders the free rotation, is about 3000 cal high.

This indicates that under normal conditions torsional vibrations around the molecule axis are carried out, with occasional jumps over the potential barrier.

We will now assume that one hydrogen atom in each methyl group is replaced by Cl and consider the conditions in *s*-dichloroethane. In the presence of polar Cl atoms, the dipole method may be used successfully.

[21] J. B. Howard, *J. Chem. Phys.*, **5**, 442 (1937); B. L. Crawford, W. H. Avery and J. W. Linnett, *J. Chem. Phys.*, **6**, 682 (1938); G. B. Kistiakowsky and F. Nazmi, *J. Chem. Phys.*, **6**, 18 (1938); G. B. Kistiakowsky and W. W. Rice, *J. Chem. Phys.*, **7**, 281 (1939); G. B. Kistiakowsky, J. R. Lacher and F. Stitt, *J. Chem. Phys.*, **6**, 407 (1938); *J. Chem. Phys.*, **7**, 289 (1939); F. Stitt, *J. Chem. Phys.*, **7**, 297 (1939).

On purely geometrical grounds the idea is as follows: There exist two preferred positions; the cis-position in which both Cl atoms lie in one plane with the nuclear linkage and on the same side of it, and the trans-position in which they are opposite to one another; on rotation around the single C—C bond, the two states become identical; such isomers have been termed *rotation isomers* by K. L. Wolf.[22] Smyth has calculated the variation of internal molecular potential for this case (see Fig. 10); $\varphi = 0°$ is the cis-, $\varphi = 180°$, the trans-position. The curve shown has been obtained by making definite assumptions regarding the position of the dipole

TABLE 30

DISTRIBUTION OF MOLECULES TO THE VARIOUS ENERGY STATES IN DICHLOROETHANE

Energy state	Energy × 10^{-14} erg	Number of Molecules	
		for 223° abs.	for 323° abs.
0	0.09	100	100
1	0.28	94	96
2	0.47	89	92
3	0.66	83	88
4	0.84	78	85
5	1.03	74	81
6	1.22	69	78
7	1.41	65	75
8	1.59	61	71
9	1.78	58	68
10	1.96	54	66
20	3.76	30	44
30	5.47	17	30
40	7.12	10	20
75	12.18	2	6

moments in the molecule, and this is open to certain objections. However, we shall not go further into this now, because, by and large, the relationships are probably valid.[23] We see that the cis-position is unstable (due to the repulsion of the Cl atoms), but the trans-position is stable; the energy difference is about 2000 cal. per mol, which is considerably greater than the mean kinetic energy available, on the average, to one degree of freedom. We must therefore expect slow torsional vibrations of greater amplitude about the trans-position; their frequency is estimated according to H. A. Stuart at about 10^9–10^{10} per sec.

[22] K. L. Wolf, *Leipziger Vorträege*, Leipzig 1931, p. 1.

[23] See H. A. Stuart, *Molekülstruktur*. Berlin 1934, pp. 92 et seq.

By applying the potential curve of Fig. 10, Smyth and his co-workers[24] have calculated the distribution of molecules between the different states and have obtained the data tabulated in Table 30 for two different temperatures. A comparison with Fig. 10 shows that at room temperature only about 4 molecules are in the 75th energy state (as compared with 100 in the position of rest) which is not sufficient to overcome the energy peak of the cis-position. It is only seldom, therefore, that the vibration in a molecule completes the cycle, i.e. passes from the trans-trough over the cis-peak again into the trans-position. We have here a case of considerably impeded rotation. The molecule must not, however, be regarded as a rigid trans-model. It is rather a case of internal mobility characterized

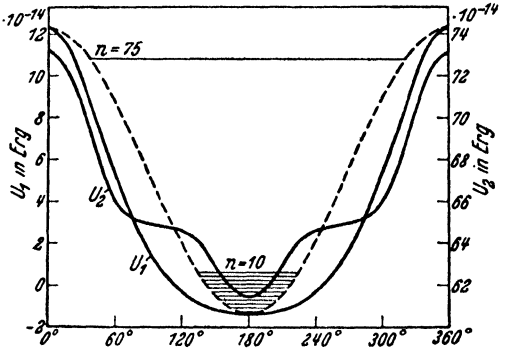


Fig. 10. Internal molecular potential of symmetrical dichloroethane. Energy in ergs per molecule as a function of the azimuth φ.
φ = 0 and 360°.....cis-position.
φ = 180°.....trans-position.

by slow and long vibrations about this position accompanied by occasional transitions over the barrier.[25]

Stuart[26] has made very interesting calculations with a number of disubstitution products of benzene; he starts from the various possible interactions of the substituents and calculates the internal molecular potential of the whole molecule; this is then compared with the deviations of the heats of combustion of the compounds from the additivity rule, with the result that considerable repulsion potentials are shown by the ortho-compounds, which practically disappear in the meta- and para-derivatives.

The results are particularly interesting in the xylenes where an internal

[24] C. P. Smyth, R. W. Dornte and E. B. Wilson, *J. Am. Chem. Soc.*, **53**, 4242 (1931).
[25] A. Turkevitch and J. Y. Beach, *J. Am. Chem. Soc.*, **61**, 3127 (1939).
[26] H. A. Stuart, *Phys. Rev.*, **38**, 1372 (1931).

molecular potential of about 3000 cal/mol is obtained from the difference in observed values for the *o*- and *p*- compounds respectively. Translated to butane, this means that—as in ethane and dichloroethane—the cis-position (see Fig. 11) is unstable while the trans-position with an amount of 2–3000 cal. per mol seems preferred. Here we have highly restricted free rotation, i.e. long, slow vibrations around the trans-position.

Similar results have been obtained with ethers and ketones, to which Stuart[27] has applied the Kerr constant and the degree of depolarization with great success, for elucidating experimentally the question of the shape of these molecules. In diethyl ether the preferred position is denoted by I in Fig. 12; around this slow torsional vibrations of large amplitude ($\approx 70°$) take place, hence it is possible that other stable systems exist besides that

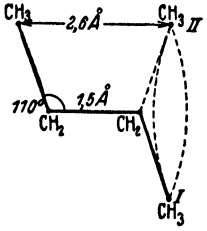


Fig. 11
I = trans-position } of normal
II = cis-position } butane
after H. A. Stuart.

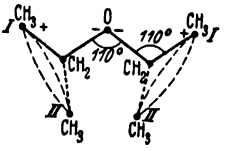


Fig. 12. I = preferred position of the diethyl ether molecule after H. A. Stuart.

shown in Fig. 12. The same is true for diethyl ketone and for the di-*n*-propyl ethers, etc.

The Raman effect affords interesting and important information on the question of free rotatory power. According to Kohlrausch,[28] it is to be expected that a continuum of configurations of a molecule having equal energies should give rise to a band in the Raman spectrum and that inhibited rotation must lead to a broadening of the Raman lines. Actually, *diffuse* Raman lines have been observed in different cases, which accord with a high internal mobility of the given molecule. On the other hand, however, a very thorough investigation of numerous mono-chlor paraffins in the *liquid state* has produced results which are not entirely in harmony with the existence of a single stable trans-position and vibrations about it.

[27] H. A. Stuart, *Z. Physik*, **63**, 533 (1930); *Ann. Physik*, **18**, 121 (1933).

[28] K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt; Ergänzungsband.* Berlin 1938; p. 155; see specially the details, ibid pp. 169 et seq.

Frequently, other symmetrical arrangements seem to be preferred in addition to the plane trans-configuration of the chain, particularly in larger molecules such as $C_{10}H_{21}Cl$ and the like. When we remember, that particles are involved which, in the liquid phase, are subject to very intense interactions and which are derived from that group of substances which tend to form molecular aggregates, we should refrain at the outset from comparison with results obtained in the gaseous state or in dilute solution. It will be convenient to consider these results only in the discussion of the liquid state (see p. 177).

If we are particularly concerned with the study of *chain* molecules, the following experiments must be specially mentioned which, by the aid of electron deflection and dipole moment, have contributed very important information on the mobility of these molecules.

R. Wierl[29] has investigated the vapor of normal hydrocarbons up to hexane by the aid of electron deflection and in them has found only two interferometrically effective distances (1.4 and 2.5 Å). This means that the chains possess such high mobility—not necessarily absolutely free rotatory power—that all greater distances capable of occurring between separated C atoms are not sharp and, therefore, do not appear in the diagram. Measurements on the vapor of 1,5-dichloropentane also point to the flexibility of the chain. In a rigid chain we should expect a distance of 5 to 7 Å between the two chlorine atoms, which would certainly give definite interference in the neighborhood of the primary beam because of the high scattering power of chlorine. In spite of careful search, however, such a value could not be found. Recent experiments of L. Pauling[30] on a whole series of chlorinated and brominated long chains (up to C_{10}) have confirmed Wierl's findings and have placed the idea of a certain internal mobility in the normal paraffin chain on an experimental basis.

We should not, of course, think figuratively in terms of models made of wooden spheres connected by wire rods which have so long been fondly used for spatial demonstration of the problems in stereochemistry. They do demonstrate very well the symmetry relationships and the cases of possible isomerism, but they give an entirely inaccurate picture of the actual space packing and of the mutual hindrance caused by adjacent links

[29] R. Wierl, *The Interference of Electrons*; edited by P. Debye; London 1931, p. 13; *Ann. Physik*, **8**, 521 (1931); **13**, 453 (1932). Cf. also H. de Lazlo, *Nature*, **131**, 803 (1933).

[30] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 8671 (1934); *J. Am. Chem. Soc.*, **57**, 2684, 2693 (1935).

in the chain. Actual conditions are much more conveniently illustrated by the use of the wooden models, as used by E. Mack or H. A. Stuart, and marketed by the Fisher Scientific Company, which give within the bounds of possibility, a very good representation of the conditions obtaining. A long non-substituted paraffin chain has about the shape, internal mobility and softness of a large caterpillar, which with limitations as to sharp bends and twists, must be regarded in its entirety as a fairly mobile structure, very different in its behavior from a pencil of the same length and diameter.

A very instructive study of the torsional mobility of a long chain paraffin has recently been made by A. Mueller.[30a] He investigated the electric behavior of two di-ketones $C_{10}H_{18}O_2$ and $C_{11}H_{20}O_2$ in the neighborhood of their melting points. The structure of these two compounds is such that the two C=O groups point in the same direction (cis-position) in one case, but in the opposite (trans-position) in the other. In both cases they are separated by a chain of 6 or 7 methylene groups. Mueller found that the two compounds show very different electrical properties in the crystalline state (as to be expected from their structure if they are rigid), but are indistinguishable above their melting points. He concludes that the hydrocarbon chain, which links the two C=O groups together exhibits a high degree of torsional flexibility.

In closing the discussion of mobility of the simple C—C linkage, mention may be made of measurements or estimations of the moments of benzene derivatives and of long chain hybrid ions or long chain α-ω-disubstituted compounds.

Fuchs[31] and Tiganik[32] have devised a formula by which the total moment of a molecule can be calculated if it possesses two separate moments, μ_1 and μ_2 which are able to rotate freely round certain axes fixed in space. In substituted benzenes, it is possible, by comparing experimental results with the requirements of this formula, to decide whether the rotary power of the polar groups is free or impeded. In *m*- and *p*-derivatives, e.g. in the chlorophenols, bromophenols, nitrophenols, etc., essentially unimpeded rotatory power of the OH-dipole round the C—O bond occurs, while in the *o*-derivatives, the mutual interaction of the substituents is so considerable that mobility is greatly impeded. There is experimental evidence

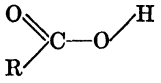
[30a] A. Mueller, *Proc. Roy. Soc.*, (A) **174**, 137 (1940); D. R. Pelmore, *ibid.*, (A) **172**, 502 (1939). Compare further A. Turkevich and J. Y. Beach, *J. Am. Chem. Soc.*, **61**, 303, 3127 (1939); B. L. Crawford and W. W. Rice, *J. Chem. Phys.*, **7**, 437 (1939); **8**, 273 (1940); E. Gorin, J. Walter and H. Eyring, *J. Am. Chem. Soc.*, **61**, 1876 (1939).

[31] R. Tiganik, *Z. physik. Chem.*, (B) **14**, 135 (1931). Cf. also W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934); L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

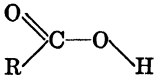
[32] R. Tiganik, *Z. physik. Chem.*, (B) **14**, 135 (1931).

to show that the rotatory power is perceived as practically free if the internal molecular potential does not exceed 10RT per mol; at higher values impedance occurs and is perceptible from the fact that the dependence of the electrical moment on temperature deviates from the 1/T curve. Group moments of the order of 1×10^{-18} (OH, CCl, NH etc.) impede one another appreciably only if they are separated in the molecule by a distance not greater than about 3 Å. This accords with the fact that *m*- and *p*-substituents have practically no opposing effect on one another.

The COOH group possesses a particularly high internal molecular potential, accurate geometrical and dynamic knowledge of which is of great importance. Measurements by Zahn[33] show that the moment of this group is about 1.51×10^{-18}, which suggests, according to H. A. Stuart, that the group assumes the following configuration



at maximum stability and executes vibrations about it only; the other position



must give a moment of 3.9×10^{-18}, whereas for the case of free rotation of the OH dipole about the C—O bond, a moment of 3.5 is calculated. Actually neither in formic acid nor in the other fatty acids could dependence of the moment upon temperature be found by Zahn.[34]

Table 31 gives a few informative data of Zahn[34] and Greene and Williams[35] on the internal mobility of simple ethane derivatives. In all examples given there is a very significant dependence of the moment upon temperature, which means that around the trans-position, which has no electrical moment, vibrations are executed which increase with rising temperature. In no instance, however, is that value of the total moment attained which is necessary for free rotation, whence it may be again concluded that only vibrations are involved which are not translated into rotation.

Of special interest to the behavior of long chains and consequently to the properties of high polymeric substances are the cases first discussed by

[33] C. T. Zahn, *Physik. Z.*, **33**, 400 (1932).
[34] C. T. Zahn, *Phys. Rev.*, **37**, 1516 (1931).
[35] E. W. Greene and J. W. Williams, *Phys. Rev.*, **42**, 119 (1932).

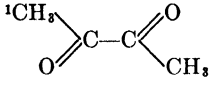
Ebert[36] and accurately investigated later by Smyth and Walls,[37] Eyring,[38] Devoto[39] and W. Kuhn,[40] in which a long chain molecule carries either a dipole μ_1 and μ_2, or a free charge at each end, so that, because of the partial mobility of the individual members of the chain and its length, the opposing influence of the terminal groups upon one another is negligible. The two moments then behave as if they were connected by a long, flexible thread, that is, they are limited in their motions only by the maximum length of the chain. If $\mu_1 = \mu_2$ we obtain under these conditions the value μ for the total moment

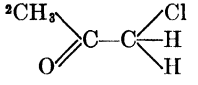
$$\mu = \mu_1\sqrt{2}. \tag{14}$$

TABLE 31

EFFECT OF TEMPERATURE ON THE MOMENTS OF A FEW ETHANE DERIVATIVES

Substance	Formula	T° abs.	$\mu \times 10^{18}$ observed	$\mu \times 10^{18}$ calculated for free rotation
Dichloroethane	$ClH_2C—CH_2Cl$	305–554	1.12–1.54	2.54
		298–588	1.27–1.57	
Dibromoethane	$BrH_2C—CH_2Br$	339–436	0.94–1.10	2.54
		347–449	0.97–1.04	
Chlorbromoethane	$BrH_2C—CH_2Cl$	339–436	1.09–1.28	2.54
Diacetyl[1]	$OCH_3C—CCH_3O$	329–504	1.25–1.48	3.20
Chloroacetone[2]	$ClH_2C—CCH_3O$	336–454	2.17–2.24	3.0





Measurements of Smyth and Walls on long saturated hydrocarbon chains, carrying two equal dipoles at their ends, have shown in fact that, within the limits of error of the method, the total moment fulfills the requirement of equation 14 (see Table 32). These molecules clearly form no rigid, flat zig-zag chain in the dissolved or liquid state, but exhibit a certain internal mobility. These results are thus in excellent agreement with previous ideas on the behavior of long hydrocarbon chains.

[36] F. Ebert, *Leipziger Vorträge.* Leipzig 1929, p. 47.
[37] C. P. Smyth and W. S. Walls, *J. Am. Chem. Soc.*, **53**, 527, 2115 (1931).
[38] H. Eyring, *Phys. Rev.*, **39**, 746 (1932).
[39] G. Devoto, *Z. Elektrochem.*, **40**, 490 (1934); *Gazz. chim. Ital.*, **65**, 1235 (1935).
[40] E.g. W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934).

Recently measurements by W. B. Bridgman[41] on ω-oxycarboxylic acids and their polycondensation products have strengthened this view. By internal esterification of ω-oxydecanoic acid, long chains of molecular weight 900–14000 were obtained and very thorough measurements of refraction and polarization made on this material in dilute benzene solution over a wide wave length range.

In the first place no anomalous dispersion could be detected, as would be expected if the molecules examined had been rigid structures with two adhering dipoles and oriented as a whole in the field. It was further found

TABLE 32

MOMENTS OF A FEW LONG CHAIN MOLECULES

Substance	Formula	Total moment $\mu \times 10^{18}$	Group moment $\mu \times 10^{18}$
Deca-methylene glycol.....	$HO \cdot CH_2 \cdot (CH_2)_8 \cdot CH_2 \cdot OH$	2.5	1.67
Deca-methylene bromide..	$Br \cdot CH_2 \cdot (CH_2)_8 \cdot CH_2 \cdot Br$	2.4	1.8
Sebacinic acid diethyl ester.....	$COOC_2H_5 \cdot (CH_2)_8 \cdot COOC_2H_5$	2.49	—
Hexadeca-methylene dicarboxylic acid diethyl ester...	$COOC_2H_5(CH_2)_{16}COOC_2H_5$	2.49	—

TABLE 33

DIPOLE MOMENTS OF HIGH POLYMERS

Molecular weight	n (monomer units)	$\mu \times 10^{18}$ (calculated)	$\mu \times 10^{18}$ (observed)
13,900	82	16.4	19.0
9,070	53	13.3	15.7
7,780	46	12.4	12.4
4,140	24	9.1	10.2
2,120	12	6.6	6.7
905	5	4.2	5.0

that the polarity of the molecules increased almost exactly with the root of the molecular weight; it can be seen from Table 33 that the values calculated from this assumption agree very well with the experimental data. A relationship of this kind is just what should have been expected, moreover, in view of the Debye equation if the individual polar groups in such chain molecules were oriented in an electric field independently of one another. This would be the situation if the long-chain molecules were not rigid but flexible. One must imagine that the molecules, under the

[41] W. B. Bridgman, *J. Am. Chem. Soc.*, **60**, 530 (1938).

influence of thermal impacts by the surrounding solvent molecules, assume a somewhat sinuous or worm-like form and that the field aligns with itself the individual dipoles in the chain and at its ends. Work of W. Kuhn[42] has been invoked to explain this effect. This author, to whom we are indebted for a series of very important studies on the internal mobility of chain molecules, has calculated that for long flexible chains, which assume an irregular serpentine and constantly changing form in the gaseous state or in solution, due to thermal agitation, the separation between the terminal groups does not increase in proportion to the number of atoms in the chain, but is proportional to the root of this number. This fact (see also p. 298) is in close relation to the law for the average path traversed by a molecule diffusing under the influence of irregular thermal impacts; indeed, generally speaking, internal molecular statistics are very similar to a diffusion phenomenon.

Experiments of Wyman and McMeekin[43] on the peptides of glycine up to heptaglycine are in agreement with the above. The increase in dielectric constant of water in the presence of dissolved peptides was determined. Wyman considered that in flexible chains the increase should be proportional to the increase in molecular weight; this held with reasonable accuracy for the higher members of the series so that this class of substances also gave the same results with respect to the behavior of long chain molecules.

d) The Double Bond and Cis- Trans- Isomerism

The double C=C bond is to some extent susceptible to quantum mechanical treatment; Pauling,[44] Slater,[45] E. Hückel,[46] and more recently R. S. Mulliken[47] in particular have tried, by employing different methods, to derive criteria for the form of the charge distribution corresponding to the aliphatic and the aromatic double bond. It has been proved repeatedly that this chemical primary valence is produced by 4 electrons, two of

[42] W. Kuhn, *Kolloid-Z.*, **76**, 258 (1936); *Z. anorg. allgem. Chem.*, **49**, 858 (1937); *Z. Elektrochem.*, **42**, 692 (1937); comp. also H. Eyring, *Phys. Rev.*, **39**, 746 (1932); L. Laskowsky and R. E. Burk, *J. Chem. Phys.*, **7**, 465 (1939); W. F. Busse, *J. Phys. Chem.*, **36**, 2862 (1932).

[43] J. Wyman, *J. Am. Chem. Soc.*, **58**, 1482 (1936); **60**, 328 (1938); *J. Phys. Chem.*, **43**, 143 (1939). Cf. also W. B. Bridgman and J. W. Williams, *J. Am. Chem. Soc.*, **59**, 1579 (1937); J. H. van Vleck, *J. Chem. Phys.*, **5**, 556 (1937); J. Wyman and McMeekin, *J. Am. Chem. Soc.*, **55**, 908 (1933); J. G. Kirkwood, *Chem. Rev.*, **24**, 233 (1939).

[44] L. Pauling, *Phys. Rev.*, **40**, 891 (1932).

[45] J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

[46] E. Hückel, *Z. Physik*, **60**, 43 (1930).

[47] R. S. Mulliken, *J.Chem.Phys.*, **7**, 14, 20, 121, 339, 353, 356, 364 (1939).

which form a rotation-symmetrical charge cloud, while a charge cloud (Eigen function) characterized by a plane of symmetry corresponds to the other two. The plane of symmetry is so placed relative to the nuclear framework that the two residual valences at each C atom are perpendicular to it (see Fig. 13). By this evidence, quantum mechanics again confirms the concept outlined by organic chemists many years ago regarding the spatial structure of the aliphatic double bond and the deductions possible from it.

The loss of high axial symmetry merely indicates that the valence scaffoldings of the two C atoms are now no longer free to rotate about the bond between the nuclei so that the double bond has a *certain rigidity.* The reason lies in the fact—deducible from the charge distributions—that, to effect any change in the arrangement shown in Fig. 13, portions of the negative charge cloud, corresponding to the double bond must be brought nearer together; this is possible only by performing work against the re-

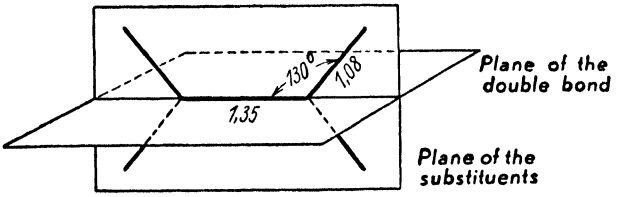


Fig. 13. Geometrical arrangement of valences in the double C═C bond.

pulsive forces between the different parts of the negative charge cloud, which owing to the Coulomb law repel each other.

Researches of Eucken and his co-workers[48] on ethylene have in fact afforded very striking confirmation of this concept. They deduce from the effect of temperature on specific heat a torsional or turning oscillation of fairly high frequency (750 $cm^{-1} \approx 10^{13}$ per sec.) so that the molecule represents a highly impeded one dimensional oscillator whose properties have been studied by Teller and Weigert.[49] Comparison of measurement and theory shows that the barrier of potential which has to be scaled in the transition from cis- to trans-form, lies far above kT; on this depends the stability of the two isomers and the possibility of isolating them by the methods of synthetic organic chemistry.

To obtain an insight into the probable behavior we shall refer to Fig. 14

[48] A. Eucken and K. Weigert, *Z. physik. Chem.*, (B) **20**, 161 (1933).
[49] E. Teller and K. Weigert, *Nachr. Ges. Wiss. Göttingen*, **2**, 218 (1933).

which represents diagrammatically the potential curve of a cis- trans-isomerism. There are two potential troughs—stable modifications—the cis position $\varphi = 0$ and the trans-position $\varphi = 180°$. Due to unequal distances between the substituents, they are not of equal depth; between them rises an energy peak, guaranteeing their stability, and arising from the interaction of double bond rigidity and the reciprocal effect of substituents.

The energy difference U between the minima of the two troughs is the heat of conversion of the two modifications into one another;[50] it determines for the mixture ratio of the isomers and can be calculated from the effect of temperature upon the equilibrium. It has been determined experimentally, for instance, in the case of dichloroethylene by Ebert and Büll.[51] At about 300°C the cis- form is the more stable, 63% of the molecules being in the cis- and 37% in the trans- form; the energy difference can be estimated at about 500 cal. per mol.

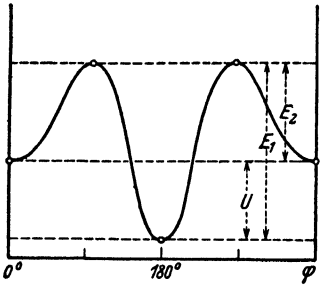


Fig. 14. Schematic curve of the internal molecular potential in the case of a cis-trans-isomerism

$\varphi = 180°$ ..... trans-position

$\varphi = 0°$ and $360°$ .... cis-position.

Stuart[52] also has investigated this problem by calculating the reciprocal effect of the two Cl atoms, and has arrived at very plausible results. Actually the cis-position was found to be preferred but its calculated stability, 1150 cal/mol, was greater than that given by experiment. We must, however, be content with this agreement in view of the inadequacy of the theory underlying the calculation.

In other cases—maleic and fumaric acid, cinnamic acid, etc.—the trans-form may be the more stable, a fact which Stuart[53] again has shown to be probable; in these cases, due to free rotation within the $CH_2 \cdot COOH$ group, there usually exist several rotation-isomeric cis- and trans- forms, a circumstance which suggests an interesting problem in re-examining the present relationships experimentally.

The energy differences E_1 and E_2 between the minima of the two potential troughs and the peak of the energy barrier separating them are the heats

[50] R. J. Corruccini and E. C. Gilbert, *J. Am. Chem. Soc.*, **61**, 2925 (1939).

[51] F. Ebert and R. Büll, *Z. physik. Chem.*, (A) **152**, 451 (1931).

[52] H. A. Stuart, *Physik. Z.*, **32**, 793 (1931).

[53] See l.c. and also H. A. Stuart, *Molekülstruktur*. Berlin 1934, pp. 95 et seq.

of activation for the transition from cis- to trans- or from trans- to cis-. They determine the thermal stability of the two forms and may be calculated from the effect of temperature on the rate of isomerization by the aid of the Arrhenius-Trautz equation. Unfortunately, the material available is very scanty; Höjendahl[54] alone has estimated from the rate of conversion of maleic acid into fumaric acid, the level of the energy peak separating the two forms as about 16000 cal. per mol; the magnitude of this value guarantees a fairly considerable stability for both types of molecule.

It would be of the greatest interest in the dynamics of organic synthesis if the very incomplete material in this field could be augmented by a rather more systematic treatment of several cis-trans-isomerisms and by equilibrium and velocity measurements.

e) Internal Molecular Dynamics and Statistics

In the theoretical treatment of small molecules—in the simplest case, of a diatomic dumb-bell molecule—we can either formulate a vibration equation based simply upon suitable application of force and solve this according to the rules of classical mechanics aided by quantum postulates, or we can proceed—by introducing a suitable potential—from the Schrödinger equation, integrate this and so arrive at the stationary conditions of the structure investigated (Eigen values) and likewise at expressions for the distribution of the charges in space (Eigen functions). The internal molecular motions are then a direct consequence of the potential characteristic for the molecule. In diatomic molecules, this problem can be accurately solved, in tri- or polyatomic molecules it is necessary to employ approximation processes, which quickly become ambiguous and involve a large amount of calculation. The whole is to be regarded as a dynamic treatment of molecular processes and constitutes an extreme aspect of the possible assertions about internal molecular motions.

We have seen, on the other hand, that there is a second type of internal motions particularly in very large and mobile molecules, which do not arise from the action of intra-molecular forces but which, on the contrary, are so disposed that during their execution, the potential of the molecule remains constant. These motions are caused by the thermal energy of the individual parts of the large molecule and can best be compared to the chaotic motion of the molecules in a perfect gas. It is natural, therefore, in studying this kind of internal molecular motion, to employ methods similar to those that have proved useful in the theoretical treatment of

[54] K. Höjendahl, *J. Phys. Chem.*, **28**, 758 (1924).

gases, namely statistical. In the limit, we have to proceed as if the individual parts of the molecule were entirely free to move and the cohesive forces replaced by purely geometrical conditions to insure the molecule against disintegration and, furthermore, that the fundamental principles of molecular structure are valid. It is just a matter of counting configurations, regarded as equal in energy value and compatible with geometrical demands; we employ as a first approximation stationary statistics.

Later, of course, we are forced to the conclusion that there are very few motions within a molecule that actually proceed quite free of forces and that most of them include a great variety of rotations and vibrations, which are associated with small energy differences and can, therefore, be realized equally well under the influence of temperature variations. Consequently, in addition to stationary statistics, we have to work with energy statistics and to take into account the energy differences by the aid of a Boltzmann factor. In terms of the gas theory, this phase corresponds with the van der Waals theory of real gases.

We shall show by a very simple example how these ideas can be transformed into mathematical relations, for it will appear later that many an important property of high polymeric substances is connected directly with the internal motions of large, chain or reticulate molecules. E. Wöhlisch[55] in 1927 advanced the idea that the tendency of rubber and muscles to contract is traceable to the thermal motion of molecules and K. H. Meyer[56] showed in 1932 that it is not a question of the motions of entire molecules, but of links in the principal chains which cause the contraction of the extended chain by their thermal motions. The quantitative demonstration of this idea was furnished by H. Mark and his coworkers[57] and independently by W. Kuhn;[58] the experimental proof occupies an important position in the field of high polymers.

We shall choose for the calculation a normal hydrocarbon chain, a case which was treated by E. Guth, W. Kuhn and H. Eyring,[59] and assume first that there is completely free rotation over the whole extent of the chain.

[55] E. Wöhlisch and R. de Rochemont, *Z. Biol.*, **85**, 406 (1927); **87**, 353 (1928).

[56] K. H. Meyer, G. v. Susich and E. Valko, *Kolloid-Z.*, **59**, 208 (1932); H. Mark and E. Valko, *Kautschuk*, **6**, 210 (1930).

[57] H. Mark, *IX. Congr. Chim. Madrid*, **5**, 197 (1934); E. Guth and H. Mark, *Monatsh.*, **65**, 93 (1934); E. Guth and H. Mark, *Naturwiss.*, **25**, 353 (1937); H. Mark, *Nature*, **141**, 670 (1938).

[58] W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934); **76**, 258 (1936); **87**, 3 (1939).

[59] H. Eyring, *Phys. Rev.*, **39**, 746 (1932) has developed an equation for the most probable length of a long chain as long ago as 1932; cf. also E. Guth, *J. Applied Phys.*, **10**, 161 (1939) and L. Laskowsky and R. E. Burk, *J. Chem. Phys.*, **7**, 465 (1939).

Later, we shall have to adapt the results of the calculation nearer to actuality on the basis of information in the final sections. The chain to be treated consists of C atoms which may be joined by single linkages. When extended, it possesses the known, plane, zig-zag form determined by the tetrahedral symmetry of the C atoms which is actually found in the crystal lattice and probably holds approximately also in liquid paraffins because of their group structure. Free rotation and even vigorous torsional vibrations are in these cases non-existent, being excluded by the strong inter-molecular forces.

The extended form of the chain represented in Fig. 15 is, however, only one of very many forms having equal energy values, for we can perform rotations round any of the $(n - 1)$ single C—C bonds, while preserving the tetrahedral angle, without having to perform any work. Since the chain in gas or in solution (i.e. in the free state) is always in thermal equilibrium with its surroundings and is always subject to random impacts from all directions, it will assume in course of time—in accordance with fundamental laws of statistics—all positions of equal energy value and will actually perform all motions possible to it, just as the molecule of a perfect gas subjected to thermal impacts will occupy all the space available to it, in accordance with energy relationships.

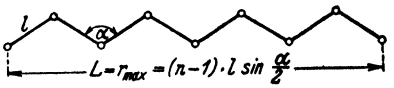


Fig. 15. Extended form of a normal paraffin chain.

It is evident from the above that it is meaningless to speak of a definite shape of the chain if, by that, we mean a configuration that remains temporarily fixed over a long range. It would be just as inappropriate to speak of a fixed location of the molecules in a gas. These are in fact always moving, and the chain is in constant sinuous motion. As in all statistical treatment—acknowledging the impossible—we abandon any attempt to assign definite states to the individual molecules. Rather we integrate all those micro states belonging to a given macroscopically definable state capable of definition and reproduction by measurement of macroscopic parameters. In a perfect gas, volume is chosen; in the chain having a certain degree of free rotation, there are several possibilities for the choice; having regard to the later application of these considerations to the elasticity and viscosity of long chain substances, we shall take the distance between the ends of the chain as such a parameter.

In order to start with the simplest possible conditions, we shall consider an isolated chain molecule, for example, an unbranched hydrocarbon chain with n links, i.e. with $(n + 1)$ C atoms (see Fig. 15); n should be a

number between 10^2 and 10^4. This model is actually a considerable simplification as compared with natural or artificial rubber, because methyl groups and double bonds are absent, but it serves for the immediate study of the principal properties of such a chain. Later we shall have to remember that the free rotatory power assumed for this chain does not actually exist and that the different chains of a macroscopic specimen mutually impede one another to some degree.

According to information in the preceding sections, the individual links are 1.54 Å long and the angle between the valences, α, is about 109°; if we extend the chain completely so that it has the shape illustrated in Fig. 15, its length is given by

$$L = r_{max} = (n - 1) \cdot l_0 \cdot sin \frac{\alpha}{2}$$

This maximum length of the chain, as is immediately evident from the illustration, is attained only under one condition, namely that all the bonds lie in one and the same plane and form the zig-zag strip; the maximum possible distance between the ends, r_{max}, which denotes complete extension of the chain, can, therefore, be obtained only in one single way.

If, however, we desire the ends of the chain to be at some other distance apart, e.g. a distance r, when $r < r_{max}$, this can be effected in a number of different ways; indeed, because of the internal mobility of the chain, we may arrange the individual links in many different ways and still have the two terminal C atoms separated by the distance r. If we imagine a large number—say, 1000—of such chains scattered at random on the floor, and then measure the distances between the ends for every chain and draw up statistics, it is very unlikely on grounds of probability that the maximum distance will be found frequently, since it can be obtained only in one way; any shorter distance can be obtained by a large number of configurations and will, consequently, be found much more frequently in actual conditions.

To each theoretical distance r between the ends of the chain there is a definite number of possibilities of realization, which, following Boltzmann, we can term the complexion belonging to r. To calculate this complexion as a function of r, we must make certain assumptions regarding the structure of the chain and its mobility. If l_0 denotes the length of a single link, n the number of links and α the angle between two successive links, and completely free rotation is assumed, then the probability that the ends of such a chain will be separated by the distance r, is given by

$$W(n, l, \alpha, r) r^2 dr = 3 \sqrt{\frac{6}{\pi}} \frac{1}{n^{3/2} \cdot l_\alpha^2} \cdot e^{-\frac{3r^2}{2n \cdot l_\alpha^2} \cdot r^2 dr} \qquad (15)$$

In this,

n = number of links

l_0 = length of each

α = valence angle

$$l_a^2 = l_0^2 \frac{1 + \cos \alpha}{1 - \cos \alpha}$$

r must naturally always be less than r_{max}. It is evident from (15) that there is a most probable distance λ between the two chain ends, namely, that value of r at which the function given by (15) has its maximum. This value, as an easy calculation shows, is

$$\lambda = l_0 \cdot \sqrt{\frac{2}{3}} \cdot \sqrt{n}. \tag{16}$$

The length r_{max} can, however, be attained only in one way, and similarly, small values of r—very short distances separating the ends of the chain—are ruled out statistically.

For the case $n = 30$, W is shown as a function of r in Fig. 16. $W(r)r^2\,dr$, like the well-known Maxwell-Boltzmann distribution curve, is thus asymmetrical; it also has greater breadth on account of the smaller number of statistically independent elements. The result is that we cannot regard the most probable value as the only one likely to be present, as we would in the ordinary statistical treatment of gases. We must, rather, consider neighboring values and attach much greater significance to fluctuation phenomena than in gas statistics. We shall return later to this point, when the occurrence of x-ray interferences in stretched rubber are discussed.

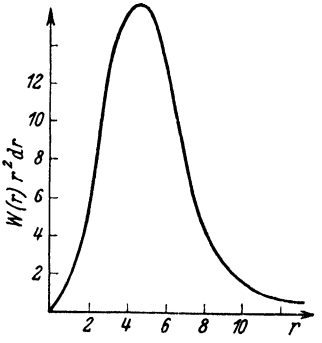


Fig. 16. Distribution function for $n = 30$.

The above considerations invite the assumption that a chain in thermodynamic equilibrium with its surroundings—and subject to thermal impacts from all sides—itself assumes that state which exhibits the greatest number of possibilities of realization. This is no more than the application of the Boltzmann statistics to a single elongated molecule and will meet with no objection so long as there are sufficient independent elements present for statistical treatment. It has been mentioned previously that

the position is not as favorable as the one existing in the statistics of gases, where the number of independent systems in one mol is of the order of 10^{23}; a chain of 3000 to 4000 links will, however, consist of 500 to 600 strictly independent component systems. I.e. after about seven or eight links, the influence of the first will certainly be so far annulled that the ninth link may be regarded as practically beginning a new element. It will, of course, be necessary to pay special attention to fluctuation phenomena.

With these limitations, and by applying the Boltzmann law, we may ascribe to an isolated primary valence chain an entropy

$$s = k \, ln \, W$$

and try to derive its final properties from it. It will be found, first, that invariably, such a chain can, of itself, change only to a state of higher entropy, i.e. of greater probability, and that work must be performed to put it into a state of lesser probability. If, therefore, we are dealing with a chain whose ends are separated by r and wish to extend it to the maximum length L, we must perform an amount of work A corresponding to the entropy difference $s_r - s_L$. This expenditure of work results in a heating of the chain on rapid extension, by an amount

$$A = Q = s_r - s_L = k[ln \, W \, (r) - ln \, W \, (r_{max})]$$

This exactly corresponds to the heating of an ideal gas on adiabatic compression, during which there is an entropy loss, because space previously accessible to the gas is now no longer available. This reduces the number of realization possibilities and hence the probability of the system.

The pressure p of a gas is exerted by random molecular impacts, which seek to enlarge the volume available to the gas and consequently to increase the number of configuration possibilities, which means an increase in entropy. Exactly in the same way, the stress σ on the ends of a stretched valence chain, caused by the random thermal motions of the individual links, tends to shorten the length of the chain, because the shorter length has greater possibilities of realization. Hence, it is more probable and corresponds to a higher entropy. Formulated, these points become

$$p = +\left(\frac{\partial s}{\partial V}\right)_T \cdot T$$

$$\sigma = -\left(\frac{\partial s}{\partial (\delta l)}\right)_T \cdot T \qquad (17)$$

δl = change in length

We now understand why rubber-like materials must heat on stretching and cool on relaxing, in complete analogy to the behavior of ideal gases and in contrast to normal crystalline elasticity.

In perfect gases the internal energy U is independent of volume, so that in rubber a region may be defined as ideal in which the internal energy is independent of tension. Experiments have shown that in lightly vulcanized samples at about 250% extension the internal energy is, in fact, only very slightly dependent upon length. In real gases and in rubber preparations which do not conform to these special conditions, the properties differ and, because of intermolecular forces, the internal energy becomes dependent upon volume or upon the extent of stretching.

We shall now attempt to establish an equation of state for the ideal rubber by analogy with an ideal gas. We start with equation (17). If we introduce $k \ ln \ W$ for s and eliminate W from equation (15) we obtain:

$$\sigma = 3kT \frac{1}{nl_0^2} \cdot \frac{1 - cos \ \alpha}{1 + cos \ \alpha} \cdot \delta l \tag{18}$$

δl = elongation of a single chain

σ = stress

just as one gets for a mol of an ideal gas the relation.

$$p = \frac{RT}{V} \tag{19}$$

Therefore, we seem to be justified in interpreting (18) as the equation of state for ideal rubber. It combines the tension σ with the elongation δl and represents the extension curve of a single valence chain.

Experimentally, however, one always obtains such a curve using a piece of rubber large enough to be handled. Let this have an original length l and let it acquire a certain elongation Δl as a result of the stress. Therefore, we must pass from formula (18) which relates to a single chain molecule to another equation which holds for a macroscopic piece of material. This was done by W. Kuhn[60] and H. Pelzer.[61]

We consider a unit volume of rubber and assume that there are Z chains contained in it. When we put the sample under a certain finite tension Σ, it undergoes an elongation Δl. Now, as a first approximation Kuhn made the assumption that the entropy of the macroscopic piece of rubber is given by the sum of the entropies of the separate chains. This is,

[60] W. Kuhn, *Kolloid-Z.*, **68**, 2 (1934); **76**, 258 (1936); **87**, 3 (1939).

[61] H. Pelzer, *Monatsh.*, **71**, 444 (1938); cf. also H. Dostal, *Monatsh.*, **71**, 144, 309, 346 (1938).

of course, only an approximation and we shall see later what change we have to make in this preliminary hypothesis.

With such assumptions we obtain

$$\Sigma = Z \cdot \sigma = Z \cdot kT \frac{3}{nl_0^2} \cdot \frac{1 - \cos \alpha}{1 + \cos \alpha} \cdot \Delta l \tag{20}$$

$$= E \cdot \Delta l$$

$$E = Z \cdot kT \frac{3}{nl_0^2} \cdot \frac{1 - \cos \alpha}{1 + \cos \alpha} = Z \cdot k'T = R'T$$

From (20) one sees that the macroscopic modulus of elasticity E of rubber-like substances is proportional to the absolute temperature. This fact was proved by the experiments of K. H. Meyer, I. S. Ornstein, and their collaborators[62] carried out for the first part of the elongation curve. The equation (20) further shows that there is proportionality between the tension Σ and the elongation Δl, a fact which also stands in fair agreement with many experimental investigations of the first part of the elongation curve of rubber having a low degree of vulcanization.

A further evaluation of relation (20) was given by Kuhn. The number of chains in the unit volume is closely connected with the average molecular weight of a single chain. One finds

$$Z = \frac{\rho \cdot N}{M_f}; \; M_f = \text{molecular weight of the mobile parts of a chain,}$$

and introducing numerical values one gets,

$$E = 7 \cdot RT \cdot \rho \frac{1}{M_f} \tag{21}$$

Therefore, the modulus of elasticity can be used to determine the molecular weight of the mobile part of the single chains. If one starts from the experimental values, which lie between 10^5 and 10^6 dynes per cm^2, one obtains for the molecular weight of the rubber chains values between 20,000 and 100,000, which are in good agreement with other quantitative data for such substances.

Up to now we have confined our considerations to the behavior of an isolated chain molecule with a certain amount of internal mobility. We may summarize by saying that this preliminary study gives

a) A range of elasticity of the correct order of magnitude;

[62] I. S. Ornstein, J. Wouda and J. G. Eymers, *Proc. Acad. Sci. Amsterdam*, **32**, 1235 (1929); **33**, 273 (1930); K. H. Meyer and C. Ferri, *Helv. chim. Acta*, **18**, 570 (1935).

b) Proportionality of the modulus with the absolute temperature,

c) Molecular weight of the correct order of magnitude.

All these consequences of the statistical theory of rubber elasticity are in fair agreement with the experiments.

We may thus feel encouraged to start with some improvements over the theoretical equations, keeping in mind the different points which have been neglected. If we want to approach more closely the conditions in a real rubber sample and to bridge the gap between it and the ideal one we have considered hitherto, we have to introduce two kinds of refinement, namely

a) geometrical and
b) dynamical ones.

a) Passing from the equation of state of an isolated valence chain to a macroscopic piece of rubber, we have assumed that the behavior of the latter can be derived by a simple process of multiplication. This, of course, cannot be true. One has to take into account that in the original sample the entangled chain molecules are distributed entirely at random. If we stretch the material in a given direction the behavior of each individual chain will depend upon its position with reference to the direction of stress. Kuhn has shown that a process of averaging the behavior of the individual chains due to their spatial positions has to be carried out.

Furthermore, it seems to be of interest to investigate the consequences of assuming that the chains do not move independently of each other, but that they stick together at certain adhering points. Kuhn has shown that one visualizes the rubber as being an irregular network of flexible chains linked together at certain points, each chain having a tendency to roll up owing to the thermal motion of the molecules.

H. Pelzer has developed the statistical theory in this direction and has obtained the following relation for the modulus of elasticity:

$$E = \sqrt{2} \cdot RT \cdot \rho^{1/2} \frac{\alpha}{M \cdot l_0 \cdot n} \tag{22}$$

n = number of links in one chain; l_0 = length of each individual link;

M = molecular weight of each individual link;

α is proportional to the number of chains parallel to the stress.

This equation gives the correct order of magnitude for E and combines the elastic behavior with the different quantities which describe the assumed model.

Pelzer also succeeded in working out a theoretical extension curve which agrees fairly with the experiments, even outside the limit of proportionality between stress and elongation. This extension curve is represented by

$$\sigma = \sqrt{2}\,\frac{kT}{l_0 n^{1/2}} \cdot \frac{\Delta l}{l} \cdot \frac{2l + \Delta l}{l + \Delta l} \tag{23}$$

The present short treatise, which is intended merely to illustrate general principles of internal molecular statistics and to indicate their application to rubber elasticity, was chosen in view of this latter point and of the possibility of explaining certain features of the viscous flow of high polymeric substances (compare page 290). It may, however, be remarked that many other characteristic constants of high polymeric substances—osmotic pressure, double refraction etc.—are related to the internal mobility of long chain or reticulate structures.

TABLE 34

DIFFERENT METHODS OF DETERMINING THE PROPERTIES OF MOLECULES

Method \ Problem	Nuclear distances	Size of the valence angle	Deformability of the valence angle	Symmetry	Internal mobility	Natural vibrations	Characterization of definite groups	Secondary valences, crystal lattice forces	Complex molecules
Scattering of x-rays by a crystal ..	++	++	−	+	−	−	−	++	+++
Scattering of x-rays by a gas ...	++	++	+	+	++	−	−	−	+
Scattering of electrons by a gas .. .	++	++	+	+	++	−	−	−	+
Analysis of the rotation structure of the molecular spectrum (infra-red).. ...	+	+	−	−	−	−	−	−	−
Analysis of vibration bands of the molecular spectrum (infra-red and Raman).....	−	−	+	++	−	++	++	−	+
Temperature curves of molecular heats .	+	−	+	+	++	++	−	−	−
Determination of the permanent electric moment.	−	++	+	+	++	−	++	−	++
Determination of the polarizability (Depolarization measurements and Kerr effect)....	−	+	−	+	++	−	+	−	+

Conclusion

In concluding the discussion on molecular size, shape and internal mobility, we recall once more the experimental methods which have

TABLE 35

DIFFERENT METHODS OF DETERMINING THE PROPERTIES OF MOLECULES

Method	Type of substance investigated	Principal precise results obtainable	Results not obtainable with accuracy
Scattering of x-rays in crystals	Fairly complex molecules (hexamethyl benzene, chrysene, stilbene, stearic acid)	Nuclear distances[1] of atoms, valence angle, symmetry of molecules, all in the solid state. Molecular aggregates, directions of strongest secondary valences in the lattice	Free rotatory power, deformability and natural vibrations
Scattering of x-rays in gases	Only simple molecules (CCl_4, C_2H_6, C_6H_6)	Nuclear distances,[1] valence angle, mobility	Natural vibrations
Scattering of electrons in gases	Only relatively simple molecules (as above)	As above, see also foot note[1]	
Rotational fine structure of molecular spectra (infra-red and Raman spectrum)	Only very simple molecules (NH_3, C_2H_4, HCOOH)	Nuclear distances (generally in excited state); valence angle, deformability, isotopes	Natural vibrations
Permanent electric moment of the molecules	Relatively complex molecules (diphenyl derivatives, pentaerythrite, tetranitromethane)	Valence angle, free rotatory power, symmetry in free state, group moments	Nuclear distances, natural vibrations
Polarizability of the molecule (depolarization and Kerr effect)	Relatively complex molecules (Pyridine, di - n - propyl ether, methyl ethyl ketone)	Valence angle, symmetry, internal mobility in free state	Nuclear distances, natural vibrations
Vibration spectrum of the molecular, infra-red and Raman spectrum	Only relatively simple molecules (C_2H_6, C_6H_6, vinyl acetylene)	Group frequencies, symmetry, natural vibrations	Nuclear distances
Temperature curve of molecular heats	Only simple molecules (C_2H_4, C_2H_6)	Symmetry, mobility, natural vibrations	

[1] With x-rays, the nuclear distance is not determined directly but the distance of the centers of gravity of the negative charge shells; with electrons, the nuclear distances directly.

furnished all the information here reviewed, and show in two tables the comparison between the statement of the problem and the experimental possibilities. Table 34 enumerates the different types of problems and indicates the methods best suited to their treatment. A dash means that the method is unsatisfactory for the problem in question while one or more crosses indicate increasing degrees of usefulness.

Table 35 gives similar information differently arranged.

With this review, the section on the nuclear framework of molecules and their internal motion will be brought to a close and we shall pass on to a discussion of the forces which, on the one hand hold the molecules together (primary valences) and on the other, combine single molecules into larger structures—associates, micellae—and finally into macroscopic phases—liquids, crystals, and so on.

C. PRIMARY AND SECONDARY VALENCES

The first two sections of this discussion have given an outline of the present knowledge of nuclear framework and internal motions in molecules; it will now be necessary to amplify and to differentiate the information by a survey of the intra- and inter-molecular forces and to explain how conclusions may be drawn from atomic distances, valence angles, vibrations and rotations, regarding the primary valence forces which hold a molecule together. Although forces must be given prominence as causes, the path of research has been in the reverse direction. The causes have been inferred from the effects of primary valences, i.e. from the existence, form and internal mobility of the molecule. It seems reasonable, therefore, to follow the inductive way here.

Experience teaches that, even after saturation of primary valences and formation of a molecule, the resulting bodies are always able to exert further forces on others of the same or different nature. These forces are considerably weaker than the first, they differ significantly in their mode of action and they are accordingly termed residual or secondary valences. They are the forces that unite molecules into associates, complexes, aggregates and micellae and to them ultimately, the macroscopic, condensed phases—liquids, mesophases and crystals—owe their existence. Although, as will be shown later, and as is customary in all concepts of natural science, it may not be possible always to draw an entirely sharp distinction between these two types of valences, and frequently the question remains open whether a given atomic group is held together by primary or secondary valences, the distinction has furnished such clear insight into the many-sidedness of the phenomena, especially in the field of organic chemistry, that its usefulness cannot be doubted, even if it cannot be applied to the last detail.

We shall, therefore, make this distinction of forces in the realm of molecular dimensions the basis of further consideration and begin with the discussion of the primary valences.

1. Chemical Primary Valence

In examining those chemical compounds which have strong forces of cohesion, it happens that the nature of the interaction between atoms

of the same or nearly the same size may yet be very different. All the chemical and physical properties of the molecules suggest that there are several types of primary valence forces which in some cases appear sharply defined and in others are more or less overlapping. If we consider the three molecules NaCl, Cl_2 and Na_2, we have before us three representatives of those types of linkage which serve to cover the existing experimental data:

the heteropolar linkage between oppositely charged ions,
the homopolar linkage between neutral atoms,
the metallic linkage between similarly charged particles.

This classification has proved useful in considering isolated molecules but has assumed much greater importance in investigating crystals. Since conditions in the condensed phases are presented in greater detail in Section D, we shall turn our attention now mainly to the three types of linkage mentioned above and it will be shown how far it is possible, within the classification, to postulate ideas regarding the origin, magnitude and potential of those forces which unite atoms into a molecule.

a) The Heteropolar Linkage between Oppositely Charged Ions

There are a great many chemical compounds which are known to consist of oppositely charged ions. In the molten state or in aqueous solution they conduct the electric current by simultaneous movement of these ions into which they dissociate; they can be excited to (infra-red) vibrations, in the course of which charged particles are vibrating against one another, they form crystal lattices in which, according to evidence from interferometric measurements, charged ions are undoubtedly in juxtaposition, and they proclaim through a series of other properties their heteropolar character. NaCl, CaO, $AlCl_3$, K_2PtCl_6 may be cited as examples.

We are indebted to W. Kossel[1] and G. N. Lewis[2] for the simple and successful theories of closed inert gas-like electron shells which are produced from the atoms of the chemical elements by the loss of loosely bound electrons (valence electrons) or by the acquisition of such electrons, thereby forming extremely stable systems. The atoms lose their motile electrons or replenish their unsaturated shells and are thus converted into positive or negative ions.

If the electron clouds of these ions are not too large—as in the elements at the beginning of the Periodic System—they may be considered as nearly rigid, charged spheres, which are attracted by virtue of their electric charges. The equilibrium position is produced by the co-action of a force of attrac-

[1] W. Kossel, *Ann. Physik*, **49**, 229 (1916).
[2] G. N. Lewis, *Valence and Structure of Atoms and Molecules*. New York 1923.

tion and a force of repulsion both of which may be derived from potentials. The relationships can best be expressed by a potential curve which represents the energy of the molecule as a function of the distance between the two atomic nuclei, and present knowledge is best complied with if the attraction potential is based upon Coulomb's law and the repulsion potential expressed either through a higher power of r according to Born[3] or in accordance with quantum-mechanical theories of Born and Mayer[4] through an exponential function. The total potential V for univalent ions then assumes the form

$$V = -\frac{e^2}{r} + \frac{b}{r^n} \tag{24}$$

$$V = -\frac{e^2}{r} + be^{-\frac{r}{\rho}} \tag{25}$$

e = electrical charge, n, b and ρ are constants which are characteristic for the two ions.

and has the form represented graphically in Fig. 17. Equation (24) gives accurate values for the internal distance and the dissociation energy of heteropolar dumb-bell molecules and has proved most useful—as will be shown later in greater detail—in representing different properties of ion lattices as well.

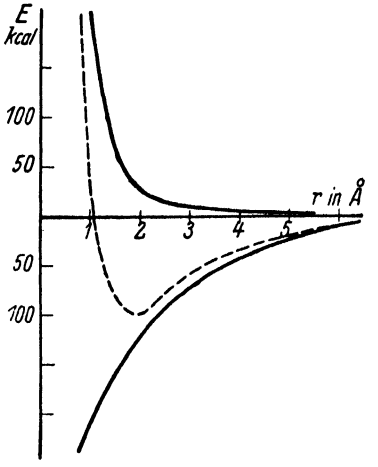


Fig. 17. Potential curve E in Cal. per mol as function of r according to equation (24).

Recently, exact information has become available regarding the spatial distribution of negative charge clouds between united ions, so that we can supplement conditions expressed mathematically in equation (25) by an actual diagram of the arrangement of the charges in space. By a remarkable increase in the precision of interferometric measurements with x-rays, H. G. Grimm and his co-workers R. Brill, C. Hermann and C. Peters[5] have succeeded in determining very

[3] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932).

[4] M. Born and M. Goeppert-Mayer, *Handbuch der Physik*, 2nd ed., Berlin 1933; Vol. 24, 2nd part, p. 722.

[5] H. G. Grimm, R. Brill, C. Hermann and Cl. Peters, *Naturwiss.*, **26**, 29, 479 (1938); *Ann. Physik*, [5] **34**, 393 (1939).

accurately the electronic density in ionic lattices by the aid of Fourier analysis developed by W. L. Bragg. They found in the rock salt lattice that the positively charged atomic nuclei bind their negative charge clouds very firmly and that over a long intermediate zone practically no negative charge exists. Fig. 18 shows a section through the charge distribution between a Na and a Cl ion in the lattice and makes it clearly evi-

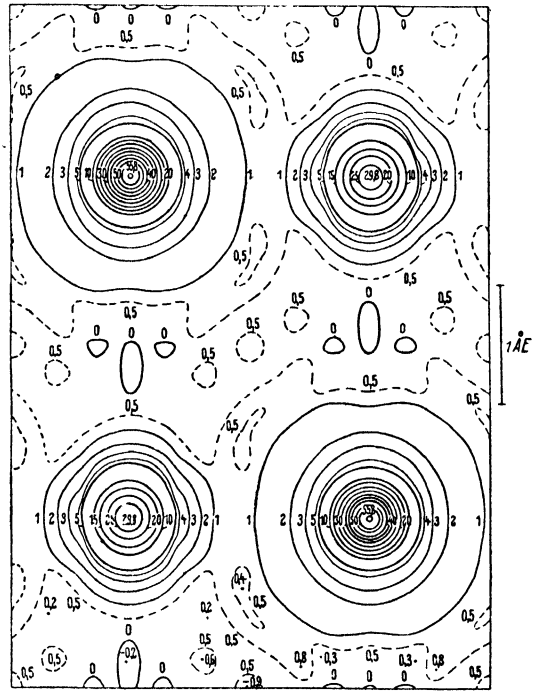


Fig. 18. Electronic density in the Na-Cl lattice; the large ions with the high charge density represent Cl, the others Na; at the bond the charge density is zero.

dent that the density of the charge, at increasing distance from the atomic nucleus, falls off very rapidly and practically disappears over a range of nearly one Å.

On passing to heavier elements, the charge clouds become larger and less rigid, so that those, particularly of the negative anions, are deformed under the influence of the forces of attraction of the cations. This polarization or deformation of the ions which has been especially studied by

Lewis,[6] Langmuir,[7] Haber[8] and Fajans[9] gives rise to an additional force of attraction whose potential may be calculated by

$$V = -\frac{\alpha \cdot e^2}{r^4} - \frac{2e^2\alpha^2}{r^7} \tag{26}$$

and may be added to the Coulomb and quantum mechanical terms of equation (25). The expanded potential expression agrees satisfactorily with experiment and at the same time leads us from the extreme heteropolar linkage to the homopolar. For example, the more strongly the negative charge cloud of the anion, which now bears the excess charge of this ion, is drawn over to the cation, the more marked is the disappearance of the charge-free region of Fig. 18, characteristic for the pure ionic structure; hence, the less can we speak of two sharply separated spherical particles and the more do conditions approach the homopolar type of linkage now to be discussed.

b) *The Homopolar Linkage between Neutral Atoms*

In molecules of numerous elements—H_2, N_2, O_2, F_2, etc.—and in nearly all organic compounds, an entirely different type of linkage prevails. All properties in the solid, liquid and gaseous state indicate that the molecules of these substances are combinations of neutral atoms. The usual chemical representation of this type of linkage by a valence bond expresses in a very diagrammatic but truthful manner the absence of heteropolarity and the preference for definite primary linkage directions, in contrast to the spherically-symmetrical Coulomb field. More recently, G. N. Lewis in his octet theory has aimed at a refinement, in the sense that he invokes for each simple homopolar valence two electrons—each arising from one of the two conjugated atoms—an improvement in the theory which has been completely vindicated by subsequent quantum mechanical calculations. While the heteropolar valence concept is acknowledged to be very useful, furnishing, as it does, a structural model of oppositely charged ions and the quantitative relationship in equations (24) and (25), the corre-

[6] G. N. Lewis, *Valence and Structure of Atoms etc.* New York 1923.

[7] I. Langmuir, *J. Am. Chem. Soc.*, **41**, 868 (1919).

[8] F. Haber, *Verh. Phys. Ges.*, **21**, 750 (1919).

[9] K. Fajans, *Z. Elektrochem.*, **34**, 510 (1928); cf. also J. E. Mayer and M. Goeppert-Mayer, *Phys. Rev.*, (2) **43**, 605 (1933) and M. L. Huggins, *J. Chem. Phys.*, **5**, 143, 527 (1937).

sponding explanation of homopolar valence by the octet theory remained hypothetical and a quantitative proof was at first lacking.[10]

It was only the application by Heitler and London[11] of the Schrödinger equation to the problem of the hydrogen molecule that brought decisive changes and made possible the formulation of a potential function for this type of linkage also. The fundamental idea of the quantum mechanical theory, a detailed exposition of which would lead us much too far afield, (it can be studied in original works and in articles such as that of M. Dunkel and K. L. Wolf[12]), is as follows: If two neutral hydrogen atoms come near each other, their electrons gradually enter into reaction. Whereas a sodium

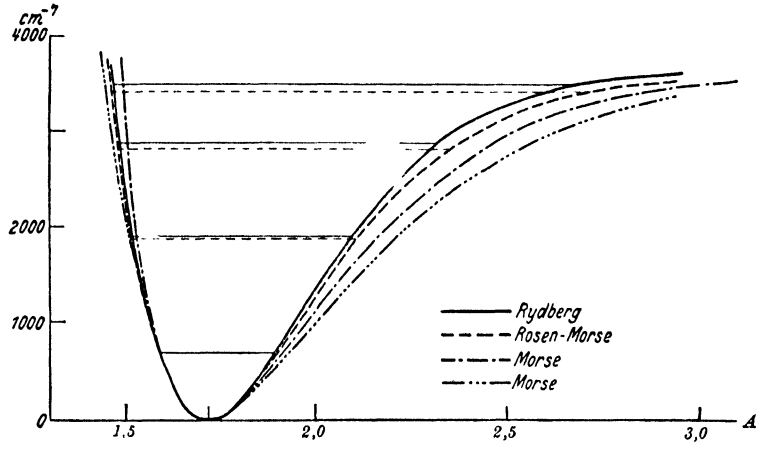


Fig. 19. Potential curves for homopolar linkages.

and a chlorine atom, on approaching to within 2–3 Å, combine in such a way that the former loses its loosely bound electron and the latter fills up its uncompleted shell, no such electrostatic dovetailing can occur in the case of two H atoms because of their identity. Rather, an interplay sets in between the two positively charged nuclei and the two electrons, the result being that in the finished molecule the two electrons envelop both nuclei with a cloud of extended charge and weld them together into a coherent and symmetrical structure.

Mathematical treatment leads to a potential function which, like (24),

[10] G. Briegleb, *Zwischenmolekulare Kräfte und Molekülstruktur*. Stuttgart 1937, p. 23 et seq.

[11] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

[12] M. Dunkel and K. L. Wolf, *Müller-Pouillet, Lehrbuch der Physik*, Vol. 4, part 3, p. 579.

expresses the total energy of the molecule as a function of the distance between the two H nuclei; it can be exactly calculated in the case of H_2 and in a few other instances. The agreement with experiment is satisfactory. Since an exact expression for the potential is possible only in the simplest cases and, even in these, the calculation is fairly complicated, we are usually content with approximate functions, which express the play of forces within a homopolar molecule just as equation (24) or (25) does for a heteropolar. Several authors have made proposals in this direction; an expression of Morse[13] is frequently used of the form

$$V = D\left\{e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\right\}. \tag{27}$$

It is particularly illuminating because the constants D and ν^{r_0} representing dissociation energy and nuclear distance in the position of rest have a direct physical significance. Other proposals which have proved more or less satisfactory in certain cases have been advanced by Rosen and Morse,[14] by Teller and Pöschl[15] and by Rydberg.[16] Fig. 19 shows the general form of the homopolar valence potential and indicates at the same time how much the various mathematical expressions differ from one another.

Recently an interesting study of the potential curve of the single, double and triple carbon-carbon linkage was made by Fox and Martin.[16] They start from an expression of the form

$$V = D\left(\frac{n}{m-n}\right)\left[\left(\frac{r_0}{r}\right)^m - \frac{m}{n}\left(\frac{r_0}{r}\right)^n\right] \tag{28}$$

where D is the energy of dissociation and is given by

$$D = \frac{kr_0^2}{m \cdot n}$$

r_0 = atomic distance in the equilibrium position
k = bond constant.

for all carbon-carbon linkages this equation assumes the form

$$V = D\left(\frac{r_0}{r}\right)^{4,55}\left[4{,}55\ ln\frac{r_0}{r} - 1\right] \tag{29}$$

[13] P. M. Morse, *Phys. Rev.*, (2) **34**, 57 (1929).

[14] P. M. Morse and N. Rosen, *Phys. Rev.*, (2) **42**, 143 (1932).

[15] G. Pöschl and E. Teller, *Z. Physik*, **83**, 143 (1933); cf. also P. M. Davidson, *Z. Physik*, **87**, 364 (1934).

[16] R. Rydberg, *Z. Physik*, **73**, 376 (1932); J. J. Fox and A. E. Martin, *J. Chem. Soc.*, **1938**, 2106; **1939**, 884.

If the different values for D are put into this relation r_0 can be calculated and compared with the experimental values. Table 36 shows the result of this calculation and exhibits a very satisfactory agreement between theoretical figures and experiment.

It should be especially emphasized that the quantum theory of the homopolar linkage is not exhausted in the formulation of this potential function. In the hands of Herzberg,[17] Hund,[18] Hückel,[19] Mulliken,[20] Pauling[21] and Slater[22] it has been used semiquantitatively to elucidate the existence of spatially defined valence directions, the free rotatory power around the single C—C bond (see p. 53), the rigidity of the double bond (p. 66), and the character of the aromatic linkage. These services of the modern atomic theory to chemistry are described fully in two books by L. Pauling[23] and H. Hellmann,[24] and in a recent monograph by L. Pauling. It would lead much too far astray to describe the content of this theory but the results will be referred to in many places.

TABLE 36

Bond	$k/10^5$ dyne/cm	r_0 obs. in Å	r_0 calc. in Å
C≡C	15.6	1.20	1.208
C=C	9.8	1.33	1.326
C—C arom.	7.6	1.40	1.395
C—C aliph.	4.4	1.56	1.556

If now, we pursue the matter to its end, namely to the distribution of the individual charges, (Eigen-functions), we must expect that, as a result of the common electron shell, which constitutes the homopolar bond, a certain accumulation of negative charge takes place along the line connecting the two atoms. Actually, H. G. Grimm[25] and his co-workers have

[17] G. Herzberg, *Leipziger Vorträge*, Leipzig 1931, p. 167.

[18] F. Hund, *Ergeb. exakt. Naturw.*, **8**, 147 (1929).

[19] E. Hückel, *Z. Physik*, **60**, 423 (1930); **70**, 204 (1931); **72**, 30 (1931); **76**, 628 (1931).

[20] R. S. Mulliken, *Phys. Rev.*, **40**, 751 (1932); *J. Chem. Phys.*, **7**, 339, 353, 356, 364 (1939).

[21] L. Pauling, *Phys. Rev.*, **40**, 891 (1932).

[22] J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931).

[23] L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics*. New York 1933. See also the article of L. Pauling in H. Gilman, *Organic Chemistry*. New York 1939. See *The Nature of Chemical Bond*, Ithaca 1939.

[24] H. Hellmann, *Quantenchemie*. Leipzig und Wien 1937.

[25] H. G. Grimm, R. Brill, C. Hermann and Cl. Peters, *Naturwiss.*, **26**, 29, 479, (1938); *Ann. Physik*, [5], **34**, 393 (1939).

shown, in their analysis of the diamond lattice already mentioned, that in exploring the charge density along a C—C bond, no region entirely free from charge is encountered. On the contrary, between the two atomic nuclei closely enveloped by negative electricity (Fig. 20), a charge bridge is found having an average density of 1.97 electrostatic units per Å^3. In contrast to the isolated closed charge clouds of the ions, we have here two electron shells blending with each other in which the valence direction is precisely fixed by the fact that there is no point of vanishing charge along this direction in space. The charge clouds which produce the

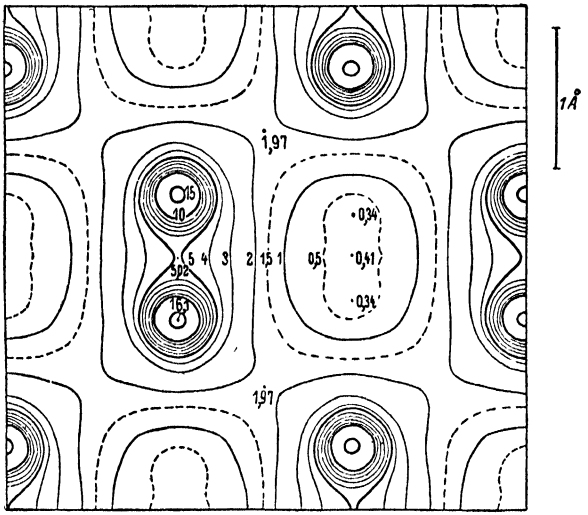


Fig. 20. The points of charge density 16.1 represent the positions of the centers of gravity of the C-atoms in the diamond lattice.

homopolar primary valence are fixed in space and form the valence scaffolding of the atom concerned.

This note brings us to the third primary valence linkage, viz., the metallic.

c) *The Metallic Linkage*

The metals do not follow the laws of either heteropolar or homopolar valence; rather there exists a characteristic new form of linkage concerning which we can say with certainty only that we know very little about it. The metallic linkage is practically or entirely unconcerned with the high polymeric organic substances to which special reference has been made

in the foregoing pages. The following brief note is given for purposes of completeness.

Everything points to the fact that in a metal, positively charged ions are embedded in an electron gas distributed over the whole crystal. This type of linkage can be conceived as arising from the homopolar, if the bond electrons abandon their sharply defined circuit in space and begin to permeate the whole lattice. They should not then be regarded merely as free, because they now move continually within the three-dimensional periodic field of the atomic lattice; they are, however, not bound to a given atom but are distributed over the whole lattice region and, just for this reason, are the cause of the high electrical conductivity which is so characteristic of the metallic state.

A potential expression for Na has been proposed by E. Wigner and F. Seitz,[26] which represents the binding energy very well and corresponds

TABLE 37

A Few Properties of the Metallic Linkage

	Wigner and Seitz	Slater	Experimental
Heat of sublimation (Cal./mol.)	25.6	9	26.9
Lattice distance in Å	4.2	3.2	4.23
Compressibility in cgs	1.6×10^{-11}	—	1.0×10^{-11}

roughly to the functions (24) and (27) in the other types of linkage; it will suffice to indicate in Table 37 the applicability of the expressions under test by a comparison between observed and calculated values.

The idea of widely dispersed electrons has been demonstrated experimentally by H. G. Grimm[27] through an accurate Fourier analysis of the Mg lattice. He showed that in this type of linkage, just as in the diamond, charge bridges lead over from one atomic core to another; spatial plotting indicated the presence, not of sharply delimited charge clouds but throughout the whole lattice. K. Froelich[28] has given a detailed account of this field of research in his book on the electron theory of metals; there is also the very comprehensive summary by A. Sommerfeld and H. Bethe in the *Handbuch der Physik.*[29]

[26] E. Wigner and F. Seitz, *Phys. Rev.*, **43**, 804 (1933); **46**, 509 (1934).
[27] H. G. Grimm etc. loc. cit.
[28] K. Fröhlich, *Elektronentheorie der Metalle.* Berlin 1936.
[29] 2nd ed., Vol. 24; Berlin 1933.

2. The Secondary Valences

While the heteropolar primary valence and the metallic linkage possess the ability to build up entire crystals from single units of NaCl or Na, the same forces serving to unite more and more new particles, it is characteristic of the homopolar primary valence that it very often ceases to act after the union of a few atoms and the aggregation becomes saturated. Such forces always give rise to a closed molecule which—as we shall see in considering high polymeric substances—comprises small groups of atoms and are closely knit structures.

Experience shows, however, that even after saturation of the primary valences inside the resulting molecules, forces still remain operative, which are generally known as residual or secondary valences. The first quantitative statements about these intermolecular forces were made by van der Waals in his theory of real gases when he introduced the internal pressure, a/V^2, so that we frequently speak of van der Waals forces.

The present state of our knowledge allows us to assume that these van der Waals forces between saturated molecules owe their existence to three different effects:

the orientation effect of rigid dipoles to which Keesom[30] first directed attention,

the induction effect of polarizable particles especially considered by Debye[31] and

a wave mechanical interaction of internal molecular electron motions, investigated by London and Eisenschitz[32] and by Slater and Kirkwood.[33]

a) The Orientation Effect of Rigid Dipoles

A dipole molecule (see p. 29) behaves at large distances as a neutral structure. However, on approach sufficiently close to be comparable with the distance d between the two charges, say, to 4 or 5 Å, the separation between those charges becomes significant. The particle can then influence similar particles by attraction between the unlike poles of each.

The equations for the dipole attraction may easily be derived from purely electrostatic considerations, and it will suffice here to describe the

[30] W. H. Keesom, *Physik. Z.*, **22**, 120, 643 (1921); **23**, 225 (1922).
[31] P. Debye, *Physik. Z.*, **21**, 178 (1920); **22**, 302 (1921).
[32] F. London and R. Eisenschitz, *Z. Physik*, **60**, 520 (1930).
[33] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

two special cases in which the dipoles are parallel or anti-parallel to each other (see Fig. 21). In the former case the potential V is given by

$$V_p(r) = -\frac{\mu_1 \cdot \mu_2}{r^3}, \tag{30}$$

in the latter by

$$V_a(r) = -\frac{2\mu_1 \mu_2}{r^3}. \tag{31}$$

It is presupposed that the distance r between the molecular centers of gravity is large compared with the distance between the charges d in any individual molecule. For the case $r = 5d$, the error in using (31) amounts to about 4%, at $r = 2d$ it is about 30%.

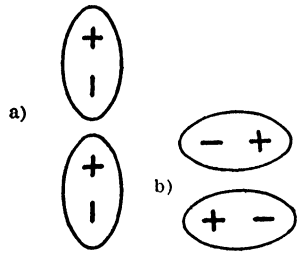


Fig. 21. Different positions of two dipoles with mutual attraction*

a) parallel Eq. (30)
b) anti parallel Eq. (31)

The meaning of this can be shown in an example: the dipole moment of the H_2O molecule amounts to about 1.8×10^{-18}; on dividing by the unit charge of 4.8×10^{-10} e.s.u., we obtain, according to the equation

$$\mu = e \cdot d$$

a value of about 0.4 Å as the effective distance of the charges from one another; we can therefore calculate the mutual actions of forces of two water molecules at the distance of 3–5 Å with tolerable accuracy from (30) and (31); with the proviso, of course, that there are no other forces acting between them (see p. 93). Were the centers of gravity of the molecules able to approach to 1.5 Å, which is impossible, owing to the repulsion of the charge clouds, it would no longer be legitimate to employ equation (30) and we should have to use another, somewhat more complicated equation.

Since a grouping which is established under the influence of the dipole force is always counteracted by thermal agitation, the orientation effect is highly dependent upon temperature.

b) The Induction Effect

This concerns the influence of the polarizability of the molecules. A molecule containing readily movable charges acquires a moment μ_i when placed in a field F, such that

$$\mu_i = \alpha \cdot F$$

α = polarizability.

Due to such moment (either alone or in conjunction with other existing moments), there results a mutual interaction between this and other neighboring molecules. Usually the permanent dipole of another molecule serves to induce the field; in this event the following relationships hold:

a) The inducing dipole μ lies parallel to the induced; in which case the potential is

$$V_p(r) = -2 \cdot \frac{\mu^2 \alpha}{r^6} . \tag{32}$$

b) The inducing dipole is perpendicular to the induced; then the equation is:

$$V_s(r) = -\tfrac{1}{2} \cdot \frac{\mu^2 \alpha}{r^6} . \tag{33}$$

Since the polarizability is a molecular constant this component of the van der Waals forces is less dependent upon orientation and therefore upon temperature than is the orientation effect.

c) *The Quantum Mechanical Interaction of Internal Electron Motions (Dispersion Effect)*

If we continue the quantum mechanical calculations which lead to the homopolar primary valence, we arrive, as a second approximation, at a further force effect between structures already saturated with respect to primary valence. From their magnitude, the distance between the interacting particles and also from the dependence of potential upon distance, these forces must be ascribed to secondary valences. Since they are related to the scattering of different wave lengths by the molecule, i.e. to the effect of frequency upon polarizability (dispersion), they are frequently called dispersion forces. They are obtained, according to London,[34] and Slater,[35] from the two equations

$$V(r) = -\tfrac{3}{4} \cdot \frac{\mathfrak{J} \cdot \alpha^2}{r^6} \text{ V} \quad \text{according to London and Eisenschitz} \tag{34}$$

$$V(r) = -\frac{\alpha^{\frac{1}{2}} \cdot n}{r^6} \cdot 7{,}07 \cdot 10^{-21} \text{ V} \quad \text{according to Slater and Kirkwood} \tag{35}$$

$\mathfrak{J}$ = energy of ionization
α = polarizability
n = number of electrons in the outermost shell.

---

[34] F. London, *Z. physik. Chem.*, (B) **11**, 22 (1930).
[35] J. C. Slater, *Phys. Rev.*, **37**, 2 (1931).

It is assumed that the interaction is between unexcited molecules and that the freely movable particles act on one another at a distance r which is large compared with their own diameter. If, as frequently happens, we wish to determine the interaction between larger molecules—paraffins, benzene, naphthalene etc.—we must resolve the total effect into the forces between separate, adjacent parts of molecules and recognize that the equations are applicable only if the distance of these particles from one another is greater than the cube root of the polarizability.

Since, in most of the atomic groups concerned—CH, CCl, CO, etc.—the polarizabilities lie between 2 and 5×10^{-24}, we see that for a mutual approach of 3–5 Å (equilibrium distance of secondary valence forces), this condition is sufficiently approximated to warrant an estimation of the effect.

TABLE 38

VAN DER WAALS ATTRACTION CONSTANTS FOR THE INERT GASES

	$a \times 10^{24}$	$\mathfrak{Z}$ (in Volts)	$a_{\text{theor}} \times 10^{-4}$	$a_{\text{exp.}} \times 10^{-4}$
He	0.20	25.5	4.8	3.5
Ne	0.39	25.6	25.8	21
Ar	1.63	17.5	144	135
Kr	2.46	14.7	254	240
Xe	4.00	12.3	432	410

In fact, if formula (34) is applied to the forces of attraction acting between atoms of the inert gases, there is very remarkable agreement with experience. Certainly these forces, in view of the spherical symmetry of the charge shells in the inert gases, can be attributed neither to orientation nor to induction effects; in them we have the pure dispersion effect, and the principle of its calculation can be tested fairly rigidly by comparison with experimental values. A glance at Table 38 shows that from He to Xe the increase of the van der Waals force constant a occurs very satisfactorily, and that the theoretical values agree astonishingly well with the experimental. We should remember that no factors other than polarizability and energy of ionization have been used in this calculation.

Since these two magnitudes are constants specific to the molecule itself, the dispersion effect is not dependent upon temperature.

d) Co-action of the Three Types of Secondary Valences

In the majority of cases the three special types of force just mentioned will contribute jointly to the molecular interaction responsible for the

van der Waals attraction. The total effect, then, is the sum of a component independent of temperature, a component slightly dependent upon temperature and a component strongly dependent upon temperature. The individual contributions are summarized in Table 39. We see that

TABLE 39

CONTRIBUTIONS OF THE DIFFERENT FRACTIONS OF THE VAN DER WAALS FORCES

	Dispersion forces	Induction forces		Orientation forces	
Appearing in	All molecules	Dipole molecules	Quadrupole molecules	Dipole molecules	Quadrupole molecules
The contribution to potential depends upon	$-r^{-6}$	$-r^{-6}$	$-r^{-8}$	$-r^{-3}$	$-r^{-5}$
Dependence on temperature	nil	slight		fairly marked	

TABLE 40

VAN DER WAALS ATTRACTION CONSTANTS FOR POLYATOMIC MOLECULES

1	2	3	4	5	6	7
Substance	$\alpha \times 10^{24}$	b_0 cm³/mol	$\mathfrak{Z}$ in volt	$a \times 10^{-6}$		
				van der Waals	Calculated by London	Calculated by Slater
HCl	2.71	53.5	13.7	3.66	2.12	2.56
HBr	3.85	58.9	13.3	4.42	3.83	3.93
CO	1.99	51.5	14.3	1.44	1.24	1.86
N_2O	3.00	58.8	11.23	3.77	1.59	3.82
H_2S	3.78	57.3	10.42	4.43	2.95	3.93
NO	1.78	34.6	14.4	1.29	1.46	2.42
N_2	1.74	52.8	17	1.34	1.09	1.45
O_2	1.57	42.5	13	1.36	0.89	1.81
Cl_2	4.60	73.0	18.2	6.32	6.03	5.48
CO_2	2.86	57.1	15.45	3.61	2.50	3.60
CH_4	2.58	57.0	14.5	2.24	1.92	2.23
C_2H_2	3.32	68.4	12.25	4.39	2.22	3.02
C_2H_4	4.10	76.3	12.2	4.45	3.10	3.84
C_2H_6	4.50	85.3	12.75	5.39	3.42	4.53

dipole force diminishes by lower powers of r than the other two effects; at greater distances, therefore, the former will predominate and at smaller distances, the latter.

A calculation by London and Eisenschitz[36] of the van der Waals a in a

[36] F. London and R. Eisenschitz, *Z. Physik*, **60**, 520 (1930).

series of polyatomic molecules shows that, even with fairly high polarity, the dispersion effect always supplies a very considerable share of the total attraction.

Table 40 gives a few data regarding the calculation of the van der Waals a for polyatomic molecules; there is always fair agreement between the measured and calculated internal pressure constant. The ratio of induc-

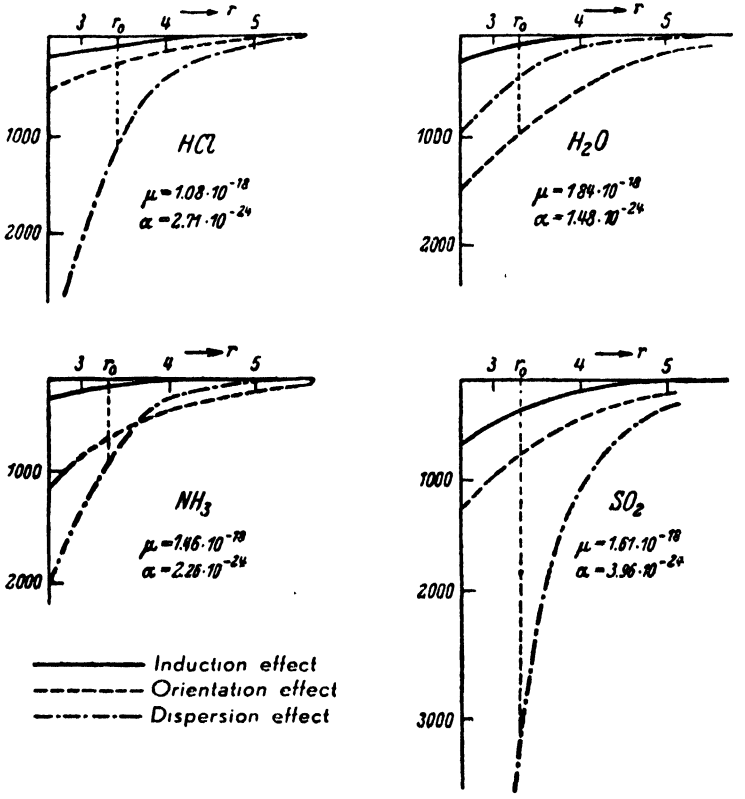


Fig. 22. Combined action of induction, orientation and dispersion effects.

tion to dispersion effect can be clearly seen from Table 41; it is evident that even with a very strongly dipolar molecule like water, the mutual polarization is only about 20% of the dispersion effect. The orientation effect of the permanent dipoles in such molecules so largely dominates the two other effects that it is not surprising that one was inclined for a long time to attribute the van der Waals forces mainly to the interaction of permanent dipoles.

Fig. 22 shows the co-action of all three effects in HCl, H_2O, NH_3 and SO_2 and demonstrates that in all cases where the distance is short the dispersion effect predominates, whereas at greater distances, the orientation effect becomes increasingly apparent; the polarization component then plays only a subordinate rôle. The ratio between directional effect and dispersion effect may be calculated directly for simple molecules; it is

TABLE 41

RATIO OF INDUCTION TO DISPERSION EFFECT

	$\mu \times 10^{18}$	$\alpha \times 10^{24}$	$\mathfrak{J}$ in volts	$\frac{\text{Induction}}{\text{Dispersion}}$
CO	0.12	1.99	14.3	0.0008
HBr	0.78	3.85	13.3	0.020
HCl	1.03	2.71	13.7	0.048
NH_3	1.50	2.21	16	0.106
H_2O	1.84	1.48	18	0.20

TABLE 42

RATIO OF DIPOLE FORCE TO DISPERSION FORCE

	HCl	H_2O	NH_3	H_2S	HCN
$\frac{\mu^2 r^3}{\alpha^2 \mathfrak{J}} 0.617 \times 10^{12}$	0.29	1.53	1.02	0.164	1.64

evident from equations (30) and (34) that it depends upon the magnitude of the quotient

$$Q = \frac{\mu^2 r^3}{\alpha^2 \mathfrak{J}} \times 0{\cdot}617 \times 10^{12}.$$

Table 42 shows values for this quotient; if they are small compared with unity, as is usually the case, the dispersion effect is predominant, if they reach unity or over, the influence of the permanent dipoles prevails.

In small, weakly polarizable molecules, having strong, easily accessible moments—H_2O, SO_2, HF—the directional effect may be so prominent that it causes the formation of double molecules. Particularly intense interactions always take place if strong dipoles are present on the one hand and easily polarizable molecular components are available, on the other. In such cases it may be anticipated that well defined portions of larger molecules interact and give rise to stable, stoichiometrically constructed complex compounds.

Although it is customary in the kinetic theory of gases, and is certainly

justifiable in the mathematical treatment of perfect gases, to regard individual molecules as rigid elastic spheres, it is in no way legitimate to do so if we are considering their interaction over short distances. On the contrary, we must bear in mind in this case that molecules—in close enough proximity—are extraordinarily sensitive and reactive. They have no less than three different possibilities of interaction and it will be the further purpose of this presentation to show what finer features enter into the formation of radicals, the aggregation of particles and later also the construction of crystals.

3. General Remarks on the Formation of Molecule Aggregates

We shall begin by discussing those cases which give rise in vapor, in solution and notably in the liquid phase, to more or less durable groups of molecules without the formation of chemical compounds capable of isolation. The arrangement brought about by the influence of molecular forces is in these cases so quickly destroyed by thermal agitation, that any two molecules remain only momentarily in close proximity and are unable to form an aggregate vibrating for a longer period about a definite position of minimum potential energy. In spite of this, the tendency to association as such may be quite appreciable, because, when a molecular group breaks up, each of the components immediately joins to form a new group. Any given molecule thus nearly always finds itself in some sort of group association but never in the same one for long. Groups are always present but they very rapidly interchange their components in space and time.

a) Aggregate Formation by Dipole Forces

Relations have already been stated on page 92 for expressing in the case of parallel and anti-parallel arrangement, the potential of the mutually attracting particles as a function of the distance; these relations indicate directly the conditions under which the two dipoles assume the parallel position, and so are able to promote chain formation, and those under which they prefer to assume the anti-parallel arrangement.

The ratio r_p^3 (parallel arrangement) to r_a^3 (anti-parallel) determines this. It depends upon whether the centers of the molecules are brought nearer together by one arrangement or the other. Conditions for HF are illustrated in Fig. 23, due to G. Briegleb; in this case $r_a^3 \approx 2r_a^3$ ($44 \approx 43$) so that the question cannot be decided in the absence of further information; on the other hand, in water there is a preference for the series arrangement of the dipoles; here, $2r_a^3 \gg r_p^3$ ($128 \gg 22$) which Jona [37] was able to confirm

[37] M. Jona, *Physik. Z.*, **20**, 14 (1919).

by measuring the molar polarization at low temperatures, where the H_2O vapor is still partially associated (see Fig. 24).

Briegleb[38] was also able to obtain data on the depth of the potential trough, through which such favored positions are stabilized with regard to the individual effects; we obtain for water, for a distance 2.8 Å between the centers of gravity, a binding strength of the dipole pair of 3500 cal. per mol. We arrive at similar values for H_2F_2, while methyl fluoride, on account of the increase in distance caused by the CH_3 group, shows a weaker association tendency. If we pass to longer chains, the anti-

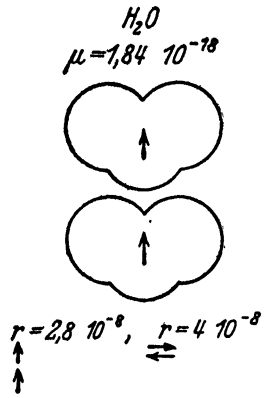


Fig. 23. Association of HF to H_2F_2.

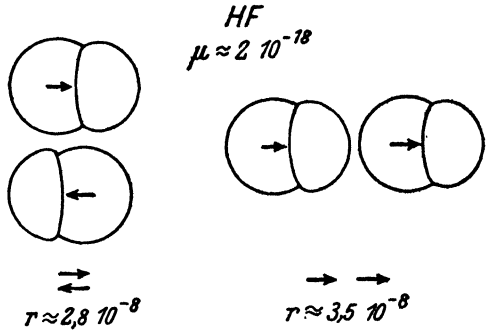


Fig. 24. Association of H_2O to double molecules.

parallel arrangement of the dipole molecules gradually prevails, as is readily apparent on geometrical grounds. The addition of water to ketones, which, according to Stuart,[39] Wolf[40] and Meerwein[41] should conform to the pattern shown in Fig. 25 due to Briegleb,[42] is of interest. In this, the spatial screening of the C=O dipole favors the appearance of a chain-like series arrangement.

If a dipole—C=O, OH, NH_2—is heavily loaded with purely homopolar groups, it may happen that the minimum distance within which the polar

[38] G. Briegleb, *Zwischenmolekulare Kräfte und Molekülstruktur*. Stuttgart 1937, p. 52 et seq.

[39] H. A. Stuart, *Z. Physik*, **51**, 490 (1928).

[40] K. L. Wolf, *Z. physik. Chem.*, (B) **2**, 39 (1928).

[41] H. Meerwein, *Ber.*, **62**, 999 (1929); **66**, 411 (1932).

[42] G. Briegleb, l.c. book p. 57.

groups of two molecules can approach is so great that the directional effect becomes less consequential than the dispersion effect of the apolar groups. That is, when the r values associated with the centers of gravity of the dipoles are large, the apolar groups can naturally approach much closer. The properties of the molecules involved then resemble very closely those of the corresponding hydrocarbon. An excellent example of this is shown in Table 43 which gives boiling points, according to Briegleb, of the isomeric butyl alcohols as a measure of inter-molecular forces.

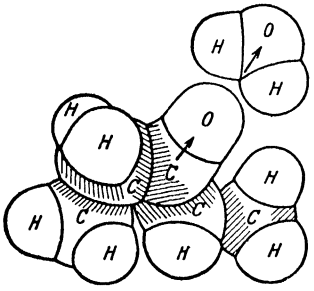


Fig. 25. Position of water on diethyl ketone.

Under the influence of a sufficiently strong dipole, even the electron shells of a symmetrical molecule, such as a tetrahedral one can be deformed so much that a considerable dipole moment results. There is likewise a possibility, under certain conditions, of a *deformation of the nuclear framework.* For example, Ulich[43] was able to demonstrate a very considerable dipole moment (2.46×10^{-18}) in liquid $SnCl_4$, while in the gaseous state the substance has a moment of practically zero and exhibits complete tetrahedral symmetry. The same is true with $AlCl_3$, $TiCl_4$ and other metallic halides. Moreover, highly symmetrical molecules may deform one another, as we may infer, for example, from the lattice of the monoclinic modifications of CBr_4 described by Mark.[44]

TABLE 43

BOILING POINTS OF THE ISOMERIC BUTYL ALCOHOLS

Substance	Boiling point
C_4H_9OH normal	117
secondary	99
tertiary	83
C_5H_{12}	37

Fig. 26 shows, according to Briegleb, the angular deformation which may occur in $BeCl_2$ under the influence of a polar organic molecule when the two are in contact. In Fig. 26 the C=O group is taken as the deform-

[43] H. Ulich, *Angew. Chem.*, **44**, 750 (1931).
[44] H. Mark, *Ber.*, **57**, 1820 (1924).

ing dipole; its influence ceases when the effective spheres of CO and Be make contact (see p. 121).

The symmetry of the electron shell is naturally altered more easily by the field of a highly polar molecule than is the nucleus. The first consequence is the induction of a moment with all the resulting phenomena already discussed. Occasionally, however, deformations of this type proceed further and lead to very interesting transition phenomena, which are intermediate between the types of linkage previously outlined. According to Meerwein,[45] they may play an important rôle, on account of their peculiar reactivity, in homogenous catalysis through the grouping and formation of intermediate compounds.

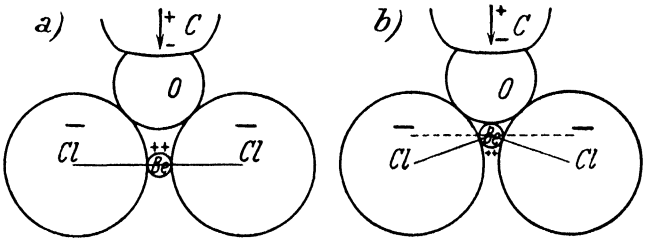
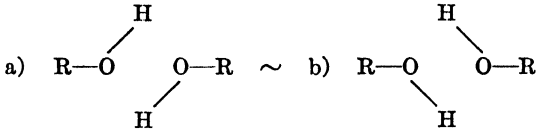


Fig. 26. Angular deformation in $BeCl_2$ by a polar molecule.

Thus, Onsager[46] has suggested that, in the association of two alcohol molecules according to the scheme of anti-parallel assemblage

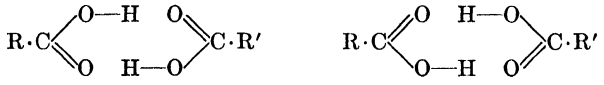


a quantum mechanical resonance effect is possible, because the two arrangements, a) and b), which result from an exchange of hydrogen atoms between the two molecules, display the same energy but have different geometrical arrangements; therefore they can give rise to a quantum mechanical exchange resonance. Such a resonance can, of course, appear only if the two structures remain sufficiently long in a favorable geometrical position. The dipole forces, however, serve to do just this. As a result of such a resonance, we may expect a particular stability of this complex with simultaneous attachment of the two H atoms to each molecule. Actually it can be observed that the Raman line of the OH frequency for

[45] H. Meerwein, *J. prakt. Chem.*, **141**, 123 (1934).
[46] L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).

alcohols in transition from gaseous to liquid state is practically extinguished, which can readily be explained in terms of the above.

Similar conditions obtain, according to Gilette and Sherman,[47] in the interaction of two carboxyl groups leading to the formation of the well known *double molecules of fatty acids.* The formulas indicate



that, by the exchange of two hydrogen atoms, it is possible to construct two arrangements of the atoms which are equal in energy value but different geometrically. In terms of quantum mechanics, this corresponds to the case that several Eigen-functions (possibilities of geometrical arrangement) belong to one and the same Eigen-value (total energy of the system) and the term *degeneration* will be applied to it. The result of this degeneration is that an intermediate stage consisting of both arrangements above is produced, which is more stable with regard to energy than either one of them. According to Sidgwick,[48] this intermediate may be considered as one in which the two hydrogen atoms are continually changing places at a definite frequency between the two molecules. The dipole attraction contributes to this effect viz.: in the first place, it produces the arrangement depicted above—which gives rise to resonance—at the same time helping to stabilize it over a long period in face of the destroying influence of thermal agitation. We, therefore, have before us a case in which dipole force and quantum mechanical effect (namely an exchange effect of the first order) reinforce each other.

Recently a very interesting survey on the hydrogen valence (*hydrogen bond or bridge*) was given by Huggins.[49] The Table 44 gives brief information regarding the energy of dissociation which is needed to break hydrogen bridges between different atoms, Table 45 regarding the length of these bridges. It seems that this bond not only plays an important rôle during the formation of molecular compounds, but it also influences to a very high degree the cohesion and the symmetry of crystals. In high polymeric chemistry, hydrogen links seem to be important factors in the structure of cellulose and keratin.

[47] R. H. Gilette and A. Sherman, *J. Am. Chem. Soc.*, **58**, 1135 (1936).

[48] N. V. Sidgwick, *Electronic Theory of Valence.* Oxford 1929.

[49] M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936); cf. also J. M. Robertson, *Science Progr.*, **23**, 663 (1939); E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937); S. C. Stanford and W. Gordy, *J. Am. Chem. Soc.*, **62**, 1247 (1940).

A considerable *deformation of the electron cloud* seems to result also in BF_3, $AlCl_3$ and $AlBr_3$ under the influence of strong dipoles, in the sense that, through this additional polarization effect, the bonds between the central metallic atom and the halogens become more polar. Thus, according to Klemm,[50] by addition of the molecule of NH_3 to $AlBr_3$, the character of the AlBr binding is displaced towards the polar side, so that, ultimately, by the entrance of more NH_3 molecules, the molecular addition compound $AlBr_3 \cdot NH_3$ is converted into an ionic interstitial compound $[Al(NH_3)_3]^{+++}Br_3^-$.

Briegleb and Lauppe[51] were able to detect in the Raman spectrum a similar effect in the molecular association between $AlCl_3$ and ether.

TABLE 44

LENGTH OF HYDROGEN BRIDGES

Bridge	Length in Å
F—H—F	2.25–2.51
O—H—O	2.50–2.30
N—H—N	2.65
N—H—F	2.63
N—H—O	2.76–2.88

TABLE 45

DISSOCIATION ENERGY OF HYDROGEN BONDS

Bond	Dissociation energy in cal. per mol
F—H—F	6.2
O—H—O	5.9–10.15
C—H—N	6.1–7.8
N—H—F	6.0
C—H—O	4.1–6.0
N—H—O	6.0–6.8

b) Aggregate Formation by Dispersion Forces

It has previously been shown that dispersion and induction forces decrease with distance between interacting molecules to a much greater extent than do the dipole forces ($\backsim r^{-6}$); they can therefore be mutually effective only when the particles are very close together. Experience confirms this expectation. While, as explained above, the force effects between dipole molecules in the gaseous state and also in the state of more or less dilute solution may induce the formation of associations of long duration, the corresponding effectiveness of the dispersion forces is restricted to the production of very transient groups in the liquid state, possibly also in very concentrated solutions.

Briegleb[52] has suggested that the individual particles in molecular groups whose composition fluctuates in space and time must on the average

[50] W. Klemm, *Z. anorg. allgem. Chem.*, **200**, 367 (1931).

[51] G. Briegleb and J. H. Lauppe, *Z. physik. Chem.*, (B) **28**, 154 (1935).

[52] Cf. G. Briegleb, book l.c. p. 50 et seq.

always arrange themselves preferably parallel to the axes or planes of their maximum polarizability, so that molecular interaction is strongly promoted by maximum packing density of rod-shaped or laminated molecules, since the forces depend so much upon distance. Later, in discussing the liquid phase, we will describe in detail the experimental methods on which present ideas about liquid structure are based; in anticipation it may be observed that both the interferometric investigation with x-rays, the Kerr effect and the degree of depolarization prove beyond doubt the existence of such clusters and show that non-polar chain molecules, e.g. paraffins, olefines, etc., orient themselves parallel to their long axes, whereas laminated ring systems, such as benzene, naphthalene, etc. arrange themselves parallel to the plane of the ring. The well known experiments of Langmuir on the behavior of monolayers are excellent examples for the aggregation of long chain molecules.

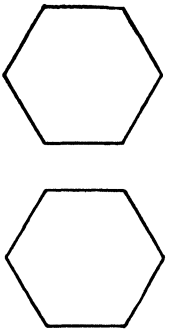


Fig. 27. This position of the two benzene rings is not favorable to the formation of an *association configuration.*

De Boer[53] estimated the magnitude of the effect in benzene. If we calculate, from quantum mechanical postulates on electron distribution in the benzene nucleus, the interaction between two benzene molecules in the position of Fig. 27, we must assume—on the basis of the effective radii of the H atoms given in Table 11—a distance of 3.5 Å between the centers of the two rings. At the same time we should remember that easily mobile and therefore highly polarizable charge components near the center of the ring (which, according to E. Hückel,[54] correspond per ring to about the equivalent of two electrons, and are responsible for the aromatic character of the molecule), cannot approach very closely and are screened from one another by the highly stable periphery of the ring. If, however, the two benzene rings are placed in the position of Fig. 28, their centers can approach each other to within a distance of about 2.6 Å and the easily polarizable components of both charge clouds can lie directly opposite each other.

An estimation shows that the energy of interaction in the Fig. 28 position is about three times as great as that of Fig. 27 and its absolute value is about 10^3 cal. per mol. The formation of groups or clusters offer-

[53] J. H. de Boer, *Trans. Faraday Soc.*, **32**, 10 (1936).
[54] E. Hückel, *Z. Physik*, **70**, 204 (1931); **75**, 628 (1932).

ing resistance to thermal dissociation is thus feasible. De Boer has suggested that in polystyrene the benzene rings in close spatial proximity may probably assume the parallel arrangement shown in Fig. 28 and it is conceivable that through this mutual effect the original flexibility of the polymethylene chain is very adversely affected, so that the resilient properties of the substance diminish at ordinary temperature. Polystyrene does, indeed, possess rubber-like properties to a certain degree at higher temperatures where the mutual effect of the substituted benzene rings, which *per se* is not very great, becomes even less.

In conclusion, a few rules governing boiling points may be mentioned. The boiling points of hydrocarbon chains are known to rise with length of chain and to fall in branched chains having the same number of carbon atoms, because, on branching, the molecule becomes more bulky and on purely geometrical grounds a denser packing of the reacting groups becomes difficult. The possible effect of geometrical packing on the boiling point is shown in Table 46, in which boiling points of normal hydrocarbon chains are compared with those of the corresponding ring systems. The open chains possess a certain measure of free rotatory power, which is opposed to a regular parallel arrangement; in the cycloparaffins, however, it is to be expected that the free mobility of the methylene groups is greatly restricted and is limited merely to vibrations of moderate amplitude. Therefore the ring-shaped molecule should be better able to form aggregates than the open chain. A glance at Table 46 shows that experiment fully confirms this expectation.

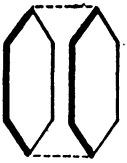


Fig. 28. Most favorable position of two benzene molecules for the formation of a group preferred on energy grounds.

TABLE 46

BOILING POINTS OF PARAFFIN CHAINS AND CLOSED RINGS

	B.P.		B.P.		B.P.		B.P.		B.P.
Pentane	37°	Hexane	69°	Heptane	98°	Nonane	150°	Heptadiene	107°
Cyclo-pentane	50°	Cyclo-hexane	80°	Cyclo-heptane	118°	Dicyclo-nonane	170°	Cyclo-heptadiene	118°

We have tried in the foregoing to outline a general picture of the mode of action of intermolecular forces in the formation of aggregates preferred on considerations of energy. Now we shall proceed to discuss a few cases in which the existence of these forces leads to the production of relatively

more stable molecular associations than those which have been investigated previously.

4. Molecular Associations and Intermolecular Forces

From the large number of previously studied molecular associations which owe their existence to the action of intermolecular forces, we shall, in this section, which is merely a preliminary to the discussion of the properties of high polymers, select only two groups and discuss them in some detail.

a) The molecular associations of unsaturated hydrocarbons and

b) The molecular associations in the carboxylic acids.

In both cases the application of the general viewpoints outlined above will afford a fairly deep insight into the mechanism of the formation of these molecular associations and throw light on the analogous relationships in high polymeric substances.

a) The Molecular Associations of Unsaturated Hydrocarbons

We shall first discuss the molecular *associations of organic nitro compounds with unsaturated hydrocarbons*, familiar since the time of Pfeiffer[55] and more recently studied in detail particularly by Briegleb,[56] Bruni,[57] Hertel,[58] Lennard-Jones[59] and other workers. All the evidence indicates that the easily mobile charge components of the aromatic and aliphatic unsaturated hydrocarbons are polarized by the strong dipole fields of the nitro groups. There ensues an attraction and the electron clouds of the two molecules are brought nearer together in consequence; the result is that the dispersion effect comes into play and the stability of the association is assured. The relatively far-reaching dipole fields therefore ensure the proximity of the two components of the association; the dispersion force stabilizes it.

This view receives strong support from the data in Table 47, for which we are indebted to Briegleb and his co-workers.[60] They show that the energy of formation of the molecular association between trinitrobenzene and various aromatic hydrocarbons increases with the average *polariza-*

[55] P. Pfeiffer, *Organische Molekülverbindungen*, 2nd ed. Stuttgart 1927.

[56] G. Briegleb, *Z. physik. Chem.*, (B) **19**, 255 (1932); **26**, 63 (1934); **27**, 474 (1935); **31**, 58 (1935); **32**, 305 (1936).

[57] G. Bruni, *Gazz. Chim. ital.*, **34**, 474 (1904); **35**, 304 (1905).

[58] E. Hertel, *Z. physik. Chem.*, (B) **11**, 59, 90 (1930).

[59] J. E. Lennard-Jones, *Trans. Faraday Soc.*, **22**, 1, 37 (1936); *Proc. Roy. Soc., London*, **45**, 475 (1931).

[60] Cf. the book of G. Briegleb, table 13 on p. 106 and table 14 on p. 107.

bility of the substances, from which latter the induction and dispersion effects can be calculated. The stability of the existing molecular association seen from Table 48 agrees entirely in order of magnitude with expectation; a dipole of the strength of about 4×10^{-18}, as in the nitro group, exerts, according to Briegleb,[61] an attraction potential of about 2000 cal. per mol on a molecule with an average polarizability of 20×10^{-24} cm^3, such as occurs in the unsaturated hydrocarbons, at a distance of 3 Å.

TABLE 47

ENERGY OF FORMATION OF THE MOLECULAR ASSOCIATIONS OF TRINITROBENZENE WITH AROMATIC HYDROCARBONS (SOLVENT CCl_4)

Hydrocarbon	Naphthalene	Phenanthrene	Anthracene
Energy of formation in Cal.	3.4	4.0	4.4
Average molecular polarizability $\times 10^{24}$	18.2	26.4	30.8
Hydrocarbon	**Styrene**	**Phenylbutadiene**	**Diphenylbutadiene**
Energy of formation in Cal.	1.81	2.15	2.88
Average molecular polarizability $\times 10^{24}$	14.18	18.85	32.6

TABLE 48

HEATS OF FORMATION OF MOLECULAR ASSOCIATIONS AS AFFECTED BY THE NUMBER OF NITRO GROUPS

Compound	s-Trinitrobenzene Acenaphthene	m-Dinitrobenzene Acenaphthene	Nitrobenzene Acenaphthene
U in Cal.	2.45	1.35	Very small
Compound	**s-Trinitrobenzene Naphthalene**	**m-Dinitrobenzene Naphthalene**	**Nitrobenzene Naphthalene**
U in Cal.	3.4	1.6	Very small
Compound	**s-Trinitrobenzene Anthracene**	**m-Dinitrobenzene Anthracene**	**o-Dinitrobenzene Anthracene**
U in Cal.	3.6	1.5	2.9

Moreover, the number of nitro groups has a very important influence, as shown by Table 48, on the bond strength of the resulting molecular association; recent measurements of Halban and Zimpelmann[62] and of Briegleb and Schachowsky[63] have proved this.

[61] Cf. the book of G. Briegleb, p. 110 et seq.

[62] H. v. Halban and E. Zimpelmann, *Z. physik. Chem.*, (A) **117**, 461 (1925).

[63] G. Briegleb and Schachowsky, *Z. physik. Chem.*, (B) **19**, 255 (1931).

It is possible from these direct experimental findings, which express the stability of the associations in terms of energy, to derive valid concepts regarding the spatial arrangement of the two components of such a molecular association. The actions of forces involved will certainly reach their maxima with a parallel arrangement of the ring planes of the two associating molecules. Figs. 29 and 30 of Briegleb,[64] seen in plan and in elevation, probably express the most favorable association of dinitroben-

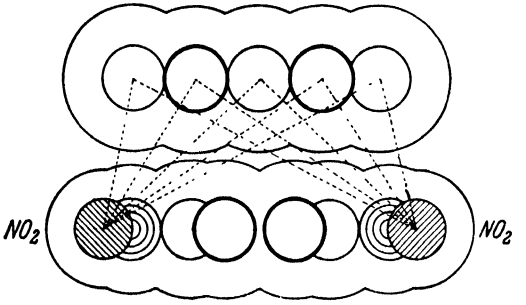


Fig. 29. Side view of the complex naphthalene (above) -p-dinitrobenzene (below); the ranges of action are indicated by the faint outlines.

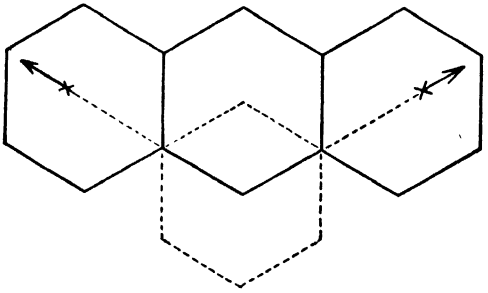


Fig. 30. Complex anthracene (heavy line) -m-dinitrobenzene (dotted line) seen from above.

zene with naphthalene and anthracene respectively. We may infer from the first figure, which represents the atoms of the two molecules and their spheres of action in the proper proportions, that such a position ensures the maximum proximity of the two charge clouds; any oblique position of one or other partner would considerably enlarge the distances involved in the interaction. Fig. 30 shows again that in this grouping, the permanent di-

[64] Cf. the book of G. Briegleb, p. 109 and 110.

poles of the nitro groups ($\mu \approx 4 \times 10^{-18}$) attain very close proximity to any particularly easily displaceable charge components found near the center of the benzene rings and can therefore polarize them especially strongly.

Before we pass to the discussion of *molecular associations* of aliphatic carboxylic compounds it may be observed that the peculiar aptness of aromatic systems for the formation of such associations is probably due to the fact that on ring closure the free rotatory power of the individual CH groups is annulled and, that, again through ring closure, larger charge components of higher polarizability are closely compressed in space thus becoming readily susceptible to the deforming effect of strong dipole fields.

TABLE 49

BINDING STRENGTH OF A FEW MOLECULAR ASSOCIATIONS BETWEEN NITRO AROMATICS AND CONDENSED RING SYSTEMS

	Binding energy of the molecular association of s-trinitrobenzene in Cal.			Binding energy of the molecular associations of anthracene in Cal.	
	U observed	U calculated		U observed	U calculated
With benzene.....	ca. 0.6	1.8	With *o*-dinitrobenzene....	3.0	2.9
" styrene.....	1.8	2.6	" *m*-dinitrobenzene...	1.6	1.5
" naphthalene...	3.4	3.1	" *p*-dinitrobenzene....	1.45	1.2
" anthracene.....	4.4	4.6	" *s*-trinitrobenzene...	4.6	3.6

Orientation associations of trinitrobenzene with styrene, stilbene and other polyenes are known; the number of associated nitro groups is generally equal to the number of the phenyl residues in the molecule. Kuhn and Winterstein[65] conclude from this, that—in the sense of the above information—the nitro-aromatics prefer interaction with the benzene nucleus to that with polyene chains.

Briegleb[66] undertook the attempt of estimating the binding strength of a whole series of molecular associations on the basis of the charge distribution, obtained by quantum mechanics, in the aromatic ring systems and in the aliphatic conjugated polyene chains; he arrived at the data given in Table 49. Comparison with a few data determined experimentally confirmed this estimation completely and gives us confidence in the accu-

[65] R. Kuhn and H. Winterstein, *Helv. chim. Acta*, **11**, 144 (1928).

[66] G. Briegleb, *Z. physik. Chem.*, (B) **26**, 63 (1934); **27**, 474 (1935); **31**, 58 (1935).

racy of other calculated energies of formation at least with regard to order of magnitude.

In conclusion, molecules other than nitro-compounds, having strong total moment or strong group moments, e.g. $AlCl_3$, quinone, phthalic anhydride, can produce with molecules possessing easily polarized groups molecular associations of remarkable stability, the production of which should be governed by the theory outlined above.

b) Molecular Associations between Carboxylic Acids

The existence of double molecules of carboxylic acids has been recognized for a long time. Fenton and Garner[67] and more recently Coolidge[68] have furnished proof in the gaseous aggregate state by measuring vapor density. Molecular weight determinations in solution were carried out some time ago by Trautz and Moschel[69] and by a number of other authors with the same result, and numerous exceptions to the Trouton and Eötvös rule in the liquid state are additional proof of the existence of associations.

We have already shown on page 63 the arrangement between two carboxyl groups which, after preliminary attraction of the dipoles, affords the possibility of a quantum mechanical exchange resonance and which is probably responsible for the production of molecular associations in chains of not excessive length. Actually, Pauling and Brockway[70] have confirmed experimentally the existence of such an arrangement in lower members of the carboxylic acid series by electron deflection. Moreover, the extensive studies carried out by Müller,[71] Trillat,[72] Langmuir and others over a long period into the arrangement of fatty acid chains in the crystal and in liquids by the aid of x-rays, all show that the interaction between the carboxyl groups is mainly that of the van der Waals forces between such molecules.

This view is also supported by the fact that on esterifying the group, the tendency to form molecular associations is completely lost. In terms of the information on page 63 there are two reasons for this. First, by steric screening, the effect of the dipole field of the COOH group is diminished and, in the absence of a mobile H atom, any quantum mechanical

[67] M. Fenton and W. E. Garner, *J. Chem. Soc.*, **1930**, 694.

[68] A. S. Coolidge, *J. Am. Chem. Soc.*, **50**, 2166 (1928).

[69] M. Trautz and W. Moschel, *Z. anorg. allgem. Chem.*, **155**, 13 (1926).

[70] L. Pauling and L. O. Brockway, *Proc. Nat. Acad. Sc. USA*, **36**, 430 (1930).

[71] Cf. A. Müller, *Proc. Roy. Soc. London*, (A) **154**, 624 (1936) and many investigations published in the same periodical in the last 15 years.

[72] Cf. J. J. Trillat, *Ann.phys.*, **6**, 5 (1926), J. J. Trillat and H. Motz, **7**, 101 (1928).

resonance effect is impossible. The H valence of Pauling[73] and Sidgwick[74] is cut out on replacing the hydrogen by an alkyl group.

Table 50 sets out the energy relationships. It is evident, at least in acids with short chains, that the energy of formation of the double molecule decreases on enlarging the non-polar group, the reason being that its presence prevents minimum approach of the carboxyl groups.

To what extent the non-polar lipoid components of long-chain hydrocarbon molecules screen the effect of the polar hydrophile, and outwardly attain the ascendancy through their own force effects, cannot be stated with certainty. It is, however, very probable that the COOH group is responsible, in the sense discussed above, for the presence of double molecules of benzoic acid in benzene; whereas, for an association effect in water, it is rather a case of interaction of benzene nuclei, because in aqueous solution the COOH groups must certainly be extensively hydrated.

TABLE 50

ENERGY OF FORMATION OF DOUBLE MOLECULES OF SIMPLE CARBOXYLIC ACIDS

	Formic acid	Acetic acid	Heptoic acid	Benzoic acid
B.P.	374.3°K	391.3°K	496.3°K	—
U in Cal.	14.3	13.8	7.05	5.6

Moreover, the well-known experiments of Adam,[75] Langmuir,[76] Rideal[77] and others on the spreading of fatty acids and other long-chain compounds on the surface of water show that in the adsorption of the COOH groups by the water surface, the tensile properties of the resulting film are mainly determined by the parallel orientation of the chains under the influence of non-polar dispersion forces and depend in characteristic fashion on chain length and on the extent of branching. In addition, Traube's law on the heats of adsorption of homologous fatty acids confirms the influence of the lipoid fraction of these molecules. We shall return later to the very marked interaction between different types of molecules in the liquid phase in the section on solutions. Here, in concluding the discussion of well-defined molecular associations, the above data may be sufficient.

[73] L. Pauling, *Proc. Nat. Acad. Sc. USA*, **13**, 359 (1928).

[74] N. V. Sidgwick, Ann. Rep. Chem. Soc. **30**, 110 (1933); *Properties of Covalent Link.* Ithaca 1933. cf. also M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936).

[75] N. K. Adam, *The Chemistry of Surfaces.* 2nd Ed. Oxford 1938.

[76] I. Langmuir, *Colloid Chemistry.* New York 1926.

[77] E. K. Rideal, *Surface Chemistry.* 2nd ed., London 1930.

c) *Calculation of the Molecular Cohesion*

A few quantitative data have already been given regarding the magnitude of the intermolecular forces, which show that, generally speaking, secondary valence forces exist of the order of 500–5000 cal. per atom or atomic group, while the chemical primary valences are found in the region of 20,000–200,000 cal. per mol.

A very interesting paper by M. Dunkel[78] will now be cited which is of similar importance to the secondary valences as is Table 51 for the primary valence.

We should like to see a table prepared also for the intermolecular forces, to which the term molecular cohesion has been applied by K. H. Meyer because of their importance to the structure of the solid and liquid phase in which the secondary valence forces radiating from the principal groups are tabulated, at least, according to the order of magnitude of their energy dimensions.

For the data in Table 18 the *dissociation energies* of the primary valence bond, i.e. the *heats of combustion*, had to be used, but now we must consider the energy of overcoming molecular cohesion, which is measured by the *heats of sublimation* and *vaporization* or by the *van der Waals constant a*. For the latter, and for the *Sutherland constant* closely allied to it, van Laar[79] has already established certain additive relationships. These are expressed even more definitely in the well known Traube rule for the heats of adsorption of homologous series, which, according to Eucken,[80] are closely related to the heats of vaporization.

Heats of vaporization doubtless constitute the best experimental material for deducing such relationships. M. Dunkel[81] has collected data for some years and has estimated from them the molar cohesion of the principal typical groups of organic molecules. The difficulty which arises here in contrast to the Fajans-v. Weinberg[82] calculation of the primary valence forces is due to the fact that, because of the large absolute values in the first case, the effect of temperature on these forces, i.e. the influence of specific heats and of chemical constants, can be ignored, while the experimental vapor pressure curves would lead to completely erroneous heats of vaporization if the specific heats were neglected. Measurements at

[78] M. Dunkel, *Z. physik. Chem.*, (A) **138**, 42 (1928).

[79] J. J. van Laar, *J. chim. phys.*, **14**, 3 (1915).

[80] A. Eucken, *Z. physik. Chem.*, (A) **134**, 280 (1928).

[81] Cf. M. Dunkel and K. L. Wolf, *Müller-Pouillet, Lehrbuch der Physik*, Vol. IV, 3, p. 579.

[82] K. Fajans and A. v. Weinberg, *Ber.* **53**, 1347, 1519 (1920); **55**, 2829 (1922).

very low temperatures would be of greater value but these are practically non-existent. Dunkel then sought to sift out, to some extent quantitatively, the contribution of certain groups to the heats of vaporization, in the following way.

The vapor pressure of a substance is determined by two factors: the gain in energy on evaporation and the ratio of phase volumes at absolute zero which are available to a molecule in the solid or gaseous state respectively. The first factor comprises the heats of vaporization whose temperature dependence is determined by the difference between specific heat in vapor and in condensate; the second factor measures the *a priori* probability that we are concerned with a molecule in the condensed or in the free state and is proportional to the chemical constants of the particular

TABLE 51

MOLAR COHESION OF DIFFERENT ORGANIC GROUPS

Group	Molar cohesion in cal. per mol	Group	Molar cohesion in cal. per mol
$-CH_3$ $=CH_2$	1780	$-NH_2$	3530
		$-Cl$	3400
$-CH_2-$ $=CH-$	990	Only approximately known:	
$-O-$	1630	$-F$	2060
$-OH$	7250	$-Br$	4300
$=CO$	4270	$-J$	5040
$-CHO$	4700	$-NO_2$	7200
$-COOH$	8970	$-SH$	4250
$-COOCH_3$	5600	$-CONH_2$	13200
$-COOC_2H_5$	6230	$-CONH-$	16200

substance. The boiling point rules and the other rules mentioned above lead us to suppose that in homologous series both factors are combined additively as are other properties of such molecules. Mathematical checking has confirmed this conjecture. Within certain limitations there was very satisfactory additivity of the two constants in the vapor pressure formula. Table 51 records the molecular cohesion increments for the most important groups in organic compounds. By its help and with the equally approximate additive term corresponding to the chemical constants, the boiling points in homologous series may be calculated in good agreement with experiment.

The limitations previously referred to are related to the mutual disturbance and interaction of individual groups in the molecule; the additive

influences are then masked by the constitutional. Thus, it is not possible to make up the increment of the carboxyl group additively from the increments of the hydroxyl and carbonyl groups, although it is feasible, according to Eucken,[83] to do this for the dipole moment to a first approximation. For the increment of the heat of vaporization, not only the rigid dipole but to a large extent also the polarizability of the newly formed groups has to be taken into consideration. Excellent examples for the vectorial additive superposition of separate group dipoles to dipole moment of the whole molecule have been furnished recently by polarization measurements and tabulated by Debye[84] in his book on "polar molecules." In particular, the approach of groups to oppositely charged ions (COOH and NH_2) requires a special treatment.

The modern experimental methods of investigating dipole molecules attributable to Debye have greatly extended our knowledge regarding the connection between dipole character and chemical constitution and concern essentially these constitutional influences. If, however, we compare only homologous or polymeric homologous series with one another, and confine the evidence to these substances, we can construct to a first approximation the molar cohesion of such organic compounds additively from single increments. Consequently, in these series, with increasing molecular weight the molar cohesion also increases nearly proportionally to chain length.

From the relation between dipole character, polarizability and constitution, it follows that isomeric compounds with the same or similar atomic grouping, can never be distinguished quantitatively on the basis of van der Waals forces, for the component moments possible in organic molecules all lie below 5×10^{-18}; they can at one time be somewhat strengthened by superposition and at other times weakened, but not to the extent that there is a very considerable difference in their external effect. The polarizabilities of the groups concerned are also of the same order of magnitude. If, however, two substances of the same empirical composition are on the one hand soluble or volatile, on the other completely insoluble and incapable of distillation, we must conclude from our present general knowledge of intermolecular forces that the molecular weights of the two substances differ. Should we wish to ascribe quantitative differences in molar cohesion to different arrangement of the individual groups in the molecule, then we must assume *ad hoc* a new type of association

[83] A. Eucken, *Physik. Z.*, **30**, 397 (1930); *Z. Elektrochem.*, **28**, 6 (1922).
[84] P. Debye, *Polar Molecules*. New York 1929.

forces, previously unknown, although there is no other evidence in organic chemistry for their existence.

In the present chapter, which has been devoted essentially to the discussion of intra- and inter-molecular forces, reference has repeatedly been made in describing the latter, to the behavior of substances in the condensed phases, i.e. in the liquid and solid phase, in order to obtain criteria; it is now time to proceed to a comprehensive discussion of the structure of solids and liquids, in which our knowledge of the magnitude, form and internal mobility of molecules and the forces uniting them will find very effective application.

D. CRYSTAL STRUCTURE, LATTICE FORCES AND CHEMICAL STRUCTURE OF THE UNIT CELL

In order to reduce to some extent the mass of confusing facts brought to light by research on the properties of crystalline solids in recent years, it has been necessary to evolve a suitable classification and to form into groups individuals of known similarity. With this object in view, it soon appeared that two characters were particularly suitable as governing principles: firstly, the forces of cohesion in a crystal and secondly, the crystal symmetry.

In course of time two systematic methods of considering solids were evolved in parallel, one of which placed emphasis on the type of lattice-forming forces, while the other relied mainly on lattice symmetry. At first it seemed as if there were no relation between the two methods of classification, because lattices with the same symmetry were found which certainly owed their cohesion to entirely different forces and conversely, similar forces resulted occasionally in very different symmetries. On further investigation, however, it appeared that considerations of symmetry occasionally furnished important evidence on the type of lattice forces, although they gave no indication of their magnitudes.

It appears advisable in the present discussion to describe both classifications of crystals in as great detail as our present knowledge permits and to emphasize their interaction at those points which are connected with the structure of high polymeric substances.

I. CLASSIFICATION OF CRYSTALS FROM THE ASPECT OF FORCES

From the fundamental researches of W. H. and W. L. Bragg,[1] V. M. Goldschmidt,[2] H. G. Grimm,[3] L. Pauling[4] and others, the facts are most

[1] Cf. especially the fundamental books of W. H. and W. L. Bragg on *X-rays and Crystal Structure*, 4th edition, London 1924; *Crystalline State*, London 1934. Very extensive information can also be found in R. W. G. Wyckoff's book on *The Structure of Crystals*, 2nd edition; New York 1931; and in the monograph of G. L. Clark, *Applied X-rays*, 3d edition; New York 1940.

[2] V. M. Goldschmidt, *Ber.* **60**, 1263 (1927); *Naturwiss.*, **14**, 477 (1926).

[3] H. G. Grimm, cf. esp. his article in the *Handbuch der Physik*. Berlin, 1st edition 1926; 2nd edition 1936. Vol. 24, part 2.

[4] L. Pauling, *Proc. Roy. Soc. London*, (A) **111**, 181 (1927).

TABLE 52

CLASSIFICATION OF CRYSTAL LATTICES ACCORDING TO THEIR BOND TYPE

(H. G. Grimm)

Bond type	Lattice type Class of compound	Compounds AB		Compounds AB_2		Further examples of different lattice types
		Lattice type	C.N.	Lattice type	C.N.	
Ionic linkage	Ionic lattice (salts)	CsCl	8	CaF_2	8.4	AlF_3
		NaCl	6	TiO_2 (Rutile)	6.3	ZrF_4
				TiO_2 (Anatas)	6.3	
Metallic linkage	Atomic lattice (metals)	CuZn	8			K
		TiC	6	LaC_2		Cu_5Zn_8
		NiAs (?)	6	FeS_2 (?)		Fe_5Zn_{21}
Atomic linkage (Homopolar linkage)	Atomic lattice (diamond lattice)	ZnS (Wurtzite)	4	SiO_2	4.2	Al_2O_3
		ZnS (Zincblende)	4	OCu_2	4.2	Si_3N_4
Atomic linkage or ionic linkage in two directions, van der Waals linkage in one direction	Layer-lattice	BN	3	CdI_2	6.3	$CrCl_3$
		LiOH	4	MoS_2	6.3	AsI_3
				$CdCl_2$		
Van der Waals linkage between the molecules; atomic linkage within the molecule	Molecular-lattices	CO	1	CO_2	2.1	CCl_4
		Cl_2	1			$CO(NH_2)_2$
		CH_3Cl	1			

C.N. = Co-ordination number.

conveniently represented by recognizing four different force effects in the lattice of a crystal. These are:

a) The heteropolar primary valences between oppositely charged ions,
b) The homopolar primary valences between neutral atoms,
c) The metallic primary valence and
d) The van der Waals secondary valence forces between saturated molecules.

Conditions are simplest if the same force is effective in all three spatial directions in the given crystal; in this case true ionic lattices, true atomic, metallic and molecular lattices are obtained. It may happen, however,—and these cases will later be shown to be of special interest—that in one and the same lattice different types of forces prevail in the different directions in space, and result in mixed lattices and transition phenomena which will be discussed after the simple cases.

The nature of each of the four above named forces is already known to us from the discussion of intra- and inter-molecular forces and it remains only to describe here the type of product that results if these forces are lattice-forming. Table 52 gives a summary of pure lattice types, arranged according to the lattice forces acting.

1. The Ionic Lattice

The development of the experimental technique for investigating crystal structure by x-rays led first to the study of the simplest inorganic substances, i.e. the binary salts, and to the elucidation of their space lattices. The abundant data thus obtained were naturally an inducement to a search for conformity to rules.

Researches of W. L. Bragg,[5] K. Fajans,[6] H. G. Grimm[7] and L. Pauling[8] have thrown light on the fundamentals of these laws and the comprehensive work of V. M. Goldschmidt and his co-workers[9] has formulated them decisively and proved them with much new experimental material. The principal results of this crystallo-chemical research are the following:

1. To a first approximation, the individual ions in the structure of solid bodies behave as rigid spheres. Each of them, e.g. the univalent Na ion, the divalent Fe ion, etc. possesses a definite ionic radius which is specific to it and persists practically unchanged in the passage from one lattice

[5] W. L. Bragg, for instance *Phil. Mag.*, **40**, 169 (1920); see also the fundamental book, cited on page 9, ref. 1).
[6] K. Fajans, *Z. Physik*, **2**, 299 (1920).
[7] H. G. Grimm, l.c. on p. 117.
[8] L. Pauling, l.c. on p. 117.
[9] V. M. Goldschmidt, *Die Gesetze der Kristallchemie.* Oslo 1925.

to the next. Table 53 gives a few examples. It is evident from this table, for example, that the range of the Na ion in the solid state is to a great extent independent of the partner with which it builds up the lattice. Deviations from this rule amount on an average to about 1–2%, if the lattice types compared are similar to one another (commensurable structures).

By the aid of the concept of rigid ions, Goldschmidt has been able to show that the ratio of the ionic radii is of decisive importance for the appearance of one or other lattice types in binary salts. He applied an idea that A. Magnus[10] first used in the elucidation of the co-ordination numbers, namely, that a system of spheres of different size is stable if the smaller of these spheres exactly fill the space formed by the larger ones.

Fig. 31 (a) shows, for example, that the space between four Cl ions, which have a radius of 1.8 Å is just filled exactly by the quadrivalent

TABLE 53

IONIC RADII OF VARIOUS ALKALIES AND ALKALINE EARTHS

Ion	Ionic radius calculated		
	From the fluoride	From the chloride	From the bromide
Li^+	0.68	0.76	0.79
Na^+	0.98	1.00	1.01
K^+	1.33	1.33	1.33
NH_4^+	—	1.36	1.49
	From the oxide	From the sulphide	From the selenide
Mg^{++}	0.78	0.80	0.81
Sr^{++}	1.27	1.19	1.21

positive silicon ion with the radius 0.4 Å, while the space formed by six chlorine ions would be too great for one silicon ion; it would not fit firmly into it but would move loosely. In contrast, six fluorine ions of radius 1.3 Å, in forming an octahedron, provide the exact amount of space required by a quadrivalent silicon ion, as shown in Fig. 31 (b). If eight fluorine ions are combined in cubic arrangement, the resulting space is too large for the silicon ion, but is exactly filled by the rather larger osmium ion as shown in Fig. 31 (c). Magnus explained in this simple way the increase in co-ordination number from 4 to 6 and to 8 or from the ratio of the ionic radii. The application of this idea to the elucidation of the different types of lattice has led Goldschmidt to an extensive classification of ionic lattices which is in excellent agreement with experimental evidence.

[10] A. Magnus, *Z. anorg. allgem. Chem.*, **124**, 291 (1922).

2. To a second approximation, there are certain small but systematic departures from the rigid spatial behavior of ions in the solid state: the ionic radius depends upon the co-ordination number and generally increases with increasing co-ordination number. This raises the question of whether an increase in the number of like ions within a co-ordination sphere can, by their mutual repulsion, leave a larger cavity for the central ion, so that a larger requirement of space should be allowed. Table 54 will give an idea of the magnitude of this effect. Experience shows further that the difference in the space requirement (calculated from the ionic radius) may amount in the Pb^{2+} ion, for example, to 11%; the absolute values of the differences come to tenths of an Ångstrom. As a matter of experience, they find very little expression in the general properties of crystals—melting point, hardness, refractive index, and so on—and do not influence essentially the strength of the bond between the central atom and the coordinated atoms.

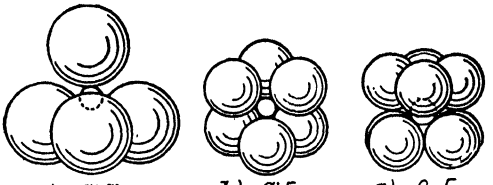


Fig. 31. Geometrical explanation of the different co-ordination numbers according to A. Magnus.

TABLE 54

CHANGE IN DISTANCE ON CHANGE IN CO-ORDINATION NUMBER

Transition from co-ordination number	To co-ordination number	Reduction in distance of
8	6	3%
6	4	5–7%
12	8	3%
12	8	3.5%

3. In addition to the above mentioned purely geometrical aspects, there is also a dynamic property of the ion which has a considerable influence on its crystallo-chemical behavior; its polarizability, or, according to Fajans,[11] its deformability. If a negative ion with readily movable electrons (e.g. iodine) enters the field of a small positive ion, the charge cloud of the former will attract the positive ion, the nucleus will repel it and the deformed ion will be characterized, not only by its charge, but also by an induced dipole moment. While formerly the interaction of the two

[11] K. Fajans, *Naturwiss.*, **11**, 105 (1923); *Z. Krist.*, **61**, 18 (1925).

ions was described by two spherically symmetrical Coulomb fields, we must now take into account the axially symmetrical dipole field of the deformed ion; while previously the centers of gravity of the masses and charges coincided, this is no longer the case, but a portion of the negative charge of the deformable ion is deposited preferably between the nuclear centers of gravity.

Goldschmidt has shown by a large body of evidence that the polarization of an ion is very essential for the lattice type, particularly in the sense that, in the absence of polarization, highly symmetrical groupings are preferred, whereas—due to the lower symmetry of the deformed ion—the result of increasing polarization is always a less symmetrical arrangement. Accordingly, we obtain lattice forces of different strengths in different

TABLE 55

RELATION BETWEEN HARDNESS AND LATTICE STRUCTURE

	BeO	ZnO	ZnS	ZnSe
Particle distance	1.65	1.97	2.35	2.48
Hardness	9	5	4	3-4
	CdSe	HgSe	ZnTe	CdTe
Particle distance	2.63	2.63	2.64	2.80
Hardness	3	2.8	3	2.8
	CC	SiC	SiSi	GeGe
Particle distance	1.54	1.89	2.35	2.43
Hardness	10	9.5	7	6

directions, the rigid or at least approximately rigid ionic radius loses its significance and the behavior of a given ion is to a high degree dependent on its neighbor, its size and polarizing action. Compounds with highly polarizable constituents consequently form a whole series of lattice types which exhibit a wide range of physical and chemical properties; their melting points, hardness, solubilities, etc. differ even in order of magnitude from one another. Table 55 gives a few examples taken from Goldschmidt's extensive experimental data.

The following conclusions may be drawn from a review of the above mentioned results of x-ray examination of inorganic, solid substances: to a first approximation, every lattice component in the lattices of salts, metals and intermetallic compounds is characterized by a definite space requirement, corresponding to a definite particle radius. This particle radius is,

however, to a second approximation, not a fixed magnitude, but it depends upon the number of the surrounding particles, possibly oppositely charged. In non-rigid ions, e.g. in all heavy metal ions, however, the purely spatial concept is no longer adequate, and to understand the actual conditions, it is necessary to consider, in addition to the Coulomb interaction of fixed charges, their deformability as well. The fact that there are ions of every polarizability, leads to inorganic lattices of the most diverse structural types having, therefore, widely differing physical properties.

The application of these ideas by Goldschmidt has furnished not only a classification of existing lattice types, but has led to a very real understanding of the properties of solids, and to the prediction of a whole series of binary compounds which in the meantime have been prepared in part, and so has confirmed the foregoing laws of crystallo-chemistry, both with regard to their range of existence and their physical properties.

The following deductions for the case of the rigid ion may be drawn as a quantitative result of this method of consideration:

1. An insight into the radii (or packing) of all important ions occurring in crystals. This quantitative material, in the hands of V. M. Goldschmidt,[12] H. G. Grimm,[13] P. Niggli[14] and others, is a very productive source of many interesting conclusions regarding the stability of inorganic compounds, the tenacity and hardness of these substances and the geochemical distribution of the elements. In the present discussion, where we are more interested in organic substances, it may suffice to give an extract to include those elements which are, or may be, of importance in organic compounds. Table 56 gives a few ionic radii of such substances.

2. The possibility of determining lattice dimensions quantitatively by the aid of a suitable expression for the forces prevailing between the lattice points. One equation of two terms first used for the potential of univalent ions was

$$U(r) = -\frac{e^2}{r} + \frac{a}{r^n} \tag{34}$$

e = particle charge a and n = constants

The first term expresses the Coulomb attraction between the oppositely charged ions, the second describes the repulsive forces which arise if the two charge shells are brought too near together; values between 9 and 11

[12] V. M. Goldschmidt, *Die Gesetze der Kristallchemie.* Oslo 1925; and *Ber.* **60**, 1263 (1927); *Naturwiss.*, **14**, 477 (1926).

[13] H. G. Grimm, article in the *Handbuch der Physik.*; Vol. 24, part 2, p. 923.

[14] P. Niggli, *Der feste Körper*, Leipzig 1938, p. 1.

are obtained for n. Table 57 by Lennard-Jones[15] shows how nearly the lattice distances d and the compressibilities χ can be calculated by the use of the above equation for simple ionic lattices.

As in the case of the length of the edge of the cell, the angle may also be calculated in lattices of low symmetry, as may be seen from Table 58 due to W. L. Bragg, in which the rhombohedral angles of several carbonates have been calculated with astonishing accuracy. The change in lattice constants with pressure—the compressibility—can also be obtained to a very fair approximation.

TABLE 56

IONIC RADII IN 10^{-8} CM (INERT-GAS-LIKE IONS)

			Li^+	Be^{2+}	B^{3+}	C^{4+}	N^{5+}	O^{6+}	F^{7+}
			0.60	0.31	0.20	0.15	0.11	0.09	0.07
			0.78	0.34	—	~0.2	0.1-0.2	—	—
N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}
1.71	1.40	1.36	0.95	0.65	0.50	0.41	0.34	0.29	0.26
—	1.32	1.33	0.98	0.78	0.57	0.39	0.3-0.4	0.34	—
P^{3-}	S^{2-}	Cl^-	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
2.12	1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52	0.46
--	1.74	1.81	1.33	1.06	0.83	0.64	~0.4	0.3-0.4	—
As^{3-}	Se^{2-}	Br^-	Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}	Nb^{5+}	Mo^{6+}	
2.22	1.98	1.95	1.48	1.13	0.93	0.80	0.70	0.62	
—	1.91	1.96	1.49	1.27	1.06	0.87	0.69	—	
Sb^{3-}	Te^{2-}	J^-	Cr^+	Ba^{2+}	La^{3+}	Ce^{4+}			
2.45	2.21	2.16	1.69	1.35	1.15	1.01			
—	2.11	2.20	1.65	1.43	1.22	1.02			

The two values are obtained in two independent ways.

3. Similarly, the lattice energy—which is determined experimentally from the heat of sublimation—is also susceptible to theoretical estimation. To obtain good agreement, one must, of course, take into consideration the exchange forces of the electron shells in close proximity and the zero energy in addition to the two purely electrostatic terms of equation (34). J. Mayer[16] has done this for the halides of thallium and silver and has found very satisfactory agreement with experimentally determined data. Table 59 is a proof of this.

[15] Cf. J. E. Lennard-Jones, *Trans. Faraday Soc.*, **24**, 100 (1928); **28**, 333 (1932; *Proc. Phys. Soc.*, **43**, 461, 475 (1931).

[16] M. Born and J. E. Mayer, *Z. Physik*, **75**, 1 (1932); M. L. Huggins and J. E. Mayer, *J. Chem. Phys.*, **1**, 643 (1933).

The conditions are less simple in lattices with polarizable ions. Born and Heisenberg[17] have been able to derive a potential expression which gives the lattice energy in fair agreement with experiment. The contribution of the polarizability to the total potential lies between 10 and 20%. In addition, the frequencies of the natural vibrations of the ions in such lattices may be predicted very successfully.

TABLE 57

CALCULATION OF LATTICE DISTANCES AND COMPRESSIBILITIES

According to Lennard-Jones

Salt	NaF	NaCl	NaBr	NaI
d calcd. Å	2.30	2.85	2.99	3.19
d obs. Å	2.31	2.81	2.97	2.23
$\chi \cdot 10^{12}$ calcd.	—	3.88	4.51	5.18
$\chi \cdot 10^{12}$ obs.	—	4.20, 4.3	5.08, 5.3	7.1
Salt	**KF**	**KCl**	**KBr**	**KI**
d calcd. Å	2.63	3.13	3.24	3.47
d obs. Å	2.66	3.14	3.28	3.52
$\chi \cdot 10^{12}$ calcd.	—	6.23	7.92	8.17
$\chi \cdot 10^{12}$ obs.	—	5.63, 5.2	6.70, 6.4	8.54, 8.8
Salt	**RbF**	**RbCl**	**RbBr**	**RbI**
d calcd. Å	3.37	3.24	3.43	3.58
d obs. Å	3.66	3.27	3.42	3.65
$\chi \cdot 10^{12}$ calcd.	—	8.10	7.72	9.26
$\chi \cdot 10^{12}$ obs.	—	7.3	7.94, 8.2	9.58, 9.3
Salt	**CsF**	**CsCl**	**CsBr**	**CsI**
d calcd. Å	2.97	4.21	4.34	4.56
d obs. Å	3.00	4.12, 4.30	4.29	4.56
$\chi \cdot 10^{12}$ calcd.	—	7.71	8.58	9.31
$\chi \cdot 10^{12}$ obs.	—	5.9	7.0	9.3

If a lattice consists of a small, very compact ion and a large, easily polarizable ion, the effect of the deformation may be so great that the purely heteropolar type of bond is lost and a lattice results whose properties resemble those of a molecular lattice. Hund[18] has investigated this problem and found that layer lattices result generally in these cases, in

[17] M. Born and W. Heisenberg, *Z. Physik*, **23**, 388 (1924).

[18] F. Hund, *Z. Physik*, **34**, 833 (1925).

which the charge shell of the larger ion is powerfully attracted towards the center of the smaller one.

A further important transition type arises if, in the salts of organic compounds such as sodium benzoate or potassium stearate, a small positive metallic ion is adjacent to a negatively charged organic residue, because the latter may exert special dispersion forces in addition to van der Waals forces of other kinds and the lattice is stamped with homopolar character.

In both instances the lattice is strongly anisotropic in regard to strength

TABLE 58

RHOMBOHEDRAL ANGLE IN THE CALCSPAR TYPE

According to W. L. Bragg

Substance	Rhombohedral	α calculated	α observed
$MgCO_3$	4.61 edge in Å	103° 28′	103° 21.5′
$ZnCO_3$	4.64	103° 18′	103° 28′
$TlCO_3$	4.70	103° 6′	103° 4.5′
$MnCO_3$	4.77	102° 52′	102° 50′
$\frac{1}{2}(MgCa)CO_3$	4.78	102° 44′	102° 53′
$CdCO_3$	4.92	102° 15′	102° 30′
$CaCO_3$	4.96	102° 4′	101° 55′

TABLE 59

LATTICE ENERGIES OF SILVER AND THALLIUM HALIDES IN CALS.

	AgF	AgCl	AgBr	AgI	TlCl	TlBr	TlI
U theor.	219	203	197	190	167	164	159
U observed	217.7	205.7	201.8	199.2	170.1	165.6	160.8
Difference	−1.3	2.7	4.8	9.2	3.1	1.6	1.8

because very strong lattice forces are effective along certain directions and very much weaker ones along others.

In conclusion, we may say that simple lattices with purely electrostatic interaction between the ions can very well be governed by equation (34) and that important transition cases in the direction of molecular lattices may be obtained from them.

2. The Atomic Lattice (Diamond Type Lattice)

This comprises all lattices which cohere by homopolar primary valences in all three directions in space. The character of the linkage has already

been discussed;[19] Grimm[20] was able to prove experimentally the existence in the diamond lattice of the charge cloud causing the homopolar pattern.

This type of lattice is not always easily distinguishable from the ionic lattice, but Grimm and Sommerfeld have succeeded in establishing criteria for deciding whether an element or a compound crystallize in the same manner as diamond. The lattices to come under consideration are essentially the diamond type and the very similar wurtzite type. Elements belonging to this class are: C, Si, Ge and Sn; compounds include AlN, CSi, ZnS and CdS.

On account of the great binding energy of the homopolar valence, all these substances are very compact, high melting, hard crystals, some of which have considerable technical importance.

The absence of a simple, well substantiated potential expression makes it impossible to estimate lattice constants, angles, lattice energies and other crystal constants; it has merely been possible, by comparing several lattices of the diamond or wurtzite type, to derive empirical rules for atomic distances in relation to bond strengths, which show that, under otherwise identical conditions, the stronger linkage corresponds to the smaller atomic distance.

3. The Metallic Lattice

This type is characterized by the presence of the metallic linkage; metallic lattices show electrical conductivity, strong reflectivity and generally high melting point. The nature of the metallic link has already been indicated.

Bernal divides the metallic elements into two groups, which he designates as true and false metals (see Table 60). This distinction is sharp in many cases but in many others it vanishes almost completely. The true metals crystallize with high symmetry, they generally possess very high conductivity and show a decrease in this property on fusion; the other elements crystallize, as a rule, in lattices of low symmetry and show low conductivity which generally increases on melting. These substances represent a certain transition to atomic lattices.

The number of intermetallic compounds is extremely large and their x-ray investigation has revealed many interesting results, the description of which would lead us too far afield.

The extent to which we can express the metallic linkage quantitatively has already been shown on page 89; an excellent analysis of the corre-

[19] Comp. p. 85.

[20] H. G. Grimm and collaborators, l.c. on p. 89.

sponding charge distribution has been carried out by Grimm,[21] as previously mentioned. Table 61 compiled by Haber[22] may be added here; in this, the lattice energy of highly symmetrical metallic lattices is calculated, by analogy with ionic lattices, from the opposing effects of a force corresponding to the Coulomb force and a repulsive force, in which the repulsion

TABLE 60

DIVISION OF THE METALLIC ELEMENTS

By J. D. Bernal

	True metals (Class 1)	Semi metals (Class 2)
Substance	Alkali metals Alkaline earth metals Rare Earths Ti-Cu (without Mn) Zr-Ag Hf-Au, Th, U	Zn, Cd, Hg, Ga, In, (Tl), Ge, Sn, (Pb), As, Sb, Bi
Crystal lattice	Face- or body-centered or hexagonal close packing; Co-ordination Number 12 or 8	Loosely packed structures; Co-ordination Number 8
Change of properties on fusion	Decrease in electrical conductivity	Increase in electrical conductivity

TABLE 61

REPULSIVE FORCES AND LATTICE ENERGIES IN METALLIC CRYSTALS

According to Haber

	Li	Na	K	Rb	Cs	Cu	Ag	Al
n from the compressibility. . .	2.44	2.90	3.18	3.64	3.62	8.0	9.0	7.0
lattice energy, calculated from n.....	6.51	5.69	5.04	5.02	4.68	11.73	10.50	8.56
lattice energy found = heat of vaporization + heat of ionization.....	—	5.87	5.13	4.88	4.56	10.69	10.17	8.71

All energies are in 10^{12} erg per molecule.

exponent is determined from the compressibility. It is evident that, in contrast to the true ionic lattices, very uncertain values (from 2.44 to 9.0) are obtained for these repulsion exponents, the reason being that a binomial expression is only a mathematical aid. Nevertheless we obtain quite useful values for lattice energies.

[21] H. G. Grimm and co-workers, l.c. on page 89.

[22] F. Haber, *Sitz. Ber. Preuss. Akad. Wiss.*, **1919**, 506, 990.

The three types of lattice discussed here have the common property that their cohesion is due to homogenous valence forces in all three spatial directions; they may therefore be designated as valence lattices. Because of the magnitudes of the lattice force, they are all characterized by a more or less high heat of sublimation, great hardness and high melting and boiling point. Entirely different properties are met with in the type now to be discussed, in which secondary valences in all three directions cause the cohesion of the lattice.

4. Secondary Valence Lattices

These lattices cohere by van der Waals forces; they have a low melting point and sublime readily. The majority of organic substances crystallize in this lattice type.

a) Secondary Valences and Density

If a primary valence bond e.g. between carbon and nitrogen has a value of 1.4–1.5 Å, it may legitimately be assumed that atoms not united by primary valence must maintain a considerably greater distance. In solving the problem of the distances between adjacent atoms in neighboring molecules, it is convenient to consult first the very numerous x-ray determinations of structures available today. These indicate that the distances all lie between 3 and 4.5 Å, i.e. they are on an average 2.5 times as great as the value corresponding to a primary valence. This reflects the characteristic difference between homopolar valence linkage and van der Waals cohesive force to which we referred in discussing individual molecules.

This distance of 3–4.5 Å which corresponds to the lattice forces in molecular lattices, may, through its frequent occurrence, account for the fact that interference it produces is especially intense. Thus, for example, in the fatty acids the reflections are especially intense in those planes which contain the chains and, consequently, have the same interplanar distance that also separates the individual chains and corresponds to the lattice forces. In liquids also, where, it is true, the oriented lattice coherence is lost but where the average distances of the molecules are determined by van der Waals cohesion forces, we find very frequently indistinct interference rings; when these are interpreted, they show that a lattice plane distance of about 4 Å prevails in the liquid also, at least, statistically. From the x-ray diagrams of hydrocarbons, e.g. of liquid isoprene, an average molecular distance of about 4 Å can be calculated from the ring.

Finally, the well known researches of Adam,[23] Langmuir,[24] Rideal[25] and others on monomolecular films have shown that the distance of the separate molecules in such a film, e.g. in the simple fatty acids amounts to 4.3 Å.

These facts indicate the validity, in dealing with crystal lattices in which the molecules cohere by homopolar valences, i.e. where heteropolar, electrostatic binding plays no part, of assigning distances of 1.2–1.6 Å to the primary valences and values of 3.0–4.5 Å to the secondary valences. This hypothesis supplements the previous diagrammatic structural formulas of organic chemistry by quantitative spatial data, and provides molecular patterns which are one step nearer to reality. Further, by taking the cohesive forces into consideration, the previous mode of thought is extended, because we shall no longer be content to deduce from a rational structural formula merely the chemical behavior of the individual molecule. In addition we expect to understand the physical properties of the lattice arising from the molecule, exactly as the Goldschmidt crystallo-chemistry combines lattice properties with ionic properties for the ionic lattice. Just as in that case, we can employ here the predicted and experimental facts to prove that certain molecules which would have been admissible previously by structural chemistry cannot actually exist.

From the foregoing facts, it is possible to make a few qualitative assertions regarding the density of carbon compounds.

We know that in the diamond lattice all atomic distances are of the order of 1.55 Å, whereas in the lattice of solid methane the distance between adjacent C and H atoms must be about 2.5 times as great. Thus, it is immediately evident that the specific volume of the C atom in methane must be many times greater than that of the C atom in the diamond, and therefore the density of the latter must be many times greater. In the recent x-ray investigation of solid methane carried out by H. Moog, the mutual distance between two molecular centers was determined; it amounted to 4.2 Å; the density determination gave a value of 0.415 as compared with 3.51 in diamond. The density of the diamond is therefore eight times that of solid methane.

In graphite, the distances between adjacent atoms in the principal plane are 1.45 Å, while perpendicular thereto the smallest distance amounts to 3.3 Å. We have before us a lattice which coheres in two directions by normal primary valences and by secondary valences in the third direction

[23] Cf. N. K. Adam, *The Chemistry and Physics of Surfaces*, 2nd ed., Oxford 1938.
[24] I. Langmuir, *Chem. Rev.*, **13**, 147 (1933).
[25] E. K. Rideal, *Surface Chemistry*, 2nd ed., London 1930.

perpendicular to these (layer or network lattice; see p. 159). The densities of diamond and graphite should, by reason of the identity of the atoms and the shorter C—C distance in the reference plane of graphite, have the ratio 1.53:1; the actual density ratio is 1.52:1.

Proceeding from graphite, let us finally imagine a carbon lattice, which coheres in one direction through primary valences and in the two other directions by secondary valences. Such a structure is impossible from carbon atoms alone where tetrahedral valence holds, but we can conceive of its being realized, e.g. from a carbon chain of double bonds alone. Its density must lie, according to the distance law, between 0.8 and 1.1, according to the particular manner of separation between the chains.

The smaller the regions of primary valence in the lattice, the greater is the specific volume and consequently the lower the density. Extreme values are represented by diamond ($\rho = 3.51$) and methane ($\rho = 0.415$). The densities of all organic compounds containing only carbon, oxygen, nitrogen and hydrogen must therefore be intermediate; layer lattices have densities of about 2.2, chain or filament lattices about 1.5. The ordinary molecular lattice with closed lattice units which we shall in future refer to as micro units, following Weissenberg, must have densities between 0.6 and 1.5.

An examination of the experimental data confirms the accuracy of this theory, the principle of which is to be sought in the difference between primary and secondary valences in organic compounds which, although schematic, has been proved by experiment. In clear contrast, the heteropolar inorganic lattices extend over a considerably larger density range, because in them the polarization properties are effective in addition to spatial requirements and they produce more complicated conditions.

The result of the marked difference between primary and secondary valences in the lattices of normal organic substances is that the molecules which are familiar in the gaseous state always remain clearly recognizable as especially closely packed, correlated atomic groups; application of the molecular concept to the solid state for this class of substance, therefore, presents no difficulty. The case is entirely different for the layer and chain lattices and in the diamond. As in the ionic and atomic lattices of inorganic substances, it is impossible to delimit special atomic groups in the crystal lattice, which corresponds to the chemical molecule of the other states. A new terminology is really needed to describe the existing conditions intelligibly. In the next chapter on page 151, in discussing the different lattice types, the system of lattice units developed by Weissenberg will be briefly described.

b) *Different Types of Secondary Valence Lattices*

Lattice force can be made up of all three components of intermolecular interaction; generally each of them will contribute a definite amount to the total lattice energy and it will, as a rule, not be easy to separate them entirely. Many cases, however, are again characterized by a definite secondary valence effect, and are useful in affording an insight into the activity of secondary valences as lattice forces. These cases will be discussed in rather more detail in view of the importance of applying this knowledge to high polymers.

True dispersion forces are present to all appearances in the lattices of inert gases. These substances crystallize in very highly symmetrical arrangement—cubic face-centered—both the lattice constants and the heats of sublimation are easily obtainable experimentally. Eisenschitz and London,[26] by employing the calculation mentioned on page 93 of the quantum mechanical component of the van der Waals forces for the lattice energy of a cubic crystal, which coheres only through such force effects, have derived an equation of the form

$$U = -\frac{59}{2} \cdot \frac{\Im \alpha^2 N}{r_0^6} \tag{35}$$

N = number of molecules in the given crystal.

$\Im$ = Energy of ionization.

α = Polarizability of the lattice units.

r_0 = Distance of the lattice units.

If, by its aid, we calculate the heats of sublimation of lattices which cohere by virtue of true dispersion forces, we obtain the data given in Table 62, which agree well with the experimental values cited in column 4. Margenau[27] has improved this agreement still further by taking into account the interaction of dipole and quadrupole terms of the zero vibration.

It is interesting that in HCl and HBr, which already possess quite considerable dipoles, there is an appreciable deviation in the sense that the lattice energy calculated on the basis of dispersion force alone is too small, because interactions of a dipole nature intervene. The fact, however, that in these lattices the quantum mechanical forces play a very important part is clear from the data in Table 62 and from the calculations of Born and Kornfeld,[28] who for a long time have tried to adopt a true

[26] R. Eisenschitz and F. London, *Z. Physik*, **60**, 520 (1930).
[27] H. Margenau, *Phys. Rev.*, **38**, 1785 (1931).
[28] M. Born and G. Kornfeld, *Physik. Z.*, **24**, 121 (1923).

dipole lattice for the hydrogen halides, in which a high symmetrical spatial arrangement of parallel and anti-parallel dipoles is present (Fig. 32), resulting in a general mutual attraction. Calculations show, however,

TABLE 62

COMPARISON OF CALCULATED AND OBSERVED HEATS OF SUBLIMATION

1	2	3	4
Substance	$\alpha \times 10^{24}$ in cm³	Lattice energy calculated in Cal/mol	Lattice energy observed in Cal/mol extrapolated to 0° abs.
Ne	0.39	0.40	0.59
A	1.63	1.83	2.03
N_2	1.74	1.61	1.86
O_2	1.57	1.48	1.89
CO	1.99	1.86	2.09
CH_4	2.58	2.47	2.70
Cl_2	4.60	7.18	7.43
HI	5.40	6.50	6.21
HCl	2.63	4.04	5.05
HBr	3.58	4.53	5.52
NO	1.76	2.04	4.29

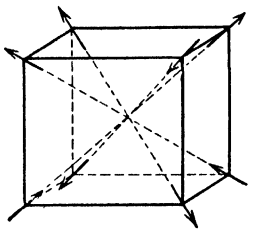


Fig. 32. Lattice with cohesion due to dipole forces alone (Born and Kornfeld).

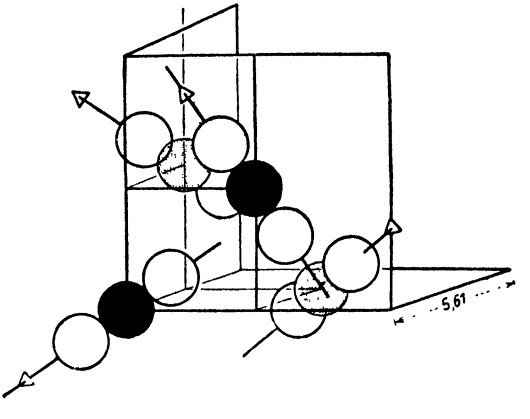


Fig. 33. Elementary cell of the CO_2 lattice; black circles are C atoms, white are O atoms.

that it is impossible to obtain the heats of sublimation found by experiment for a lattice of this type if dipole force alone is admitted.

Carbon dioxide gives a lattice which resembles Fig. 32 in structure. In it, as shown in Fig. 33, the rod-shaped CO_2 molecules lie parallel to

the spatial diagonals of a cube of edge length $a = 5.63$ Å and in such a way that any two neighboring ones are always perpendicular to one another. In this arrangement, the C=O dipoles to which may be ascribed a group moment of about 4×10^{-18}, produce, in molecules lying perpendicular to the dipole axis and separated by a distance of 3.5 Å, induced moments whose interaction with the permanent group moments may constitute the main component of the lattice force. The low boiling point of carbon dioxide (compared with H_2O or CS_2) is obviously due to the fact that the intermolecular interaction described above is only weak. Unfortunately, there is at present no accurate mathematical treatment of the lattice of CO_2, so that we cannot say to what extent the intervention of dispersion forces must be assumed. To emphasize again the true conditions, the molecule CO_2 with its proper space-filling is reproduced in Fig. 34, due to H. A. Stuart.

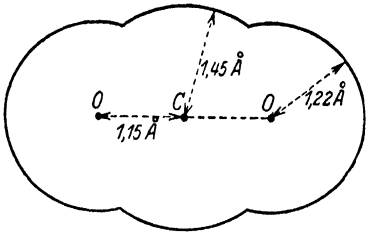


Fig. 34. Effective range of the carbon dioxide molecule (H. A. Stuart).

The ice lattice has been investigated with considerable accuracy. Its symmetry and its heat of sublimation give clear indications regarding the interaction of the OH groups, as shown especially by Bernal and Fowler.[29] Having regard to the great importance of the hydroxyl groups in cellulose and starch, it is permissible to discuss the structure of this lattice in considerable detail here, because, later, it will be possible to draw very interesting conclusions regarding the behavior of other substances with high hydroxyl content.

At present three ice modifications are known, a hexagonal type which is formed under normal conditions and two rhombic types which are formed at low temperature or at increased pressure; all have been investigated quite thoroughly with x-rays. The elementary cell of normal ice (ice I) contains 12 molecules of H_2O; each of them is surrounded tetrahedrally by four others in such a way that the distance between the centers of gravity of the oxygen atoms is 2.74 Å. Fig. 35 shows this arrangement, which can also be so represented that each selected H atom appears to be united by a primary homopolar valence to a given oxygen atom. But through the insertion of the molecule in the lattice, a second oxygen atom exists toward which the H atom is especially inclined. Each O atom is, there-

[29] J. D. Bernal and R. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

fore, surrounded by 4 H atoms which lie at the corners of a somewhat distorted tetrahedron and every H atom is common to two such tetrahedra; we thus obtain the correct ratio H:O = 2:1 and a spatial framework of the formula $(H_2O)_n$. We shall see later that the different modifications of SiO_2 conform to the same structural principle. The structure of normal ice resembles most nearly that of tridymite (see Fig. 35). This configuration corresponds not to a most compact spherical packing but to a considerably more attenuated one.

In the two rhombic phases we find similarly that a selected water molecule is surrounded by four others in tetrahedral association, so that there

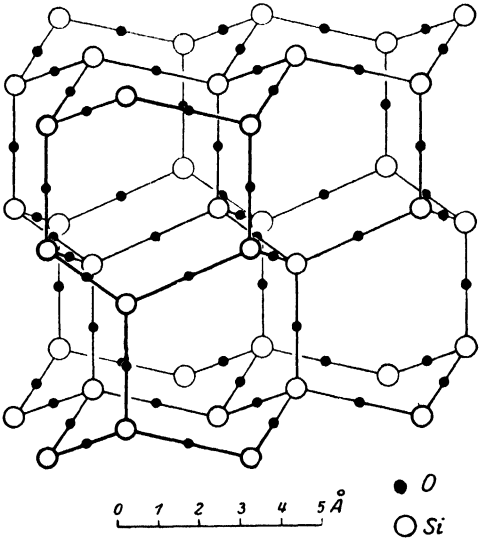


Fig. 35. Space-lattice of tridymite as pattern for the lattice of ice I.

is some deformation as compared with the regular tetrahedron; in ice II the distance between centers of gravity of adjacent oxygens is about 2.71 Å; the H atoms are difficult to locate, but we gain the impression that in these two lattices the molecular association would be largely dissolved and the structure would approach that of an ionic lattice.

For liquid water, Bernal and Fowler[30] assume that there exists a mixture possessing 3 configuration possibilities, whose quantitative ratio depends greatly upon temperature; further, that any one of the three persists over submicroscopic range and only for very short periods. In the neighbor-

[30] J. D. Bernal and R. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

hood of the melting point and up to +4° a tridymite type of configuration prevails (see Fig. 35) which arises from the ice and which will endure over a small range, even though above the melting point. At higher temperatures (4–200°) a quartz-like modification becomes more and more developed and at even higher temperature (200–340°) up to the region of the critical point there is a final configuration of closest spherical packing.

Further details on the very interesting views regarding the structure of liquid water will be added later in the section on liquids.

As an example of a molecular lattice in which cohesion is also effected predominantly by dipole forces, oxalic acid dihydrate may be discussed here, because it allows of a remarkable insight into the rôle of the water of crystallization.

H. Hoffmann and H. Mark[31] determined some time ago the elementary cell and spatial group of this substance; more recently J. M. Robertson[32] has carried out an accurate investigation of the position of the atomic centers of gravity and obtained the results shown in Figs. 36a and b. The six heavy atoms of the oxalic acid residue—excepting the H atoms whose positions could not be determined by scattering of x-rays—all lie in one plane. The distance C—C amounts to 1.43 Å which is distinctly smaller than usual (1.54) and even approaches the distance of 1.45 Å, which is characteristic for the aromatic C—C-bond. The reason for this fact probably lies in the spatial proximity of the two C=O linkages.

Fig. 36b shows the distances between the center of gravity of a water molecule and the three nearest oxygen atoms of oxalic acid residues; one sees that they lie between 2.52 and 2.87 Å. It appears, therefore, that the hydrogen atoms of the acid residue and those of the water in the lattice play the same rôle and are arranged between the oxygen atoms of the water and the oxalic acid residue. In this sense, the crystal is best regarded as oxonium oxalate with the formula

$$(H_3O)^+ - (OOC - COO) - (H_3O)^+;$$

each oxonium radical is then united with 3 oxalic residues by a hydrogen bond.

It must again be assumed here that the dipole forces first produce the configuration shown in Fig. 32 and that it is only stabilized subsequently by quantum mechanical exchange forces when the individual O and H atoms move into the places determined for them by these forces.

Considerable information regarding the details of the van der Waals link may be derived from the lattice of hexamethylene tetramine which

[31] H. Hoffmann and H. Mark, *Z. physik. Chem.*, **111**, 321 (1924).

[32] J. M. Robertson and J. Woodward, *J. Chem. Soc. London, 1936*, 1817.

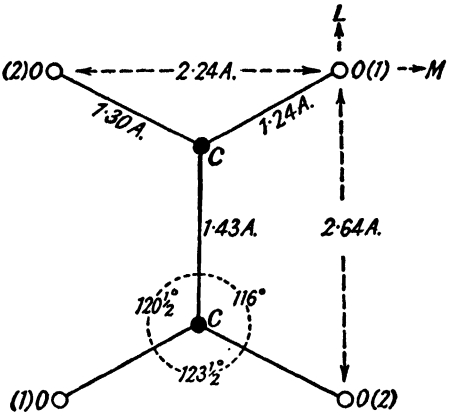


Fig. 36a. Nuclear framework of the oxalic acid molecule with H atoms omitted.

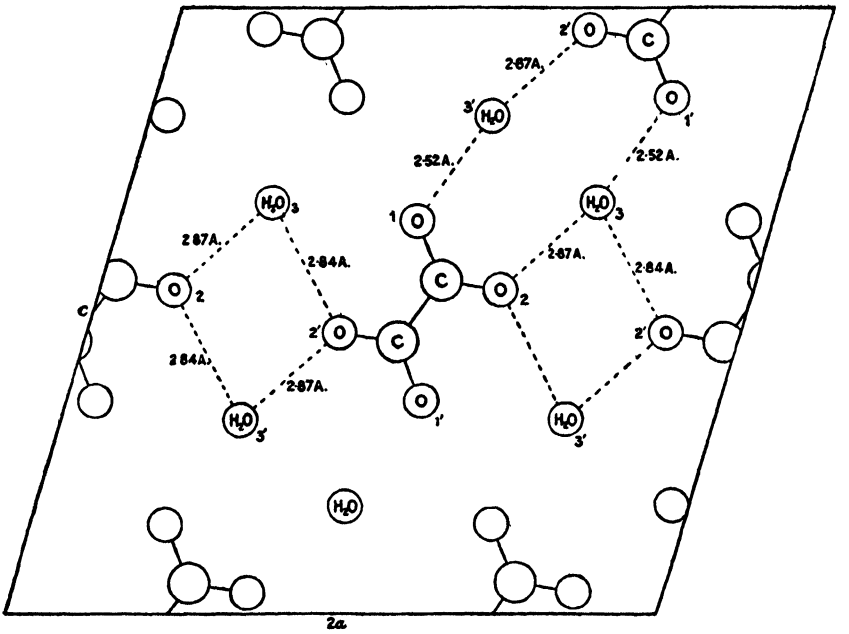


Fig. 36b. Arrangement of oxalic acid molecules in the lattice (hydrogen atoms omitted).

crystallizes with very high symmetry (see Fig. 37a). The cubic, body-centered elementary cell of this substance and the atomic center of gravity

positions were demonstrated independently a long time ago by Gonell and Mark[33] and by Dickinson and Raymond;[34] the findings of both were

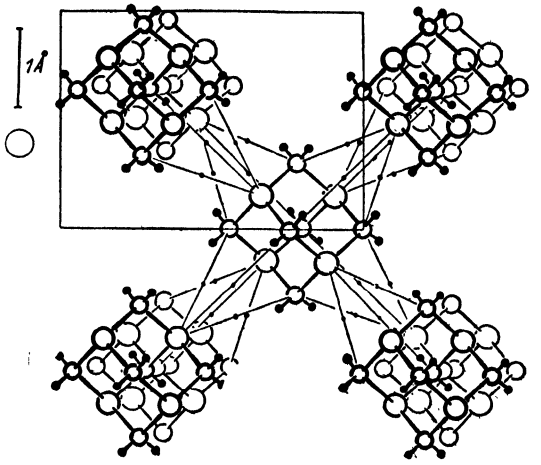


Fig. 37a. Space lattice of hexamethylene tetramine.

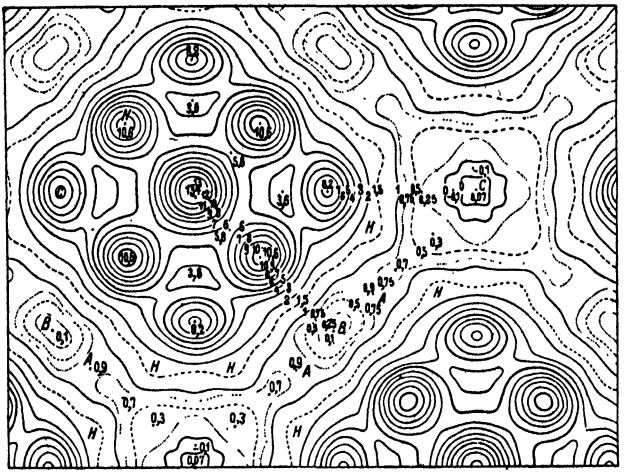


Fig. 37b. Electronic density in the hexamethylenetetramine lattice.

in complete agreement. Recently H. G. Grimm in common with Brill, Hermann and Peters[35] investigated the exact distribution of the negative

[33] H. W. Gonell and H. Mark, *Z. physik. Chem.*, **107**, 181 (1923).
[34] R. G. Dickinson and A. L. Raymond, *J. Am. Chem. Soc.*, **45**, 22 (1923).
[35] H. G. Grimm and co-workers, l.c. on page 89.

charge clouds in this lattice and found that, actually, certain regions between the closed molecules of composition $(CH_2)_6N_4$ are practically free of charge but that at other places charge bridges which, though weak, are detectable experimentally, connect one molecule with another.

The results of this research are shown in Fig. 37b; the charge distribution between the separate molecules is very interesting. At the position C, i.e. between the two upper molecules of the figure, there is a large region in which the charge has declined practically to zero—the lattice displays a fairly definite and extensive gap. Also at B, a very deep valley appears between the charge peak caused by the molecules; the electronic density in the trough amounts only to 0.1 electron per Å^2. At A, on the contrary, two charge bridges lead from the upper left to the middle molecule, which always show even at their minimum position the considerable density of 0.9 electron per Å^2. They are responsible for the homopolar bond between the molecules. The impression is gained, therefore, that the dispersion forces acting between the H atoms are the main cause of the lattice cohesion.

c) *Molecular Lattices of Long Chain Substances*

It seems particularly important to mention here the lattices of long chain aliphatic compounds in which, on the one hand, strong polar groups are present, as in the fatty acids and alcohols, and on the other, larger non-polar molecular components which give rise to dispersion forces. By reason of their filament-like form, these substances lead us gradually to the lattices of long chain high polymeric substances in which different forces provide for cohesion in different directions.

The paraffins, aliphatic fatty acids and alcohols have been investigated most thoroughly, particularly by A. Müller and his co-workers,[36] also by J. J. Trillat[37] and by Brill and Meyer.[38] In the examination of the paraffins of the formula $C_{11}H_{24}$ to $C_{30}H_{62}$, the interesting fact emerged that, with increasing temperature, the length of the chain itself remained practically unchanged, a fact connected with the strength of the primary valence bond, whereas the lattice dimensions, on the other hand, exhibited a very considerable thermal expansion. We have here the influence of thermal vibrations opposed to van der Waals forces.

It may be observed here, with respect to the conditions in cellulose and its derivatives to be discussed later, that all long chain aliphatic substances tend to a large extent to polymorphism; thus two different modifications

[36] Cf. A. Müller, *Proc. Roy. Soc. London*, **114**, 542 (1927); **120**, 437 (1928).
[37] J. J. Trillat, *C. R.*, **180**, 1329 (1925).
[38] R. Brill and K. H. Meyer, *Z. Krist.*, **67**, 570 (1928).

have already been observed for the paraffins and three for the fatty acids. The modification of the paraffins which is stable at higher temperature shows greater symmetry of the individual chain then corresponds to its elliptical cross-section; this can be understood only by assuming that the long chains in these lattices rotate about their long axes and, as a result, no longer exhibit elliptical symmetry perpendicular to the long axis but, rather, axial symmetry. Actually, the chains in the low temperature modification resume an elliptical cross-section and the free rotation turns into a normal vibration of the chain about an equilibrium position.[39]

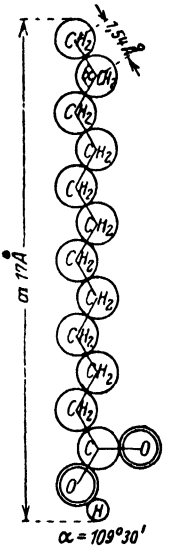


Fig. 38a. Individual Lauric acid chain in the lattice, after Brill and Meyer.

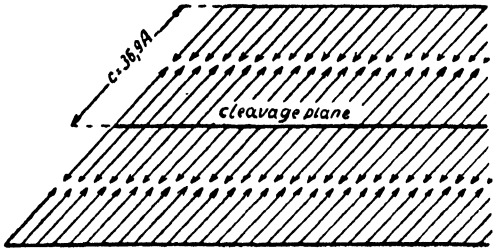


Fig. 38b. Diagrammatic representation of the arrangement of the fatty acid chains in the crystal lattice.

Fig. 38 shows diagrammatically the arrangement in the lattice of the fatty acids; the two carboxyl groups of two molecules assume the relative positions already discussed and cause, so to speak, the formation of double molecules in the lattice. Along these planes, cohesion is particularly strong, whereas only very weak forces are acting along the other surfaces occupied by the terminal methyl groups; these are the planes which cause the weakness of the whole structure and the marked laminar behavior. It is convenient now to apply the concepts regarding packing of atoms and

[39] C. S. Fuller and C. J. Frosch, *J. Am. Chem. Soc.*, **61**, 2575 (1939).

molecules in order to formulate rules regarding the volumes they assume in the solid or liquid state. It is obviously clear that a constitutive influence, namely the degree of springiness of the molecule, must also play a part in this. This has probably been the reason that numerous attempts made years ago to arrive at simple additive relationships were not always successful. Work of Kopp,[40] Lossen,[41] Gervaise-Le Bas,[42] Pope and Barlow[43] and others may be cited.

We should expect to find simple relations only in homologous and polymeric homologous series and actually can find them there, as shown by the case of the paraffin series. In the crystalline state all paraffin chains have about the same cross section of 18.5 Å^2; their length is made up of increments, as is evident from Fig. 39.

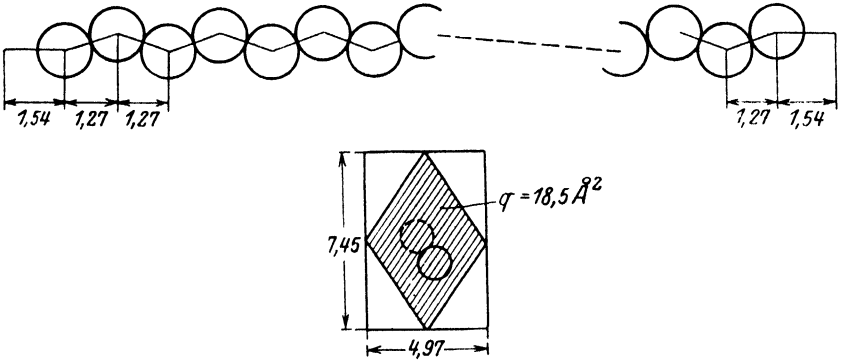


Fig. 39. Length and cross dimensions of a paraffin chain.

The volume of a single paraffin molecule of n C atoms is accordingly

$$18{\cdot}5[(n-1) \times 1{\cdot}27 + 3{\cdot}1]\ \text{Å}^3 = 18{\cdot}5\ (1{\cdot}27n + 1{\cdot}83)\ \text{Å}^3.$$

Tables 63 and 64 record the densities and volumes calculated from those densities of a few simple paraffin molecules. Column 4 gives the volumes calculated by the above formula from x-ray data for the crystalline state. Column 5 contains the quotient, which indicates how many times the molecular volume found for the liquid state is greater than that calculated for the crystalline state. The lower hydrocarbons are compared at 0° in Table 63 and the higher at 99° in Table 64.

The quotient of Columns 4 and 5 thus remains constant, so that com-

[40] H. Kopp, *Ann.*, **128**, 193 (1863).
[41] F. Lossen, *Ann.*, **214**, 81 (1882); **254**, 42 (1889).
[42] M. Gervaise-Le Bas, *Phil. Mag.* (6), **14**, 324 (1907); **16**, 60 (1908).
[43] W. J. Pope and W. Barlow, *Proc. Chem. Soc. London*, **22**, 264 (1906).

parison at the same temperature is legitimate. Inasmuch as the individual CH_2 groups, which behave essentially as independent centers of

TABLE 63

CALCULATION OF DENSITIES FROM TRUE MOLECULAR VOLUMES

	Density at 0°	Mol. Wt.	Volume of a Molecule from the Density (in Å³)	Volume of a Molecule calcd. from: 18.5 ($1.27n + 1.83$) Å³	Quotient of Volumes
Butane	0.60	58	159	128	1.24
Pentane	0.646	72	183	151	1.22
Hexane	0.677	86	208	175	1.19
Heptane	0.700	100	234	198	1.18
Octane	0.718	114	261	222	1.17
Nonane	0.733	128	286	245	1.17
Decane	0.745	142	313	269	1.16
Undecane	0.755	156	339	292	1.16
Dodecane	0.765	170	368	316	1.16
Tridecane	0.771	184	391	339	1.15
Tetradecane	0.774	198	420	363	1.16

TABLE 64

CALCULATION OF DENSITIES FROM TRUE MOLECULAR VOLUMES

	Density at 99°	Mol. Wt.	Volume of a Molecule from the Density (in Å³)	Volume of a Molecule calcd. from: 18.5 ($1.27n + 1.83$) Å³	Quotient of Volumes
Nonane	0.6541	128	320	245	1.31
Decane	0.6690	142	345	269	1.30
Undecane	0.6816	156	374	292	1.28
Dodecane	0.6930	170	402	316	1.27
Tridecane	0.7008	184	429	339	1.27
Tetradecane	0.7078	198	459	363	1.27
Pentadecane	0.7136	212	487	386	1.31
Hexadecane	0.7197	226	522	410	1.27
Heptadecane	0.7245	240	543	434	1.25
Octadecane	0.7288	254	572	457	1.25
Nonadecane	0.7323	268	598	481	1.25
Eicosane	0.7363	282	628	500	1.25
Heneicosane	0.7400	292	654	528	1.24
Docosane	0.7422	310	688	551	1.24
Tricosane	0.7456	324	714	574	1.24
Tetracosane	0.7481	338	742	598	1.24

attraction, exert approximately equal forces from group to group at any one temperature, equal distances between the molecules are to be expected.

Otherwise, only very general viewpoints can be advanced, such as the relation emphasized by Gervaise-Le Bas that ring closure leads to a decrease in volume; further, that the above mentioned springiness actually can be observed experimentally: asymmetric and irregularly shaped molecules have a greater volume than regular ones, as shown by the following comparison:

Cyclohexane $d_{19.5^0} = 0{\cdot}7788$;	Vol. of a molecule 175 Å^3
Methylcyclopentane $d_{19.5^0} = 0{\cdot}7488$;	Vol. of a molecule 184 Å^3

In liquids, molecular volume multiplied by a low power of surface tension has been shown to be an additive quantity and has been termed the parachor by Sudgen.[44] Its additivity holds over a considerably greater territory than the density relations just cited, which are true only within homologous series. The zero volumes investigated by Biltz should yield further information.

In many cases crystal form and crystal habit may be represented very clearly by space models. Although we may not be able to make such exact assertions regarding crystal structure in a given molecule as in ionic lattices, a number of qualitative relationships can be adduced. Groth, in his chemical crystallography, formulated a relation between molecular structure and crystal structure for molecular lattices and Duden and Scharff[45] many years ago inferred from the cubic crystal structure of hexamethylene tetramine a high symmetry of the molecule which was later confirmed by x-ray analysis.

It has been mentioned previously that the single groups of a long hydrocarbon chain act outwardly as independent centers of attraction; for each group in the compaction of molecules from gaseous to liquid or solid state, a definite amount of energy will be freed. In a paraffin chain, for example, molar cohesion is distributed between the individual links as follows:

$$\text{Molar cohesion in calories per member} \quad \underset{1{\cdot}8}{CH_3}\ \underset{1}{CH_2}\ldots\underset{1}{CH_2}\ \underset{1{\cdot}8}{CH_3}$$

Energy quotas of this order of magnitude are obtained if the chains are entirely surrounded by others, i.e. if they possess 8 neighbors. If only two chains exist parallel to one another, we can count on only about one quarter of the total molar cohesion,

$$\frac{[2 \times 1{\cdot}8 + 1(n-2)]}{4} \tag{36}$$

[44] S. Sugden, *J. Chem. Soc. London*, **125**, 1167, 1177 (1924).
[45] P. Duden and M. Scharff, *Ann.*, **288**, 218 (1895).

The amount of energy liberated is much less if two chains are arranged "head to head," with only the terminal groups together. It amounts then only to

1.8 Calories per mol.

The parallel orientation of the chains is, therefore, the type of assemblage in which the decrease of total energy is a maximum; accordingly it will correspond to equilibrium at lower temperature, and will also favor the formation of clusters or groups in the liquid state.

Actually, Stewart and Morrow have observed interferences in liquid fatty acids and paraffins (see later, p. 191), which point to the existence of bundles. The fundamental researches of Adam[46] and Langmuir[47] showed some time ago that film formation of fatty acids on water surfaces is due to the fact that the carboxyl groups cleave to the surface of the water while the lipoid hydrocarbon chains, in consequence of their strong molecular cohesion, form a relatively stable surface film which, itself, has a very low surface tension on account of the small secondary valence effect of the end methyl groups. If we calculate the surface tension of such a film in absolute energy units from molecular cohesion, we obtain values between 10 and 50 dynes/cm, which agree satisfactorily in order of magnitude with values determined experimentally.

Later, J. J. Trillat[48] demonstrated, by detailed experiments on the orientation of chain molecules on metal surfaces, and in phase boundaries, that the parallel arrangement of chain molecules can be detected similarly in the liquid or adsorbed state and that it plays a determining rôle for the physicochemical and technical properties of such films.

That long molecules of complicated structure are able, even in the liquid phase, to form oriented clusters or groups over large expanses is shown particularly well by the existence of the mesophases in which the presence of oriented particle groups can be detected both by optical and x-ray methods. These substances constitute a transition from true liquids to true crystals, such that any given molecule is neither freely motile as in the former nor entirely fixed as in the latter: rather it still possesses, according to the particular type of mesophase concerned (smektic or nematic state), certain degrees of freedom of rotation or deformation which make it to some extent independent of neighboring molecules. Later on, conditions in the mesophases will be discussed in rather more detail

[46] N. K. Adam, *Chem. Rev.*, **3**, 163 (1927).
[47] I. Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917).
[48] J. J. Trillat, *Journ. Phys. et Rad.*, **10**, 32 (1929).

and it may suffice here to cite the comprehensive works of Vorländer,[49] Friedel,[50] Oseen[51] and Zocher.[52]

If now, the long chain molecules are oriented parallel to a crystal lattice, the two groupings shown in Fig. 40 are possible. Simple hydrocarbons of regular shape are known to prefer arrangement 1 and consequently form laminae preferably. The paraffins, naphthalene and anthracene are especially good representatives of this type. If type 2 is assumed, the conditions are less clear; the products crystallize, as a rule, in needles (diphenyl, dibenzyl, etc.).

If, in addition to hydrocarbon residues, other polar groups of higher molecular cohesion are present in the molecule, they generally exert a special influence on the molecular arrangement in the crystal structure. The hydroxyl groups (molar cohesion 7.2 Cals.), the keto groups and, particularly, the carboxyl groups (molar cohesion 8.97 Cals.) are examples. If there is only one such group in the molecule, double molecules frequently result which are often characterized by a center of symmetry; if, however, several groups are present, a chain-like molecular arrangement appears (see p. 99) which gives rise to particularly large cohesive forces in one direction in the crystal, resulting frequently in needle structure.

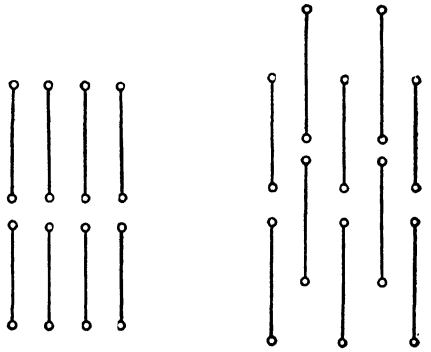


Fig. 40. Chain molecules in different arrangement in the crystal lattice.

The first case is typical for the monobasic fatty acids. In the lattice of these substances, each of two fatty acid molecules are arranged with their carboxyl groups reversed and these double molecules behave just like a paraffin of double the length of the single fatty acid. They crystallize like the paraffins in laminae and exhibit also the above mentioned marked tendency to cleavage which is caused by the low cohesion of those planes in which the acids impinge on one another at their end groups. The second, less evident, case is found, for example, in anthraquinone and hydro-

[49] D. Vorländer, *Kristallographie der Flüssigkeiten.* Leipzig 1924.

[50] E. Friedel, cf. e.g., *Z. Krist.*, **79**, 1 (1931).

[51] C. W. Oseen, *Die anisotropen Flüssigkeiten. Tatsachen und Theorien.* Berlin 1929, p. 8.

[52] H. Zocher, *Physik. Z.*, **28**, 790 (1927).

quinone and similar substances containing oxygen and having a marked tendency to needle structure.

d) Molecular Lattices and Symmetry of the Unit Cells

Asymmetrical molecules occur very frequently in organic chemistry. We would, at first, be inclined to expect, therefore, that the triclinic crystal system would be frequently met with, but actually nearly all asymmetrical molecules crystallize in the monoclinic system; their lattices possess diagonal screw axes or slip-surface planes of symmetry.

According to Reis and Weissenberg,[53] the reason is as follows: *Translation* is characteristic for the triclinic system, but a parallel arrangement of the molecules can only be expected if the directions of the strongest forces of attraction in the molecule are exactly opposite in direction to each other. In most cases, however, they are inclined at some angle and the second, adjacent molecule deviates from the parallel position. If now, we assign to a third molecule the same position with regard to the second as the second bears to the first, a symmetrical saturation results. The first and third molecules are parallel to each other and the arrangement may be continued indefinitely; it corresponds to a two-fold screw axis or a slip-surface plane of symmetry, which may be anticipated very frequently for symmetrical molecules and may lead to the formation of needle forms.

The above consideration holds only for the aggregation of molecules from the gaseous state. In solution, solvation or desolvation of the molecules comprising the crystal enters in. In compounds which contain both lipophile and hydrophile groups, it is well known that the former are solvated in solvents according to the nature of the hydrocarbon and the latter in water or in other media having strong dipole moments (see p. 29). Naturally, the unsolvated (free) groups are the ones that directly determine the association of the molecules, because their association forces are hereby completely fully saturated. On the other hand, in associations of solvated groups, only the molecular cohesion is diminished and the heat of solvation set free.

An explanation can be found in this way for the phenomenon well known in organic chemistry that both rate of crystallization and crystallizing power may greatly differ from solvent to solvent. It may be cited as an example that the higher dibasic acids crystallize from water in laminae but from hydrocarbons in quite long, thin needles, because in water the lipoid chains, as in the paraffins, promote the production of laminae, whereas in benzene the differing solvation relationships cause the produc-

[53] A. Reis and K. Weissenberg, *Z. Physik*, **34**, 406, 420, 433 (1925).

tion of needles. Conversely, azobenzene, which crystallizes in laminae from most solvents, may be obtained in needle form from dilute sulphuric acid. If the oxygen-bearing groups: carbonyl, carboxyl, etc., serve as the primary foci of crystallization, it will be convenient to crystallize from media in which these groups are not solvated. This may be related to the fact that many oxygen-bearing compounds come out particularly well from hydrocarbons and that even small amounts of moisture may hinder crystallization.

Accurate theories of molecular structure and of the size of the atoms in the molecule may be applied to the problem of isomorphic replaceability in the crystal association, which has been largely developed in the field of inorganic crystals by Goldschmidt[54] and Grimm[55] in recent years by the introduction of ionic radii. The material accumulated by Giuseppe Bruni[56] in careful researches may easily be co-ordinated and understood in the light of concepts of molecular and crystal structure. The formation of mixed crystals of phenanthrene and anthracene or naphthalene or dihydronaphthalene may be explained by the similar form and size of the molecules concerned and by the similarity of their association forces. The same is true for the series stilbene, tolane and azobenzene. Very characteristic is the formation of mixed crystals observed by Villiger[57] in 5-nitro-2,4-dichlorobenzoic acid and 5-nitro-4-oxy-2-chlorobenzoic acid. For isomorphic replaceability there is the obvious proviso that the different atoms or atomic groups of the compounds crystallizing together occupy about the same space and that, in their interchange, the association forces of the whole molecule are not essentially influenced. This is generally the case if methyl (molar cohesion = 1.8) is replaced by the same sized hydroxyl (molar cohesion = 7.2) or if hydroxyl is replaced by halogen. Since, however, in the special case investigated by Villiger, the molecule contains a whole series of other groups of stronger molecular cohesion (carboxyl and nitro-groups), the change of a hydroxyl to a halogen group cannot essentially influence the polarity and the force relationships of the whole molecule.

5. Lattices with Different Forces in Different Directions

We have hitherto described essentially lattices whose cohesion is effected by the same force in all three directions in space and have pointed out

[54] V. M. Goldschmidt, *Naturwiss.*, **14**, 477 (1926).
[55] H. G. Grimm, *Handbuch der Physik.* 2nd ed. Vol. 24, part 2.
[56] G. Bruni, *Über feste Lösungen.* Stuttgart 1902.
[57] V. Villiger, *Ber.*, **51**, 2596 (1928).

only occasional transition cases; we will now consider those substances in which different kinds of forces prevail in different directions of the lattice structure.

At the outset we may examine Fig. 40a, which, according to H. G. Grimm[58] represents the conditions very clearly. At the corners of a tetrahedron are the four extreme types of linkage described in the foregoing sections; the transition lattices lie on the edges of the tetrahedron. A glance at the figure reveals the interesting fact that the homopolar primary valence bond (a) must participate in all transition lattices; the three edges which lead from 3i to 3z, from 3i to 3m and from 3m to 3z, are void (if we ignore the hydrates and ammoniates of ionic lattices). In

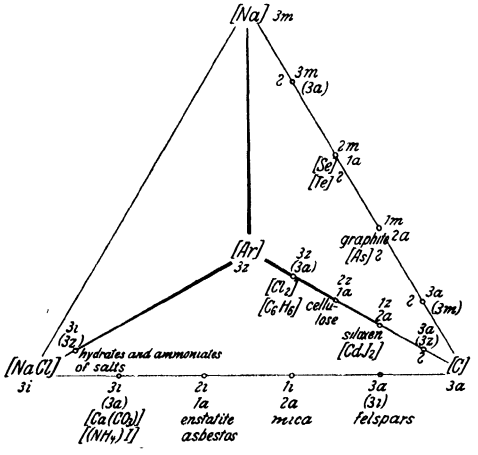


Fig. 40a. Systematic survey of crystal lattices in which different kinds of forces prevail in different directions of the lattice structure.

contrast, we find a number of very interesting compounds on the other three edges.

Consider first the tetrahedron edge from 3i to 3a. We have here substances in which the atomic (diamond type) and the heteropolar ionic linkage participate simultaneously in the lattice structure.

a) Lattices with Atomic and Ionic Linkage

Proceeding from the left side, we have in NaCl, CaO, CaF_2 etc., first, true ionic lattices. But in all compounds which contain radicals or complex ions, conditions are otherwise. Thus, for example, in $(NH_4)Cl$, it is true that the crystal lattice is certainly built up in the different directions by true ionic forces, but one of the two ions, namely, $(NH_4)^+$ owes its cohe-

[58] H. G. Grimm, *Handbuch der Physik.* 2nd ed. Vol. 24, part 2.

sion to homopolar atomic valence. Since, naturally, the lattice forces are themselves co-determined by the size and polarizability of this ion, the atomic type of linkage participates in this and in similar cases, such as $CaCO_3$, $BaSO_4$, NaCN etc., not directly, but indirectly, in the structure of the lattice as a whole. This is expressed in the diagram by inserting under the symbol (3i) for the ionic linkage in three directions, the symbol 3a in parentheses for the atomic linkage in three directions.

If we proceed further in the direction towards the atomic linkage corner of the tetrahedron, we come to lattices which cohere in two directions by ionic forces but in one by atomic forces; they belong to a definite group of silicates whose structure will be discussed later in another connection (see p. 169). Particularly well known representatives are enstatite $MgSiO_3$, diopside $CaMg(SiO_3)_2$ and asbestos. The latter at once suggest by their very marked fibrous habit that in one direction a particularly strong link prevails, namely, the atomic; it is produced in the lattice by O-Si-O chains, while in the other two directions weaker ionic forces prevail.

The next step leads to substances with one ionic and two atomic linkages; again silicates provide particularly suitable examples in the large groups of micas and chlorites. Their essentially laminar structures show very definitely that strong atomic forces are effective in two directions whereas, in the third, cohesion is produced by weaker ionic linkages.

Finally, we arrive at a class of compounds in which the lattice as such is welded together in all three directions by atomic forces, while ionic linkage is present in the individual lattice cells. Examples of such substances which, following Grimm, will be denoted by the symbol 3a (3i) are $CaTiO_3$, $KMgF_3$ and most of the feldspars. Reis has applied the term honeycomb lattice to such lattices, which also exhibit very interesting tensile properties.

After them we come along the tetrahedron edge 3i—3a to the true atomic lattices which have their typical representative in the diamond and about which everything necessary has been said previously.

If we pass now along the edge 3a—3m, we come to the

b) Lattices with Atomic and Metallic Linkages

Substances in which lattice structure is provided for in all three directions by homopolar primary valences, while the cohesion of the lattice cells is due to the metallic bond, may be present in many intermetallic compounds although nothing definite can be said here regarding the exact type of linkage involved.

On the other hand we have in graphite and probably also in Se, Sb and Bi, elements in which homopolar chemical valences are predominant

in two directions while in the third spatial direction the metallic bond comes into operation. This view is confirmed both by the strongly anisotropic mechanical behavior of the substances and especially by the high degree to which their electrical conductivity depends on direction.

There is much to be said also, according to Bernal, for assuming the existence in Se and Te of metallic linkages in two directions and to make atomic forces responsible for the cohesion in the third direction. A large series of other semi-conductors, some of which have very interesting and important technical properties, cannot yet be included in the above scheme with certainty, but lie definitely in some manner along the tetrahedral edge 3a—3m.

The last outstanding tetrahedral edge leads us to

c) Lattices with Homopolar Valence Linkage and van der Waals Linkage

These include, notably, the layer lattices which cohere in two directions by primary valences and in the third by secondary valences; examples, which we shall later discuss in greater detail, are CdI_2, MoS_2, AsI_3, talc, graphitic acid and siloxene. The anisotropy of the linkage type is very markedly expressed in them by the laminar habit and by the mechanical properties. To this type belong also reticulate filamentous lattices such as exist in vulcanized rubber and in numerous synthetic high polymers.

We come next to a type which is of very special importance to natural and synthetic organic high polymers: to the filament lattices which cohere in one direction by primary valences and in the other two by van der Waals forces. The chief representatives of this class, which will be discussed in great detail in the second volume of this work, are cellulose, chitin, rubber, proteins and a large number of synthetic high polymers such as polystyrene, polyvinyl acetate, polyacrylic esters, polyethylene oxide, etc.

The next step leads us to those compounds, discussed above, in which the lattice itself is formed in all three directions by secondary valence forces, but in which the lattice units are kept together by primary valences. We have here the large number of molecular lattices consisting of compact units, such as Cl_2, CH_4, C_6H_6 and we arrive finally at the inert gases in whose lattice-like structure only secondary valence forces participate.

We may now regard the classification of crystal lattices on the basis of cohesive forces as closed and turn to the other classification which depends mainly on considerations of symmetry. It will appear in the course of the description how these two systems finally overlap and how, particularly in those lattices which have been discussed last, they supple-

ment each other in their evidence regarding the structure of these substances.

II. CLASSIFICATION OF CRYSTALS FROM THE ASPECT OF SYMMETRY

1. General Remarks on the Symmetry of Crystal Lattices

It has been shown in the previous chapter that the study of organic and inorganic crystal structures has led to important general relationships between the forces of cohesion in atoms, ions or molecules in the lattice and the distances separating them. Almost simultaneously with this research, which was prosecuted largely by Bragg and Goldschmidt, another more geometrical method of treating the connection between crystal structure and chemical constitution was developed by A. Reis[59] and elaborated particularly by P. Niggli[60] and K. Weissenberg[61] into a general classification. In a rational crystallo-chemical treatment of high molecular substances, we must, of course, rely on both methods of consideration, which at first sight are somewhat contradictory. It is clear that, only by applying all available knowledge, the elucidation of these complicated structures can be attained. It is, therefore, necessary to outline briefly the general principles of symmetry concepts and to supplement the distance rules already mentioned by discussing the Weissenberg theory of crystal structure in greater detail.

The particular aim of an x-ray structure determination, which can be nearly always attained with macroscopic crystals and very often also with fiber diagrams and highly oriented preparations, is the measurement of the unit cell. By this we understand the smallest body from which the entire crystal can be built up merely by parallel displacement along three directions. The unit cell is determined by finding the periods of identity along the crystallographic axes. These are the distances which must be traversed along each of the preferred directions in the crystal in order to arrive at a lattice point identical with the initial one. If, in addition to these fundamental periods of the lattice, we also know the angles between the crystallographic axes, we can determine the volume V of the unit cell according to stereometric formulas.

If we multiply the unit volume by the density, we obtain the absolute weight of the unit cell in grams and, by dividing this by the weight of a hydrogen atom ($m = 1.65 \times 10^{-24}$ g), the relative weight of the unit cell

[59] A. Reis, *Z. Elektrochem.*, **26**, 412, 529 (1920).
[60] P. Niggli, *Geometrische Kristallographie des Diskontinuums*. Leipzig 1919.
[61] K. Weissenberg, *Z. Krist.*, **62**, 13, 52 (1925).

is found. If, particularly in molecular lattices, we know something regarding the molecular weight of the substance investigated from observations in vapor or solution, we can ascertain the number of atoms or molecules present in the unit cell by dividing the weight of the cell by the molecular weight. Table 65 contains data calculated for a number of typical compounds; in the case of hexamethylene tetramine, for example, two molecules of composition $C_6H_{12}N_4$ are present in the unit cell. It is known from reported structure determinations that each of these molecules is in itself very closely packed while their centers are separated by a distance of several Å.

TABLE 65

UNIT CELLS OF A FEW MOLECULAR LATTICES

Substance	Density	Volume of the unit cell in Å^3	Number of molecules in the unit cell
CO_2	1.63	176	4
Benzene	1.09	471	4
Oxalic acid	1.90	302	4
$CO(NH_2)_2$	1.33	147	2
Pentaerythrite	1.39	329	2
Metaldehyde	1.27	442	8
Isatin	1.51	645	4
Hexamethylentetramine	1.34	341	2
Stearic acid	0.94	1837	4
Anthraquinone	1.43	1931	8
Triphenyl methane	1.06	3050	8
Phthalocyanine	1.44	1200	2
Vitamin B	1.43	1648	4
Follicular hormone	1.22	1479	4

Since the unit cell combines in itself all the properties of the macroscopic crystal, it possesses its symmetry also. The spatial arrangement of the separate atoms in the unit cell is, therefore, not at random but is governed by the symmetry elements specific to the crystal. Crystallographic theory permits accurate counting and description of all combinations of symmetry elements which are geometrically possible and shows that in three dimensional space there are only 230 such possibilities. Each of them is defined by a specific group of symmetry elements and by data on their mutual positions. Such a group is accordingly termed a space group.

The above definition of a unit cell suggests a comparison with the conditions in the gaseous state, research on which has given rise to the term molecule. In a perfect gas, by progressive division, we arrive ultimately

at structures which cannot be further subdivided without loss of the chemical properties of the macroscopic phase constituted by them. We call these particles molecules and can seek in a single one of them all the chemical properties of the substance, because the assembly of many molecules to form the gaseous phase introduces no new factor, inasmuch as the individual particles exert no forces on one another in this state. In the same way, by progressive subdivision of a crystal, we may arrive at a unit cell which is the ultimate structure, embracing all the properties of the crystal; occasionally this has also been termed the crystal molecule. If, however, we compare the unit cell with the kinetic molecule, we often find that it is a multiple of the latter. We can, therefore, state: in organic molecular lattices, the smallest region which embraces all the chemical properties is usually smaller than that which in itself includes all the properties of the crystalline state.

This is easy to understand. The chemical properties are given by the structure of the kinetic molecule in the isolated state, while the sum of all the physical properties of the solid substance (hardness, refractive index, conductivity, etc.) are determined mainly by mutual interactions among the molecules; accordingly these properties can seldom be expressed by a single molecule but require for the purpose a group of molecules in association.

If the unit cell is known, the next step in structure elucidation is to search for all the symmetry elements present, i.e. we determine the space-group. By its symmetry, the geometrical conditions within the unit cell are defined. A full description of these conditions would far exceed the scope of this treatise and we can only cite the comprehensive literature on the subject, particularly Niggli's book and Weissenberg's original papers.

In order to understand the idea of the geometric systematization, the general character of the symmetry elements will be explained by a simple example. Fig. 41 represents a crystal which possesses the property of self-coincidence on rotation through 180° about the axis AA′. This is termed the symmetry property of a two-fold (digonal) axis of rotation: it is determined by the fact that in this crystal lattice all points are translated into one another on rotation through 180° about the axis AA′, as shown diagrammatically in Fig. 42. 1 changes into 2, 1′ into 2′, etc.

In addition to the two-fold, there are three, four, and six-fold axes of rotation which, in turn, possess the property of allowing a given point to appear in three, four and six positions in the unit cell.

If, now, we imagine, as shown in Fig. 43 the two points P_1 and P_2 which, on account of the four-fold axis A are a crystallographic group

(equivalent point positions) bound together by any forces, possibly by a chemical primary valence, then the four-fold axis is an expression of the fact that all four points are joined together by equivalent forces. Parallel displacement applied to individual cells, results in the formation in the crystal of closed groups, each of four appropriate points. There are, therefore, symmetry elements which, in conjunction with the specific translation periods pertaining to each crystal, permit the formation of closed point groups in the lattice (rotation axes, symmetry plane, center of symmetry). Such point groups have been termed micro-units or islands by Weissen-

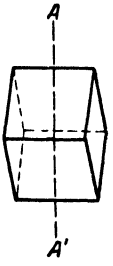


Fig. 41. Crystal with two-fold axis of rotation.

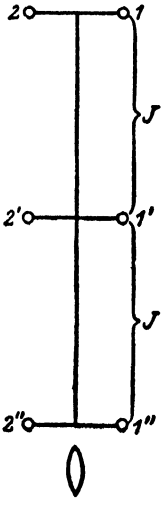


Fig. 42. Point arrangement in a two-fold axis of rotation.

berg and his method of systematization consists first in counting up all the micro-units possible in the three dimensional lattice.

Besides the above named rotation axes, there are still further axial symmetry elements, the so-called screw axes. Fig. 44 represents the point arrangement corresponding to a digonal screw axis; it is evident that the crystallographically equivalent points 1 and 2 are no longer capable of translation into one another merely by rotation through 180°, but only by a parallel displacement of the rotated points by the half identity period J parallel to the axis of rotation.

The coincidence movement thus consists of
rotation + translation.

Since the translation is conveyed through the entire crystal, an infinite number of equivalent points is produced by the screw axis from a given point 1. If now we assume a given force to be acting between the two points 1 and 2, the presence of the screw axis denotes that the same force effect extends throughout the crystal parallel to the direction of this axis (screw axes, slip-surface planes).

While a rotation axis leads to an ultimate collection of point groups, the screw axis provides, by the same type of combination, a chain of points traversing the entire crystal, which Weissenberg has named an island chain. If two screw axes are present, we obtain island networks and in the

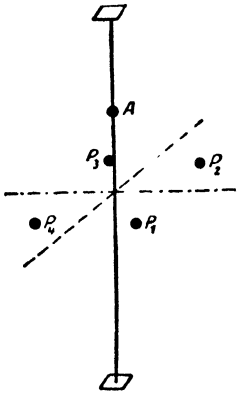


Fig. 43. Point arrangement of a four-fold axis.

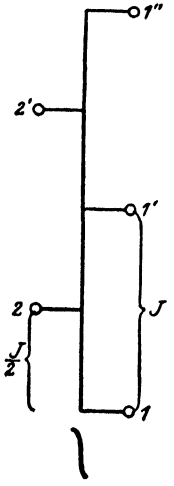


Fig. 44. Point arrangement of a digonal screw axis.

presence of three digonal screw axes perpendicular to one another we obtain island lattices.

For the present purpose we can, therefore, divide the symmetry elements into two groups:

1. Those which build up an ultimate point group (molecule) from one or more given points (atoms) (rotation axes, symmetry planes, center of symmetry) (Class I) and
2. Those (Class II) which translate the given point into an infinite number of other equivalent ones. This class gives rise either to chains or networks which traverse the whole lattice, or there results the whole three-dimensional crystal (screw axes, slip-surface planes, translation).

In a lattice whose space-group is known, the Weissenberg method allows us to determine all the possible micro-units and to indicate their symmetry. Their count indicates the extent of closed, finite atomic groups possible in the crystal lattice investigated and affords for the solid state a certain analogy with a molecular weight determination in the gaseous substance.

It is immediately evident that the micro-units will generally be smaller than the unit cells, for they possess only a portion of their total symmetry, namely symmetry of the first kind. The physical purport of the Weissenberg theory is that in all organic molecular lattices the largest possible micro-units are identical with the kinetic molecules of the substance, a concept which can be tested on all existing experimental material and confirmed, with the exception of certain cases in which association exists in the lattice (metaldehyde, acetaldehyde ammonia, etc.).

Thus, for example, in the lattice of urea, the atomic group $CO(NH_2)_2$ is the largest that can be comprised in a micro-unit; this is consistent with the expectation emphasized particularly by Willstätter[62] that in the molecular lattices of organic substances the molecules always persist as closed groups. Thus the clear idea of closed atomic groups in molecular lattices derived from distance measurements, is supplemented and confirmed by a geometrical systematization of all possible micro-units.

The relation has proved true also in lattices of inorganic substances; the micro-units are identical with the complex ions or with the molecules of the intermetallic compounds; e.g. $ZnMg_2$, CO_3, $PtCl_4$, SnF_6. In the first case there is an intermetallic linkage and in the other cases there are heteropolar ionic linkages. It is evident from this that the purely geometrical demarcation of the micro-units can tell us nothing about the physical nature of the forces between the individual parts; it will affirm only that the points capable of linkage form a closed group in the crystal, but nothing regarding the manner in which, and the force by which, they are held together.

However, by considering the symmetry elements of the second kind, the Weissenberg method furnishes information on general structural principles for the building up of crystal lattices. For this coincidence operation enables a given point to be translated into a number of others; the field of force whose point arrangement corresponds to a digonal screw axis is, therefore, of such nature that it will not be saturated after the assembly of a certain finite atomic number; rather, if a new atom or group enters, there arises a force analogous to those existing previously which

[62] R. Willstätter, *Angew. Chem.*, **32**, 331 (1919).

effects further growth of the chain. We can, therefore, briefly state the contrast between the field of force corresponding to a digonal axis of rotation and to a digonal screw axis respectively in this way: The former is saturated after the assembly of a definite number of atoms, the latter effects growth in a certain direction.[63] Nothing will be said here regarding the nature and magnitude of the forces.

If we are to understand the structure of a crystal lattice fully and are interested both in the mutual position of the atoms and the magnitude and nature of the forces, we must take into account the interval rule and the other properties of the substance in addition to the above described geometrical considerations and try to merge them into a uniform design.

Conditions are simplest and clearest in the ordinary molecular lattice, perhaps in the urea lattice. In this, the ultimate structure determination shows that the group $CO(NH_2)_2$ is closely packed but is relatively far removed from the next identical group; the Weissenberg Tables indicate that this group is the largest possible micro-unit; there is thus full concordance of the two available modes of consideration, the energy one and the geometric one; both recognize the molecule $CO(NH_2)_2$ as a particularly stable group and everything leads to the following conclusion: the urea molecule is held together in the crystal by primary valences while the lattice forces have the order of magnitude indicating molecular cohesion.

The same is true for the majority of molecular lattices already discussed.

We see that purely geometrical consideration of symmetry with particular regard to the groups included, leads to the same results as consideration of the lattice forces on dynamic lines; there are lattices which consist of isolated units firmly closed in themselves, there are lattices which are built up of chains and networks, and there are, finally, crystals in which no internal closed groups can be conceived either geometrically or dynamically; the whole crystal is held together by identical, generally very strong, forces and forms one gigantic molecule. To complete the discussion on different kinds of lattices and conclude the chapter on the solid state, we shall discuss briefly the principal lattice types from the point of view of the intimate connection of certain groups.

2. Primary Valence Lattices

The whole crystal is held together in all directions by identical forces and demarcation of a definite closed region is impossible geometrically and dynamically. Such lattices are familiar among the metals, e.g. Na, Mg, Cu, W, etc. in which cohesion is provided for by metallic bonding

[63] See e.g. H. Mark, *Ber.*, **59**, 2991 (1926).

forces; we know them also as ionic lattices, such as NaCl, CaF_2, CaO, etc., in which heteropolar primary valences determine the structure and we know that there are also primary valence lattices with homopolar atomic linkage: diamond, quartz, carborundum, zinc sulphide, and so on.

It may be added that many synthetic high polymers, as well as natural high polymeric substances which have been processed, form a three-dimensional structure cohering by homopolar valences. In most cases, of course, the regularity of the arrangement is not high enough to result in sharp and intense crystal interferences, but there can be no doubt that the substances concerned are to be classed as more or less highly deformed primary valence lattices.

First we shall take vulcanized hard rubber, in which the long primary valence chains of the natural product are reticulated by simple or multiple sulfur bridges into frameworks which intersect in all directions and give to the product its hardness, non-fusibility and insolubility. The so-called cyclized rubber is also included, because today it must be regarded as proved that, on heat treatment of natural rubber in the presence of condensing agents such as $AlCl_3$, BF_3, etc., there result not only ring structures within the individual valence chains, but also the production of bridges between the chains.

For the rest, nearly all poly-condensation products which have found technical application may be named. By elimination of water, polybasic acids and polyvalent alcohols, notably glycerine, give rise to the so-called glyptals, which in the initial stage of condensation exhibit predominantly chain character, but in later stages of the reaction give every indication of far reaching spatial reticulation. The same holds for condensation products of urea and formaldehyde or phenol and formaldehyde. In all cases, where condensation is carried far enough, we obtain solid, hard, non-fusible and insoluble products of high resistance to impact and high specific gravity.

In conclusion, it may be remarked that many natural proteins and resins—the keratin of nails, hair and feathers, colophony and others—form primary valence lattices which may possess such great regularity that they give at times very definite x-ray interferences, as shown by interesting experiments of Astbury.[64]

The properties of the primary valence lattice enumerated above—in fusibility, insolubility, strength and density—make it difficult to

[64] W. T. Astbury, *Fundamentals of Fiber Structure.* Oxford 1933. Cf. also W. T. Astbury, *Trans. Faraday Soc.*, **29**, 193 (1933); see also T. B. Speakman, *Proc. Roy. Soc.* (B) **130**, 377 (1928).

treat them according to the exact methods of physical and organic chemistry, although these same properties enhance their technical importance. The result is that data relating to internal structure are inadequate to characterize the artificial materials which play such an important part in modern industry.

3. Primary Valence Networks

Here, also, there is a complete concordance between geometric and dynamic systematization; lattices in which, according to Weissenberg, there is a possibility of linkage of the lattice points in two dimensions, and where conditions are therefore favorable to layer lattice development, may be held together by the most diverse forces. We are interested here in those cases in which primary valence networks are formed through the action of homopolar atomic linkages which traverse the entire crystal uniformly.

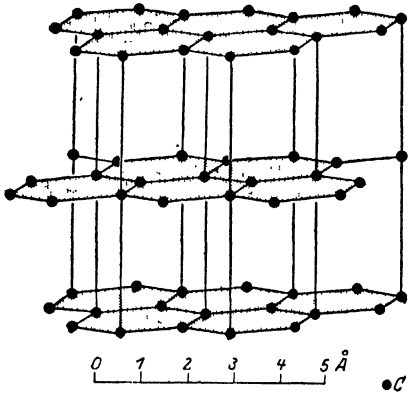


Fig. 45. Primary valence network lattice of graphite.

Thus, for example, in the graphite lattice, the micro-unit is identical with the carbon atom, i.e. no larger closed atomic group can be formed. If any two points lying in the basic plane (Fig. 45) are joined in this lattice, the bond is extended by the symmetry elements over the whole plane, but in such a way that any two consecutive planes remain free of one another. It is again legitimate from the distance rule, to identify the linkage in the reference plane with a chemical primary valence, when primary valence networks, N_1N_2 etc., are obtained which may be linked to one another by bonds of other types (layer lattices). If, at any point, however, two such networks are linked together, then the cohesion will spread by means of the symmetry elements throughout the whole crystal. The linkage within the layers themselves is, however, independent of the linkage between one layer and another. These conditions have already been discussed and allow of an explanation of the laminar form, the accompanying easy slippage, the anisotropic character of the conductivity and various other properties of graphite.

In addition to graphite, there is a series of other reticulate or layer attices. The most closely allied is the lattice of graphitic acid.

If graphite of very variable origin is treated with nitric acid or a mixture of concentrated HNO_3 and H_2SO_4, a definite swelling of the laminae is observed. Hofmann and Frenzel[65] have found that all the x-ray interferences remain practically unchanged by this; only the principal reflection lacks sharpness and shows a shift to smaller angles of diffraction which corresponds to an increase of the lattice plane distance from the normal value 3.37 Å to 3.68 and 4.1 Å. On further swelling, the material changes color and becomes brown; the inter-planar distance of the primary valence networks is now 7.9 Å.

Graphitic acid results if $KClO_3$ is added during the oxidation of graphite; green laminae are obtained which swell actively in water. In thoroughly dried condition, the distance between the carbon layers amounts to 6.4 Å and to 11.3 Å in the presence of 60% water. It is clear that here a very definite layer lattice is present in which the separate lattice planes, which are otherwise firmly bound together by primary valences, become very easily displaced with respect to one another on the infiltration of foreign atoms.

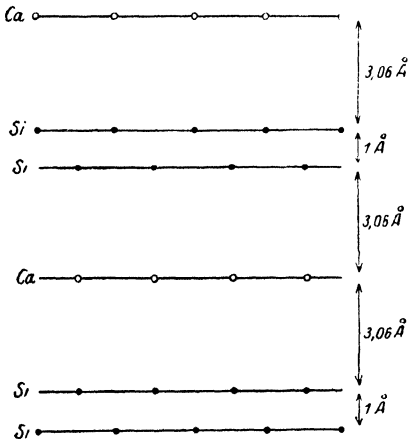


Fig. 46. Point arrangement in the layer lattice of calcium silicide after Boehm and Hassel.

Schleede and Wellmann[66] have obtained very interesting products by the action of alkali metal vapors on graphite; as x-ray data show, the atoms of the alkali metals—K, Rb and Cs were employed—penetrated between the lattice planes of the hexagons and increased their distances quite appreciably; identity periods of 21, 34, 18, 51, 22, 73 Å etc., were measured on the hexagonal axis; graphite itself had $d = 6.79$ Å.

We are just as well informed regarding the structure of calcium silicide, which was described by Böhm and Hassel as a primary valence lattice of six-membered silicon rings linked together by calcium bridges. Fig. 46 shows diagrammatically the arrangement of atoms in this lattice as elucidated by thorough x-ray structure analysis.

All the substances mentioned are characterized by extreme laminar

[65] U. Hofman and A. Frenzel, cf. e.g. *Kolloid Z.*, **61**, 297 (1932); **69**, 351 (1934); furthermore *Ber.*, **63**, 1248 (1930) and *Z. Krist.*, **86**, 340 (1933); **98**, 229 (1937).

[66] A. Schleede and W. Wellmann, *Z. physik. Chem.*, (B) **18**, 1 (1932).

habit. It would be of great interest in this connection to have an accurate knowledge of the siloxene derivatives prepared by Kautsky[67] from calcium silicide, which show the same high tendency to layering and are famed for their interesting topochemical reactions. According to Kautsky's researches, the compounds can experience chemical substitution layer for layer without losing external cohesion, a process which Freundlich has designated permutoid reaction of this crystalline system. It is a special case of a reaction which is confined to definite, spatially fixed points. Such reactions have been much investigated by Kohlschütter and termed topochemical.

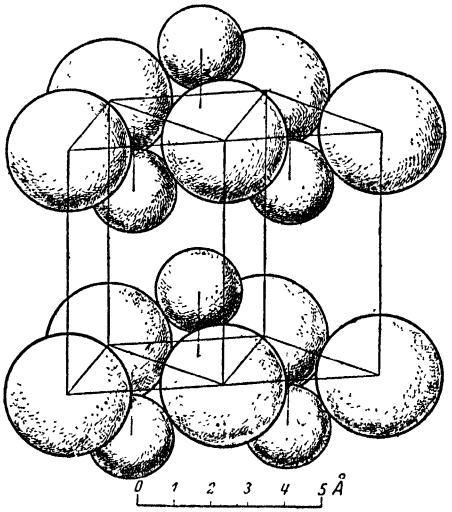


Fig. 47. Layer lattice of cadmium iodide.

The ionic lattices include also a large number of layer lattices in which the same heteropolar type of linkage is present in the layer plane as perpendicular to it; but such that, through the polarizability of the ions, the linkages are considerably greater in a given network plane than they are perpendicular to it. An example of such a heteropolar layer lattice is the lattice of cadmium iodide, represented in Fig. 47, in which the strongly anisotropic conductivity, solubility, etc. are readily understandable from the structure.

Recent researches of de Boer and his collaborators[68] on the intermicellar

[67] H. Kautsky, *Z. anorg. allgem. Chem.*, **139**, 135 (1925); **147**, 81 (1925); cf. also *Ber.*, **57**, 1665 (1925).

[68] C. I. Dippel and I. H. de Boer, *Rec. trav. chim.*, **57**, 277 (1938); cf. also *Z. physik. Chem.*, (B) **21**, 278 (1933); **25**, 399 (1934).

swelling of CaF_2 in cesium vapor are of particular interest in this connection. They show that CaF_2 prepared by sublimation is able to take up quite appreciable amounts of Cs and liberate it again by a completely reversible process.

The particular preference for a given plane is always characteristic of a marked layer lattice. Macroscopically it is generally evident as a cleavage plane and is particularly prominent by its intensity in the x-ray diagrams as the network plane of densest lines. Using deformed preparations of graphite and molybdenite, x-ray diagrams show, moreover, that the distance between the separate valence networks is not as dependable as the atomic distance within these networks. On application of high pressure, reflection from the basic plane of graphite is broadened markedly, while the distance between the crystallographic network planes perpendicular to it remain consistently sharp. This fact indicates that in the minute crystals of the preparations investigated, the distance between layer planes has been somewhat changed by the stress, whereas the primary valence network has remained rigid. A similar effect was found in other well defined layer lattices such as molybdenum sulphide and calcium silicide.

4. Primary Valence Chain Lattices

The next step in the Weissenberg system leads to the chain lattices which are characterized by the presence of a parallel set of screw axes or a set of slip-surface planes. Numerous organic molecular lattices possess this structural principle, in which the molecular groups running through the whole crystal are linked together as island chains. This linkage has no particular chemical significance, as a rule, but it corresponds to the force effects described by the screw axes, generally van der Waals cohesion forces, as, for example, in the lattice of CO_2, oxalic acid, etc.

If, however, the forces which unite the micro-units are of the order of magnitude of chemical primary valence, then we obtain chains extending throughout the whole crystal, which, in accordance with previous terminology, may be designated primary valence chains.

If experience gained from layer lattices is applied to the chain lattices, which are also frequently named fiber lattices, it is to be expected that the cohesion of the primary valence chains will stamp the whole structure and that permutoid reaction will be present to a still higher degree than in layer lattices, because here the strong cohesion due to primary valence acts only in a single direction. We may further assume that the diffraction effects of such primary valence chains will exhibit certain similarities to diffraction phenomena in linear lattices.

It is well known that a rigid collection of points irradiated perpendicularly

with monochromatic x-rays gives a diffraction pattern on a flat plate consisting of curves resembling hyperbolas. Only by the juxtaposition of several linear lattices in regular arrangement do the hyperbolas exhibit

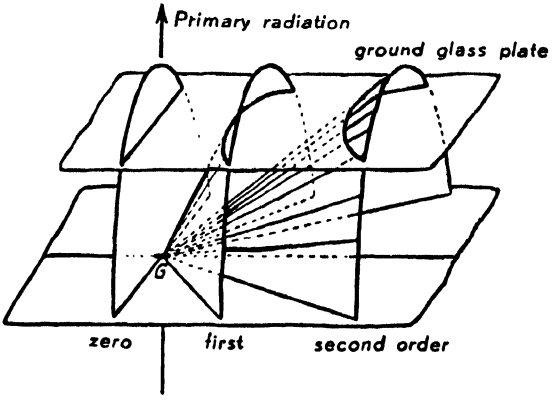


Fig. 48. Diffraction phenomenon in a linear point lattice; co-axial diffraction cones are produced.

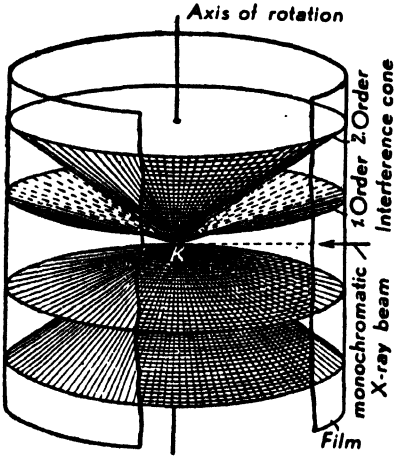


Fig. 49. Diffraction phenomenon in a linear point lattice taken on a cylindrical film; parallel layer lines are produced.

breaks, due to the additional extinctions now occurring, and change into the familiar layer lines. Fig. 48 represents diagrammatically the diffraction process in a linear lattice and Fig. 49 that in several fiber lattices placed regularly beside one another.

If, now, the regular arrangement of the single chains is disturbed by any influence, we may expect increasing smearing of the interferences along the individual layer lines. Actually it is found, e.g. in asbestos, which appears from its completely fibrous structure to belong to the group of chain lattices, that such an effect can be observed more or less clearly. Frequently the diagram of strongly mercerized or otherwise chemically treated cellulose shows definite smearing of the interference points along the layer lines, a qualitative proof that the structure concerned belongs to the fiber lattice type. It will be shown in greater detail in the next section that all x-ray and chemical evidence points to the fact that typical

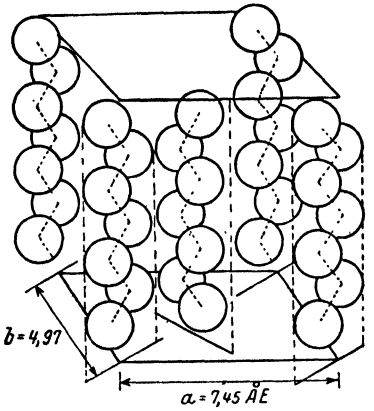


Fig. 50. Position of paraffin chains in the unit cell.

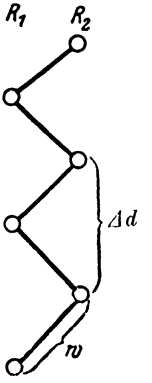


Fig. 51. The zig-zag structure of the fatty acid chains gives rise to an internal periodicity of the magnitude Δd.

fiber lattices of primary valence chains are present in the high molecular organic substances.

The relations between molecular and primary valence lattices are very clearly illustrated by a research carried out by Hengstenberg[69] at the suggestion of Mie and Staudinger on the paraffin $C_{35}H_{72}$ and extended in recent years by the very comprehensive work of Müller[70] on $C_{29}H_{60}$ and $C_{30}H_{62}$. As already mentioned, investigation of lower and higher crystallizable paraffins has indicated that the unit cell increases regularly in one dimension during growth of the carbon chain but remains of constant

[69] J. Hengstenberg, *Z. Krist.*, **67**, 583 (1928); *Ann. Physik*, **84**, 245 (1927).

[70] A. Müller, *Z. Krist.*, **70**, 386 (1929); *Proc. Roy. Soc. London.*, (B) **120**, 437 (1928); **124**, 317 (1929); *Trans. Faraday Soc.*, **25**, 347 (1929).

size in the other two dimensions. We concluded from this that the paraffin molecule in the unit cell lies parallel to the former axis (c axis), as shown in Fig. 50. If we reflect in a plane (001), which is perpendicular to the paraffin chains and coincides with the gliding planes of the lattice, we obtain a diagram which allows us to calculate the identity period along the c-axis. In the case of the paraffin $C_{35}H_{72}$ this amounts to 46.2 Å.

For measuring the two other (shorter) periods perpendicular to the chains, the crystal has to be adjusted vertically to the axis of the camera and rotated in front of a monochromatic x-ray beam. The diagram which results shows that the a- and b- edges of the elementary cell have lengths of 7.4 and 4.97 Å respectively, and that the crystal possesses rhombic symmetry.

Besides these three distances of 4.97, 7.4 and 46.2 Å, which form the elementary cell and are the true identity periods of the lattice, another spacing appears with strong intensity in the diagram. It corresponds

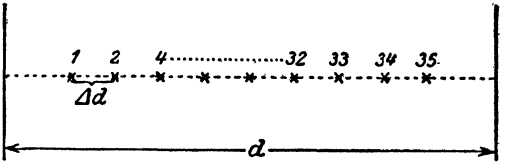


Fig. 52. The figure shows the true (intermolecular) identity period d and the internal molecular period Δd.

to a distance of about 2.5–2.6 Å. As Fig. 53 shows, this coincides with the distance between alternate carbon atoms in an ordinary zig-zag paraffin chain.

While the three above mentioned periods of 4.97, 7.4 and 46.2 Å are to be regarded as true identity periods of the lattice, the distance of 2.5 Å must be called a pseudo-identity period which has nothing to do with the lattice structure itself but is due to the great regularity prevailing within each molecule. (Compare Fig. 51.)

On proceeding along the c-axis in such a crystal, crowded network planes occur at distances of 1.25 Å, atoms with identical reflecting power at 2.5 Å, and strictly identical network planes only at 46.2 Å, a fact which leads of necessity to angulated chains of the dimensions indicated earlier. Fig. 53 shows diagrammatically how reflections lying near the point of penetration correspond to large network plane distances in the crystal lattice, whereas points lying outside correspond to the small distances within the molecule. Similar results have been obtained by investi-

gations[71] on the other long chain compounds, such as alcohols or ketones, which have been carried out in the last few years. All these studies together give us a very reliable and clear insight into the lattice structure of crystals, which are built up by chains of medium length and are of great importance for the structure of the high polymeric substances.

In the transition from pure substances (chains of exactly equal length) to mixtures (chains of slightly different length), the large network plane distances, which are characteristic of the length of the molecule, disappear and there remains only the above mentioned subdivision as sharply marked periodicity. Since this is now determinative for the identity periods along the fiber axis, molecular components and not molecules themselves are responsible for the regular repetition which produces the identity. The unit cell appears correspondingly small and the lattice has become a primary valence chain lattice.

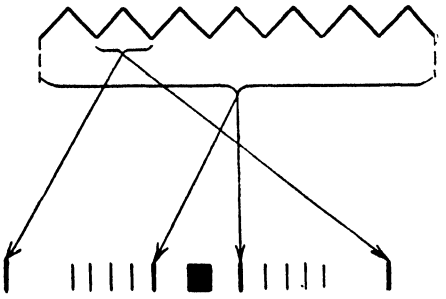


Fig. 53. Because of the Bragg reflection law large network plane distances correspond to small angles of diffraction and *vice versa*.

L. Piper[72] first found that the reflections belonging to the molecular lengths in a mixture of palmitic and stearic acids appear broadened and lie between the positions due to the pure components, a behavior which is in line with the Vegard rule for inorganic mixed crystals.

Later, long chain compounds were studied very thoroughly by Hengstenberg[73] and A. Müller.[74] While in pure substances (e.g. $C_{35}H_{72}$) the long

[71] E. Shearer, *Proc. Roy. Soc.* (A) **108**, 655 (1925); A. Müller, *Proc. Roy. Soc.*, (A) **138**, 517 (1932); **158**, 292 (1937); A. R. Ubbelohde, *Trans. Faraday Soc.*, **34**, 292 (1938); I. W. H. Oldham and A. R. Ubbelohde, *Trans. Faraday Soc.*, **35**, 328 (1939).

[72] L. Piper, *J. Chem. Soc.*, **127**, 2194 (1925); **128**, 2310 (1926).

[73] J. Hengstenberg, *Z. Krist.*, **67**, 583 (1928).

[74] A. Müller, *Z. Krist.*, **70**, 386 (1929); *Proc. Roy. Soc. London*, **120**, 437 (1928); **124**, 317 (1929); *Trans. Faraday Soc.*, **25**, 347 (1929).

period is always observable, it disappears in homogenous mixtures of similar average chain length. Chains which consist of the same members but possess different lengths, exhibit only interferences corresponding to the short periods (subdivision) and give rise to a unit cell which is indicated by the very marked periodicity within the molecule and not by the repetition of the molecule itself.

In the long chain compounds available synthetically, of a certain molecular size upwards, a separation into pure substances, i.e. into fractions of exactly the same chain length, has not yet been attained. X-ray research on the lower, pure members shows molecular lattices with long periods which in higher, impure preparations pass into primary valence chain lattices. In a few long chain compounds in which definite cells recur periodically—with Staudinger, we shall call them polymeric homologous series—this gradual disappearance of the interferences has been examined experimentally, in the greatest detail among the lower and higher polyoxymethylenes. The noteworthy fact has emerged that, after disappearance of the large periods, the small ones are not the only identity to persist, but that an intermediate periodicity is established, e.g. in the polyoxymethylenes, according to Hengstenberg,[75] which makes up the ninefold small period. This intermediate value is presumably produced by the mutual interaction of the chains.

Natural high polymeric compounds, like high molecular weight mixtures, show only reflections corresponding to the intra-molecular periodicity, so that here also primary valence chain lattices are involved.

In the case of extremely long molecules which are identical, the interferences characteristic of the large network distances are shifted very near to the point of penetration and are weak and blurred on account of the rare repetition of long molecules in the single small crystal. Under these conditions, in spite of the identity of the molecules, their very great length is responsible for the absence of all but the interference phenomenon of a chain lattice.

The method of applying the paraffins to the support also influences the sharpness of the large network plane distances. According to recent researches, there frequently exist, in long chain compounds, as previously mentioned (see p. 139), polymorphic modifications which differ from one another only by the different angle of inclination of the chains to the plane of the laminae. Probably, according to the mode of preparation of the reflecting layer, a mixture of such modifications is produced which gives rise to a lowering or a broadening of the basic reflection. Under certain

[75] J. Hengstenberg, *Ann. Physik*, **84**, 245 (1927).

conditions, this may also lead to entire disappearance of the reflection which is characteristic of the large periods.

If the individual primary valence chains are not in themselves sufficiently orientated, then the intra-molecular interferences of the individual fibers may also be blurred or entirely disappear, so that it is impossible to observe any longer a well defined x-ray pattern.

It has only been possible quite recently to obtain preparations of typical high molecular weight substances so uniform that the long identity periods can be observed directly with the x-ray spectrograph. Bernal and Crowfoot[76] have been able to measure identity periods of 67 Å and 154 Å directly in single crystals of pepsin by using a particularly precise exposure technique; a molecular weight of 40000 was obtained with 12 molecules in the elementary cell. A qualitative discussion of intensities allows the conclusion that the protein particles are dense-textured, flattened, spherical clusters with a diameter of about 30 Å.[76a]

Clark and Corrigan[77] were able to determine direct identity periods of 74.7 Å and 30.6 Å in crystalline insulin and derived a molecular weight of about 39000. Similar results were obtained by Wyckoff and Corey[78] on haemoglobin. The same authors were able to measure periods of 100 and 330 Å directly in proteins, especially in the tail sinew of the kangaroo and in quills and porcupine bristles; finally, Clark, Parker, Schaad and Warren[79] measured network plane distances of about 440 Å in collagen.

From all these results it may be assumed that synthetic high polymers, because of the non-uniformities unavoidable in their preparation, are usually poorly susceptible to x-ray analysis with regard to very long periods, but that the natural products, which are usually formed much more slowly, display a considerably higher internal molecular order with greater sharpness and definition. As in the case of the above substances they throw much light on intermolecular interferences.

[76] J. D. Bernal and D. M. Crowfoot, *Nature*, **133**, 794 (1934); D. M. Crowfoot, *Nature*, **135**, 591 (1935); cf. also W. T. Astbury and R. Lomax, *J. Chem. Soc.*, **1935**, 846.

[76a] Compare also D. Wrinch, *Nature*, **134**, 978 (1934); **137**, 411, (1936); **139**, 972 (1937); **142**, 956 (1938); I. Langmuir, *Proc. Phys. Soc.*, **51**, 592 (1939); J. D. Bernal, *Nature*, **141**, 521 (1938); **143**, 74 (1939).

[77] G. L. Clark and K. E. Corrigan, *Phys. Rev.*, **40**, 639 (1932).

[78] R. W. G. Wyckoff and R. B. Corey, *Science*, **81**, 365 (1935); *J. Biol. Chem.*, **114**, 407 (1936).

[79] G. L. Clark, E. A. Parker, J. A. Schaad and W. I. Warren, *J. Am. Chem. Soc.*, **57**, 1509 (1935).

5. Structure of Silicates

A specially good example showing how a large group of important compounds can develop all the above described types—primary valence lattices, primary valence networks and primary valence chains—is afforded by the silicates whose structure elucidation is due in the first place to the experiments of W. L. Bragg and his co-workers[80] over many years. For these very compounds the old method borrowed from organic chemistry of description by the aid of constitutional formulas was shown to be inappropriate.

The work of W. L. Bragg and also the experiments of L. Pauling[81] and F. Machatschky[82] have led to the establishment of astonishingly simple principles which render the structure and properties of these widely distributed compounds intelligible.

The main forces, which prevail in these lattices are those between the silicon and oxygen atoms which are best viewed as homopolar primary valences, although they probably have in part a certain heteropolar aspect.

We can now base the structure of the silicate lattices on the following principles.

a) Each silicon atom is surrounded by 4 oxygen atoms in tetrahedral association.

b) One oxygen atom can be chemically combined with one or two silicon atoms.

c) Two tetrahedra built up of silicon and oxygen may have one oxygen atom in common.

We may derive from these simple rules two possibilities as extreme cases.

a) The lattice consists of isolated SiO_4 tetrahedra which form islands and which have metal atoms or ions in the interstices. Each O atom belongs only to one tetrahedron; the ratio of Si to O is 1:4 or

b) each O atom belongs to two tetrahedra. Then a primary valence lattice of the composition $(SiO_2)_n$ is formed and the ratio of Si to O is 1:2.

All silicates may now be grouped between these two extreme cases, according to whether more or less of the O atoms present belong to two Si atoms. In this way we obtain:

1. The ortho-silicates with quadruple negatively charged SiO_4 ions. They possess the properties of normal, ionic-radical lattices such as $CaCO_3$ or $BaSO_4$, Mg_2SiO_4, $ZnSiO_4$ and others belonging to this class.

[80] Cf. e.g. W. L. Bragg and W. J. Warren, *Z. Krist.*, **69**, 168 (1928); **76**, 201 (1930).
[81] L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, **16**, 578 (1930).
[82] F. Machatschky, *Naturwiss.*, **26**, 67 (1938).

2. Silicates which, though polymerized, contain a finite number of Si-O groups, are formed by the union of one or more O atoms to two Si atoms in the lattice.

When two SiO_4 tetrahedra have one O atom in common, dimeric (Si_2O_7) ions result; they also are islands in the Weissenberg meaning and represent closed finite lattice units. Examples are $Sc_2Si_2O_7$, $Pb_3Si_2O_7$.

If three SiO_4 tetrahedra condense with the elimination of three atoms to a ring shaped ion (Si_3O_9), the compound $BaTiSi_3O_9$ and several others result.

TABLE 66

STRUCTURE OF THE SILICATES

Ratio Si:O	Composition and Form of the Anion	Total charge of the Anion	Charge of one Si Anion	Examples
1:4	(SiO_4) Tetrahedron	-4	-4	$Mg_2(SiO_4)$ Forsterite
2:7	(Si_2O_7) Double-tetrahedron	-6	-3	$Sc_2(Si_2O_7)$ Tortveitite
1:3	(Si_3O_9) Ring	-6	-2	$BaTi(Si_3O_9)$ Benitoite
1:3	(Si_6O_{18}) Ring	-12	-2	$Be_3Al_2(Si_6O_{18})$ Beryl
1:3	$(SiO_3)_n$ Chain	$-2n$	-2	$CaMg(SiO_6)_2$ Diopside
4:11	$(Si_4O_{11})_n$ Band	$-6n$	-1.5	$Ca_2Mg_4(Si_4O_{11})_2Mg(OH)_2$ Tremolite
2:5	$(Si_2O_5)_n$ Plane	$-2n$	-1	$Mg_2(Si_2O_5)_2Mg(OH)_2$ Talc
3:10	$(AlSi_3O_{10})_n$ Plane	$-5n$	-1.67	$KAl_2(Si_3AlO_{10})$ $(OH)_2$ Muscovite
1:2	$(SiO_2)_n$ Space network	0	0	SiO_2 Quartz
3:8	$(AlSi_3O_8)_n$ 3-dimensional	$-n$	-0.33	$K(AlSi_3O_8)$ Orthoclase
1:3	$(AlSi_2O_6)_n$ giant anion	$-n$	-0.5	$Na(AlSi_2O_6) + H_2O$ Analcite

3. Silicates with endless Si—O chains, which are formed when SiO_4 tetahedra, linked successively in a given direction of the lattice, have one O atom in common. Here we have typical primary valence chains of the composition $(SiO_3)_n$. This structure is found in the pyroxenes $CaMg(SiO_3)_2$ —$MgSiO_3$. By association of two (SiO_3) chains, an endless band is produced of the formula $(Si_4O_{11})_n$, which is present in the silicates of the amphibole and serpentine group and is characterized by very marked fiber structure (asbestos).

4. Silicates with SiO_4 networks. By linkage of (SiO_4) tetrahedra giant laminar anions are produced such that three O atoms are always common to two SiO_4 tetrahedra. They have the composition $(Si_2O_5)_n$ and are present for example in talc, kaolin and mica.

All the physical and chemical properties of these substances are in

complete harmony with the presence of primary valence networks. The layers can cohere among themselves by ionic forces or by van der Waals forces.

5. Silicates in which each O atom belongs to two (SiO_4) tetrahedra. We have here primary valence lattices which are designated honey comb lattices; the class includes the different modifications of SiO_2, quartz, tridymite and crystobalite, also the silicates of the feldspar group and the zeolites. In these the exchangeable water molecules fit into the large cavities which occur between the incompletely formed SiO_4 tetrahedra.

Table 66, due to Grimm,[83] summarizes the above remarks; it gives a very striking picture of the great variety of the lattices met with, and indicates that the silicates, which are rightly classed as the high polymeric substances of inorganic chemistry, extend in their properties over a very wide range, appearing sometimes as needle-like or laminar, soft materials and at others as hard, brittle substances.

In conclusion it may be pointed out that L. Pauling[84] has succeeded in the task of investigating in the same way the large class of heteropoly-acids of W and Mo with regard to their lattice structure.

6. Internal Mobility and Form of Molecules in Relation to Lattice Structure

The idea that molecules can change their shape is not alien to organic chemists. In ring closure between 1–5 or 1–6 positions it is always assumed that the chain curves and that the ends unite to form a ring. This concept has been represented symbolically by the formulas, but it can now be taken literally and evaluated morphologically. Unfortunately, little is known regarding the different possible states of the molecule with regard to shape but there is no doubt that research on the different types of molecular state is an important problem which will throw renewed light on many processes in the chemistry of the high molecular substances as well as of biologically important compounds.

The phenomena of polymorphism show immediately that individual atoms in organic molecules assume different arrangements under changing external conditions. Thus, for example, in tetrabromomethane the individual molecule possesses tetrahedral symmetry above 45°C., whereas below this temperature it possesses less symmetry in the monoclinic form. A change has, therefore, occurred in the positions of the bromine atoms

[83] Cf. H. G. Grimm, *Handbuch der Physik.* Second edition Berlin 1936, Vol. 24, part 2.

[84] L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, **16**, 578 (1930); see also S. D. Hendricks and W. H. Frey, *Soil Sci.*, **29**, 457 (1930).

relative to one another and to the carbon atom. Similar changes in the shapes of molecules are doubtless to be assumed in many polymorphous modifications. As previously stated (see p. 19), the tetrahedral angle is not strictly preserved in the transition from CCl_4 to $CHCl_3$ and CH_2Cl_2. Moreover, the optical activity of crystallized benzil, which vanishes in solution, points to an arrangement of the atoms which is different in the aggregate from that in the free state.

In solution and in gaseous state the concept of approximately free rotatory power leads to the inference that, at temperatures which are not excessively low, open chains, such as hexane, do not possess the same rigid rectilinear form as in densely packed crystal lattices. Rather, will the length and shape of the chains undergo thermal fluctuations; the frequency of occurrence of a given form will be determined by its *a priori* probability and by its energy content. An isolated long paraffin chain in the gaseous state, because of its heat capacity and also of the van der Waals forces exerted by the individual groups on one another, will assume a more or less strongly curved form, which is both lower in energy and at the same time statistically more probable than the straight chain (see page 72). The shape of the molecule in the gaseous state frequently differs therefore, from that in the crystal.

Particularly marked differences are to be expected in the case of molecules which possess groups with strong dipole moments (OH-, COOH-, NH_2-, CO-groups). We know from the association of acetic acid, alcohols, etc. in the state of vapor that such groups exert strong forces of attraction. Now in the crystal lattice, the molecules of normal dibasic acids are in extended parallel arrangement, as evidenced by x-ray study, and the two carboxyl groups of each individual molecule are far removed from one another and closely associated with the carboxyl of a neighboring acid. Doubtless the isolated dicarboxylic acid molecule, typified by sebacic acid $COOH(CH_2)_8COOH$, will behave differently. Due to the attraction of the two carboxyl groups, considerable curvature of the molecule to a ring-shaped structure is to be expected. In solution, the shape will depend on the solvent and will differ in those liquids which solvate principally the CH_2 group and in those which solvate the COOH group. In water, alcohol and organic acids, the van der Waals forces of the two carboxyl groups are to a large extent saturated by the solvent, but in dilute solution in benzene and the like, similar conditions should obtain to those in the gaseous state.

The behavior of acids in the surface film of an aqueous solution confirms this view experimentally. According to Langmuir and Adam it must be

assumed that in fatty acid films on water, the COOH groups lie on the surface, whereas the lipoid part is drawn into the water. According to spatial requirement, dibasic long-chain acids behave as two molecules of a monobasic acid, i.e. there is folding or curvature of the chain.

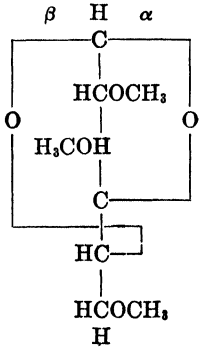
For example, the space requirement of nonylic acid amounts to 25×10^{-16} cm^2 per molecule, that of sebacic acid 57×10^{-16}. Similar relations are to be expected in amido acids, polyhydroxyl compounds etc.

It is clear that in low molecular compounds, such shape changes result in no special phenomena, but they are effective in compounds in which the macroscopic behavior is influenced by the considerable length of the chains. In this case the form changes may be accompanied by changes in the physical state (see the chapter on rubber and proteins). Generally speaking, this expectation is highest in compounds with open chains, since here the free rotation of the valences permits a change without essential energy addition. In molecules whose structure is strengthened by ring closure, they can occur very much less frequently.

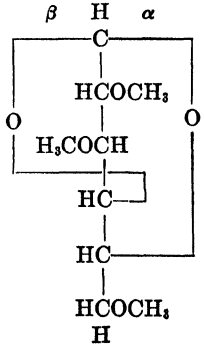
If we assume that the Bragg model represents accurately the true shape and size of the molecule, the following conclusion, which is of importance for the theory of structure and isomerism, may be drawn: Only those compounds can exist which obey the laws of space requirement outlined above, that is, which can be represented without strain by the Bragg molecular models. We arrive at the fact that two carbon atoms, united by primary valences, may not be separated by any distance greater than 1.2–1.6 Å, a requirement which places definite limitations on the bridge bonds frequently formulated in organic chemistry.

It may be shown, for instance, that of the anhydrides of 2,3,6-trimethyl glucose which would be possible according to structural theory, represented below by formulas I and II, II cannot be reconciled with this condition.

I



II



This is best seen in the spatial model of Fig. 54 which has been constructed by using Bragg's atomic diameters and the tetrahedral model. If, with the β arrangement, an anhydride bridge from 1 to 4 extends from atom 1, it must cut into the ring; this is impossible in the model. Atoms which are not united by a primary valence, cannot approach to within 1.3–1.6 Å, which means a further limitation of the space formula.

Moreover, it can be seen that an anhydride of cellobiose which contains an oxygen bridge between the carbon atom 1 of the reduced ring and the carbon atom 4 of the other ring, cannot be constructed without strain. This is important, because such a formula can occasionally be assigned to certain degradation products of cellulose

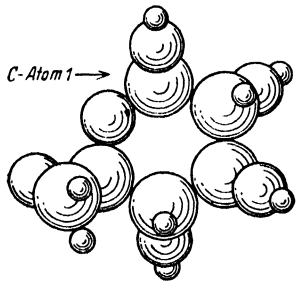


Fig. 54. Spatial model of β-glucose.

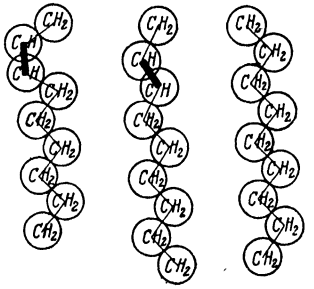


Fig. 55. Left: cis configuration. Center: trans configuration. Right: Normal paraffin chains.

In compounds of the type of camphor or cineol, cis- and trans-forms are possible from structural theory but only one type of molecule has been found. The spatial model with the double ring system shows at once that only the cis-configuration is possible, in which the groups and atoms involved stand outside on the spherical masses which form the camphor framework.

Since the tendency to mixed crystal formation and to isomorphism phenomena is essentially due to the fact that foreign molecules of similar form and similar association forces are incorporated in a lattice, the fact of mixed crystal formation can be utilized in doubtful cases for determining constitution, provided that at least the structure of one of the two compounds crystallizing together has been elucidated beyond doubt. This method, frequently used by Bruni,[85] gains considerably in conclusiveness through more accurate concepts of molecular structure. It may be

[85] G. Bruni, l. c. p. 415.

applied *inter alia* particularly to the problem of the syn- and anti-configuration.

As shown in Fig. 55, the zig-zag structure of a paraffin established by x-ray technique is closely allied spatially with the trans-configuration, whereas the cis-configuration has a totally different spatial arrangement. It is to be expected, therefore, that trans-forms resemble the long chain paraffins physically and generally crystallize together. Bruni has, in fact, proved that elaidic acid crystallizes with stearic acid and deduces from this fact that elaidic acid is the trans-form. This conclusion, which contradicts many chemical data, has been confirmed beyond doubt by Müller and Shearer[86] by x-ray investigation of the acids. The resemblance between stearic acid and elaidic acid is also evident from their similar melting points as compared with the lower melting oleic acid. We shall see in the chapter on rubber and balata that gutta percha of trans-configuration differs mainly from rubber of cis-configuration by having a higher melting point.

Bruni demonstrates in an analogous way the connection between crotonic acid and butyric acid; the trans-form is indicated for crotonic acid and the cis-form for isocrotonic acid. He further deduced, from the isomorphism of stilbene, benzal aniline and azobenzene with dibenzil, the trans-configuration of these compounds; x-ray examination clearly confirmed the trans-form for stilbene. If it is possible in this way to establish the position of the unknown double bond in a known aliphatic chain, it is possible conversely, from a knowledge of the olefine configuration, to determine the configuration of the paraffin crystallizing with it.

When Bruni shows that dimethyl succinate crystallizes with dimethyl fumarate, it means that the succinic acid ester has a structure resembling the trans-form, i.e. must have a zig-zag form—at least, as long as it is incorporated in the fumarate crystal.

Isomorphism can serve for elucidating constitution also in really complicated cases; many years ago Garelli[87] concluded from the fact that tropanine and granatanine form solid solutions in naphthalene, that they are simple bi-nuclear substances without branch chains; Willstätter,[88] Ciamician and Silber[89] proved this by chemical means.

Similar considerations established for the sterols by Bernal and Crowfoot[90] are of special importance. Definite proposals for these substances

[86] A. Müller and E. Shearer, *J. Chem. Soc.*, **123**, 3156 (1923).

[87] A. Garelli, *Ber.*, **29**, 2972 (1896).

[88] R. Willstätter, *Ber.* **29**, 393 (1896); *Ann.*, **312**, 204 (1901); **326**, 1 (1903).

[89] G. Ciamician and P. Silber, *Ber.*, **25**, 1601 (1892); **26**, 156, 2738 (1893); **29**, 481 (1896).

[90] Cf. J. M. Robertson, *Rep. Progr. Phys.*, **4**, 332 (1938).

have been made by chemists working in this field and especially by Windaus and Wieland, although preparative chemical methods have not succeeded in setting up a completely satisfactory structural formula.

Measurements on a series of sterols have supplied very informative data on the dimensions of the unit cells (see Table 67) and made it possible to calculate the thickness of the molecules and their spatial expansion in the molecular plane. The result is that the formula preferred by organic

TABLE 67

UNIT CELLS OF CERTAIN STEROLS

Substance	a (Å)	b (Å)	c (Å)	β	Thickness of molecule
Cholesterol	14.0	10.3	2×19.6	117	—
Ergosterol + H_2O	9.75	7.4	2×19.6	115	4.95
Dihydroergosterol	3×10.3	7.4	2×21.6	127	4.1
α-Ergosterol + Alcohol	12.0	5.81	2×17.8	95	—
γ-Ergosterol	10.0	6.9	2×18.5	90	5.0
Calciferol	2×10.4	7.15	2×17.8	95	5.2
Calciferol-pyro-calciferol	2×10.1	7.35	2×20.0	117	4.5
Suprasterol I	2×13.0	7.5	2×20.0	137	4.5
Suprasterol II	13.4	10.4	2×17.2	90	—
Lumisterol	2×10.2	7.25	20.4	120	4.3

chemists is incompatible with the results of the x-ray measurement. Bernal[91] deduced from his measurements that a different, flatter structural formula, proposed for discussion by Rosenheim and King, was nearer the truth, a view that has now been accepted by all research workers in this field.

Thus the interferometric measurement of molecules which are complicated even in the mind of the organic chemist, has made an important contribution to the elucidation of the structure of a very significant class of compounds.

[91] J. D. Bernal and H. D. Megaw, *Proc. Roy. Soc. London*, (B) **151**, 384 (1935).

E. MOLECULAR ARRANGEMENT IN LIQUIDS AND THE INVESTIGATION OF VERY MINUTE CRYSTALS

1. General Remarks on the Arrangement of Particles in a Liquid

While a quantitative theory for ideal and real gases has been fully developed by employing statistical mechanics, and a complete and quantitatively far-reaching idea of the structure of crystals has been provided in an astonishingly short time as a result of the discovery of v. Laue, our knowledge of the structure of liquids has made only very gradual progress. Although there is early work by G. Jäger,[1] who attempted to work out a theory of liquids based on conditions in highly compressed gases, and attained quite remarkable success in the quantitative evaluation of several constants, precise evidence regarding the arrangement of individual particles—atoms and molecules—in the liquid state has only become available in recent years.[2]

The reason is as follows: in gases the molecules are present in the free state; they move for most of the time without being influenced by any forces, so that it is possible to employ statistical methods and to obtain data which, though summary, are sufficient to characterize the macroscopic state. In the crystal, on the other hand, the mutual forces are so strong that the individual particles are maintained permanently in certain positions of equilibrium and execute vibrations about these. It is possible here to connect the structure with the properties in a purely dynamic way.

In liquids also, forces are undoubtedly present, otherwise there would be no surface tension and no heat of vaporization, but they are not large enough to offset the thermal motion of the molecules and to cause the formation of an oriented lattice. In liquids we have a state subject neither to purely statistical nor purely dynamic treatment and which has accordingly presented great difficulties for a long time.

Only in recent years has it been possible to effect changes. In the first

[1] G. Jäger, *Sitz. Ber. Akad. Wiss. Wien*, **102**, 253, 483 (1893); **105**, 97 (1896); **111**, 697 (1902).

[2] Comp. especially the monography of J. T. Randall, *The Diffraction of X-rays and Electrons etc.*, London 1934 and *Second Rep. Viscosity.* Amsterdam 1938; p. 1.

place we are indebted to Prins[3] and Debye,[4] who rely on the diffraction patterns which can be obtained for liquids with x-rays and deduce from them quantitative relationships for the molecular arrangement of spherical particles. Later, other authors, particularly Raman and his co-workers,[5] Stewart,[6] Trillat[7] and Kratky,[8] have studied theoretically and experimentally the conditions in liquids consisting of non-spherical particles and have arrived at a concrete idea of the arrangement in the region of molecular dimensions.[9]

As a result, it may be said that the individual particles of a liquid do not, like those of a perfect gas, assume at random all possible positions and orientations in space, but that their mutual arrangement resembles very largely that of the crystalline state. In this sense we may conceive of the liquid as an aggregate of numerous very small crystals in which each individual does not show exactly the arrangement characteristic for it in the crystal but assumes a series of temporary positions. These small crystallites (each consists only of 10–100 atoms) are only very short lived; they disband continually and recrystallize, so that a given particle belongs for an instant to one of these small aggregates, then to none, then to a subsequent one which has been formed in the meantime, and so on. Kistler has proposed to term these groups *cybomas*, and it seems to be very reasonable to adopt such nomenclature to have a short expression for the situation just described.[9a]

In the gaseous state, the molecules traverse relatively large paths, then suddenly collide with one another, thereby suffering an entire change in direction; in the crystal lattice the individual atoms vibrate about quite definite fixed equilibrium positions; on the other hand, a molecule in the liquid state moves slowly from place to place with persistent, irregular vibrations; it executes a Brownian motion of very small free path, during which its center of gravity exhibits additional vibrations, being always under the influence of other adjacent molecules.

[3] J. A. Prins, *Physica*, **6**, 315 (1926); *Z. Physik*, **56**, 617 (1929); *Nature*, **123**, 84 (1929); *Naturwiss.*, **19**, 435 (1931).

[4] P. Debye, *J. Math. Phys.*, **4**, 133 (1925); *Physik. Z.*, **31**, 348 (1930). Compare also H. Eyring; *J. Chem. Phys.* **4**, 283 (1936); J. E. Lennard-Jones; *Proc. Phys. Soc.* **43**, 471 (1931). J. Frenkel; *Trans. Faraday Soc.* **33**, 58 (1931).

[5] C. V. Raman, *Phil. Mag.*, **47**, 671 (1924); *Indian J. Phys.*, **3**, 225 (1929); **3**, 399 (1929); **4**, 195 (1929).

[6] G. W. Stewart, *Rev. Modern Phys.*, **2**, 116 (1930); *Phys. Rev.*, **31**, 1, 174 (1929); **32**, 153 (1929); **35**, 726 (1930).

[7] J. J. Trillat, *Trans. Faraday Soc.*, **29**, 495 (1933).

[8] O. Kratky, *Physik. Z.*, **34**, 482 (1933).

[9] Cf. also K. F. Herzfeld, *J. Applied Phys.*, **8**, 319 (1937).

[9a] S. S. Kistler; *J. Phys. Chem.* **39**, 79 (1935).

The method which gives the clearest insight into the conditions prevailing is the scattering of x-rays in liquids; this will be briefly discussed below.

2. Scattering of X-Rays in Liquids

Well developed crystals were such convenient objects for structure elucidation by x-rays, that much time elapsed before experiments on the scattering of x-rays in liquids were designed with the requisite accuracy for satisfactory theoretical treatment. Compared with the wonderful point and line diagrams of crystals, facilitating exact calculation, the liquid exposures did not at first seem very promising. For they consist, in most cases, only of one or a few blurred rings, the measurement of which at best gave two or three data which had to suffice for theoretical interpretation. Conditions changed when Zernike and Prins[10] and Debye[11] showed that it was necessary to go further than mere measurement of the rings and to consider the dependence of the scattered intensity on the angle point by point. The authors named demonstrated clearly that the scattering of x-rays by liquids is an effect made up of two components which must be considered separately if the total effect is to be interpreted quantitatively.

Debye,[12] to whom, particularly, we owe the clear recognition and calculation of the two effects, has named them inner and outer interference.

The inner diffraction effect is produced when the individual particles of the atom capable of vibration, i.e. the electrons contained in the atoms, are dispersed and give rise to secondary radiations which interfere with one another. In a liquid built up of single atoms—A, Kr, Xe, Hg, Ga—the result is that, on account of intra-atomic interference, the dependence of intensity distribution on the angle of diffraction is already affected. This influence is generally expressed by a factor, which, because of its origin, is called the atomic form factor; its action is that more intensity is scattered in the directions near the primary beam than if the interaction of the individual electrons is not taken into account.

If we are concerned with a molecule composed of several atoms—H_2O, CCl_4, C_6H_6 etc.—we have to imagine that the individual atoms, which have definite positions in the molecule, also send out secondary waves which interfere with one another and cause a further change of the angular dependence of the scattered radiation; intramolecular inter-

[10] F. Zernike and J. A. Prins, *Z. Physik*, **41**, 184 (1927).
[11] P. Debye, *Physik. Z.*, **31**, 384 (1930).
[12] P. Debye, *Physik. Z.*, **31**, 797 (1930).

ference is added to atomic interference and the molecular form factor must be taken into account as well as the atomic.

The internal effect is clearest in the scattering of x-rays or electrons by molecules in the gaseous state and its study in the gas phase has provided the very interesting evidence on molecular structure which has already been discussed in the first section.[13]

If now, the atoms or molecules, which are entirely independent of one another in the gaseous phase, condense to the liquid phase, certain distance relationships are established between them; the result is that even the secondary radiations proceeding from the different particles interfere with

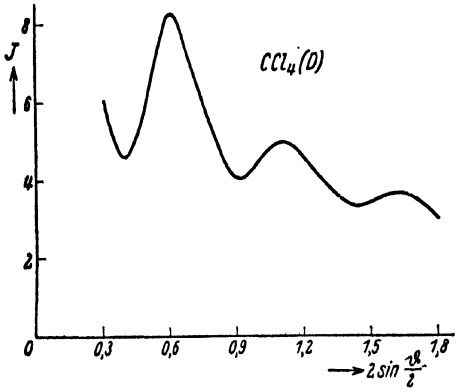


Fig. 56a. Intensity curve of CCl_4 vapor.

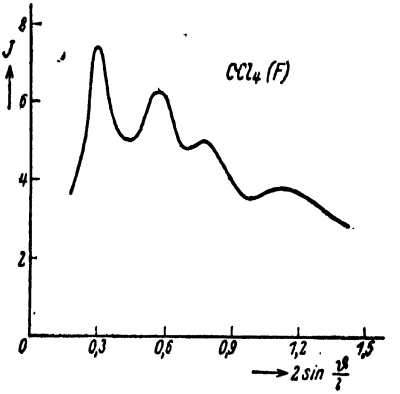


Fig. 56b. Intensity curve of CCl_4 liquid

one another and cause additional modification of the laterally scattered intensity. This intensity dispersion is caused by the grouping of the individual particles in the liquid, so that it is possible to deduce information about this grouping. Conditions are naturally simplest in the monatomic liquids and the first quantitative results were obtained in their investigation.

The extent to which the intermolecular phase relations may change the whole aspect of the diagram may be seen by a comparison of Fig. 56a and Fig. 56b, both taken from a fundamental publication of Debye and Menke.[14] Carbon tetrachloride was chosen in one case in the state of

[13] It should be mentioned here that also the critical state of gases has been investigated with x-rays; comp. W. H. Barnes, *Chem. Rev.*, **23**, 29 (1938).

[14] P. Debye and H. Menke, *Physik. Z.*, **31**, 797 (1930).

vapor and in the other as liquid. The curve in Fig. 56a shows the effect of the angle on scattered intensity for the case of CCl_4 molecules while entirely independent of one another in space. It represents the purely internal effect and, on the basis of the interference theory, gives insight into the symmetry and distances in the carbon tetrachloride molecule (see p. 19).

The curve in Fig. 56b shows entirely different conditions. The first maximum is displaced much nearer to the point of penetration. This indicates the very frequent occurrence of some distance in the liquid which exceeds the intramolecular distances of the individual atoms; for according to Bragg's reflection law

$$n\lambda = 2d \sin \varphi \tag{37}$$

angle of diffraction φ and distance of the scattering particles d are in reciprocal proportion to one another. The appearance of intense reinforcement in the neighborhood of the point of penetration points to large distances between centers of scattering capable of interfering with one another, while lines, points or bands further removed from the primary beam indicate a smaller distance within the scattering body. On comparing the two diagrams, we see that the maximum of the external effect in Fig. 56b corresponds to about half the abscissa value of the maximum of the internal effect (Fig. 56a) and we may infer as a rough approximation that any distance occurring frequently in the liquid must be about double the distance generally appearing in the diffraction pattern for the chlorine atoms in the molecule of carbon tetrachloride. Since the latter amounts to about 2 Å, we may deduce from a comparison of the two diagrams that a distance of about 4 Å must occur very frequently in the liquid.

It is an approximation to regard this as the average intermolecular distance of individual particles in the liquid and to obtain in this way a first idea of the structure of the liquid phase.

We shall not, however, be content with this rough average value but will attempt something more accurate regarding the distribution of the atoms and molecules in the liquid, just as it has been possible to interpret the diagram of a crystal to give the complete elucidation of its fine structure. The theoretical analysis of the process of scattering by particles in random arrangement, such as occurs in liquids, has shown that it does not suffice to establish the existence of certain maxima—as seen in Fig. 56a and 56b—and to derive from them, as was done there, the presence of definite average distances as an approximation. It is necessary to record the whole course of the scattering curve point by point photo-

metrically and to deduce, by the aid of harmonic analysis, the arrangement of the particles in the liquid from the laterally scattered intensity as a function of the angle.

It has only been possible hitherto to apply this method with strictness to monatomic liquids, but the results obtained have allowed very promising analogies to be drawn regarding the arrangement in liquids which do not consist of spherical particles.

a) The Scattering of X-Rays by Monatomic Liquids

Two methods are possible for elucidating conditions in monatomic liquids such as argon, krypton, mercury, gallium etc. The first has been adopted particularly by Prins,[15] Zernike,[16] Mark[17] and Kratky.[18] Its principal assumption is that monatomic liquids possess a structure which may be regarded as distorted hexagonal or cubic close spherical packing and seeks to prove this assumption by experiment. The other method, which is stricter and more far reaching in its consequences, has been adopted by Debye and Menke,[19] by Prins and Zernike,[20] and by Kirkwood.[21] It seeks to infer directly the average distribution of the scattering centers in the liquid by harmonic analysis of the intensity distribution found experimentally.

Since the former method of treatment has the advantage of simplicity and the latter that of mathematical exactness, we shall describe them both briefly and show that they lead to the same results.

Prins and Mark many years ago expressed the view that the arrangement of the atoms in liquid mercury may be regarded, to a fair approximation, as close spherical packing strongly distorted by internal diffusion. This view is based on a very simple estimation. If we construct from mercury atoms the densest possible hexagonal packing, with specific gravity 13.6, the distance between two neighboring atoms works out at 3.26 Å. If, on the other hand, we take the x-ray diagram for liquid mercury given in Fig. 58, a particularly intense maximum is evident, which must certainly be ascribed to the external effect, since a monatomic liquid is involved. If, as an approximation, we regard it (see p. 178) as representing the average distance of adjacent atoms in the liquid and insert its angular

[15] J. A. Prins, *Physica*, **6**, 315 (1926).
[16] F. Zernike, *Z. Physik*, **41**, 184 (1927).
[17] H. Mark, *Z. Physik*, **54**, 505 (1929).
[18] O. Kratky, *Physik. Z.*, **34**, 482 (1933).
[19] P. Debye and H. Menke, *Physik. Z.*, **31**, 797 (1930).
[20] S. A. Prins and F. Zernike, *Z. Physik*, **41**, 184 (1927).
[21] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 919 (1939).

distance from the primary radiation in the appropriate interference equation, we again obtain 3.26 Å for this mean value. To a rough approximation, therefore the inter-atomic distance which prevails in hexagonal close spherical packing holds also in the liquid pattern.

Consideration of this average value will not suffice and it is desirable to have a more accurate conception of the mutual positions of the atoms in the liquid. Kratky has extended the view of Prins and Mark in this direction and has discussed in greater detail the distortion of the hexagonal lattice which serves as the initial arrangement. We arrive at a result most easily by assuming that all possible arrangements of the atoms in the liquid can be produced by starting with an ideal lattice arrangement and allowing each atom a definite displacement of its position relative to its neighbors. The same is true for a vibrating crystal lattice, but in this case the displacements occur relative to a rigid, geometrically ideal framework (the point lattice at absolute zero). In liquids, however, displacements should always be stated relative to the neighbors which are likewise removed from their rest positions; the result is that the relative displacement of two atoms increases with distance, whereas in the vibrating crystal the relative displacements from the rest position are constant for the individual atoms.

We shall now imagine the origin of a co-ordinate system fixed in some special atom and consider a lattice point at any distance r from it. The scattering, which is calculated for this lattice point on the basis of the above theory, is then a measure of the distortion of the lattice at this point, and at the same time is also a measure of the mobility possessed by an atom r units away from the initial atom.

To invest this method of consideration with formulas, we proceed from the above mentioned central atom and establish progressively in every direction in space, the distances of the surrounding atoms. In this way we obtain statistics of the inter-atomic distances within the liquid, the quantitative determination of which is the object of the investigation.

It is convenient to imagine a thin spherical shell described around the initial atom, the radius of which is allowed to increase gradually so as to include, during the expansion, the atoms present in concentric spherical shells. The radii of these shells are then plotted as abscissae and the values W for the density of distribution of the atoms in the shells as ordinate. If we establish, for example, that a shell of radius r contains exactly n atoms, the density of the atoms in the shell is

$$W(r) = \frac{n}{4\pi r^2}. \tag{38}$$

If we apply the calculation to the lattice of hexagonal close spherical packing, we obtain the diagram shown in Fig. 57. On moving out from the atom at the origin, we meet at first with no other atomic centers of gravity because there is a characteristic minimum interatomic distance for this lattice. It amounts to 3.26 Å, as mentioned before, so that we come to the first atomic center of gravity only at this distance. The coordination number in the lattice of hexagonal close spherical packing is 12, so that 12 Hg atoms are present in the spherical shell of radius 3.26 Å and the ordinate, $W(r)$, gives a value for r of 3.26. If we continue the construction, we obtain sharp lines at definite distances fixed by the symmetry and the distance relationships in the lattice, which indicate the presence of atoms in the appropriate spherical shells. A mere glance at Fig. 57 shows that actually, in the distortion of such an arrangement, a distribution with several maxima results, the first of which is predominant however.

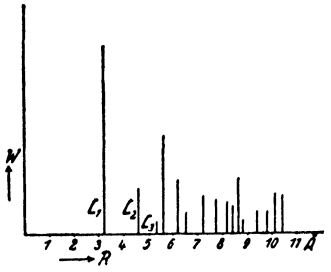


Fig. 57. Distribution of atomic centers of gravity in hexagonal close packing.

A more accurate treatment, again due to Kratky, indicated two further maxima, which, although not corresponding exactly in height to the experimental data, agreed very well with them in regard to position. Fig. 58 gives a comparison between the distribution function calculated by Debye and Menke from the experimental intensity distribution of the scattered radiation (upper curve), and the distribution derived by Kratky; the latter was calculated on the basis of a hexagonal close spherical packing subject to a certain distortion of the arrangement (middle curve); finally there is shown the curve for the cubic close spherical packing (lower curve). It is evident that there is good agreement with experiment, particularly for the hexagonal close packing.

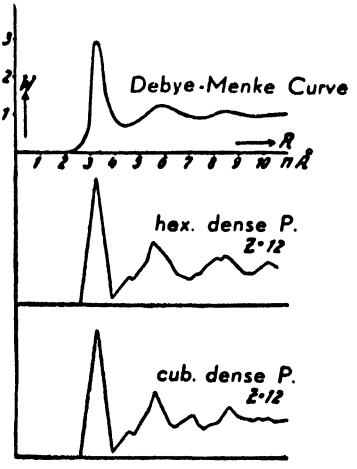


Fig. 58. Comparison of experimentally determined distribution curve of Hg with a distorted hexagonal or cubic spherical packing.

This comparison is illustrated even more clearly by Fig. 59 in which the position distribution, according to Debye, is indicated by a heavy line, the hexagonal close packing by a dotted line and the cubic packing by a thin line. It is evident that, at least as a first approximation, the concept of a distorted close packing for the arrangement of spherical structures is very probably near the truth.

The procedure of Debye and Prins is still more exact. Here, relying on the strict relations of the interference theory, a mathematical connection is devised between the scattered intensity I as function of the angle of deviation ϑ and a distribution W as function of r, which indicates the degree of probability that, on proceeding from a given initial atom in any direction in space, another atom appears after traveling the distance r.

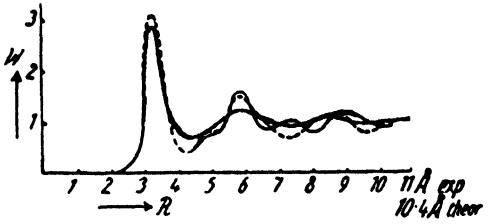


Fig. 59. Comparison of three curves for the arrangement of atoms in a monatomic liquid.

W and I are combined by an equation derived independently by Zernike and Debye, of the form

$$N\rho(1 - W) = 2\frac{V}{\lambda^3}\int_0^\infty s[1 - E(s)] \sin(2\pi\rho s)\, ds, \tag{39}$$

in which

$$E(s) = \frac{2I(s)}{(1 + \cos\vartheta)N\psi^2}.$$

In this

$\rho = \frac{r}{\lambda}$; λ = wave length

$s = 2 \sin\frac{\vartheta}{2}$; ϑ = angle of deviation

N = number of atoms in the irradiated volume V

ψ = atomic form factor

Experiment supplies the I value corresponding to each value of s or ϑ. We can therefore compute E as a function of s (compare Fig. 60) and integrate the right-hand side of (39) stepwise, either graphically or numerically. After performing this calculation, the right-hand side represents a function $F(\rho)$ of ρ (or of r) from which the desired distribution function W may be calculated using equation (39). We obtain

$$W(r) = 1 - \frac{F(r) \cdot \lambda}{N \cdot r}. \tag{40}$$

By this process we obtain a continuous, smooth distribution function $W(r)$ such as is given by Debye and Menke for mercury in Fig. 58. The distance from the initial atom is chosen as abscissa and is plotted directly in Å in the figure. If we imagine a given atom in liquid mercury as fixed

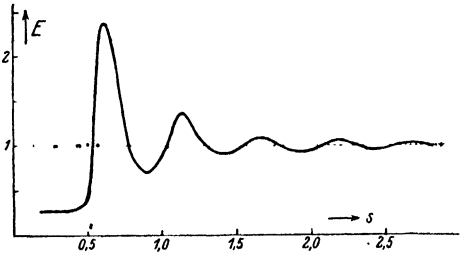


Fig. 60. Experimental scattering curve $E = f(s)$ for Hg.

and a volume element combined with it at a distance r, the ordinate of the curve in Fig. 58 represents the probability that the center of another mercury atom lies within that volume element.

Experiment gives a zero value for W quite close to the initial atom, because the atoms are unable to interpenetrate, owing to the repulsive forces acting between the negative charge clouds. The function represented by equation (40) expresses a different behavior, because the repulsive forces between the atoms have not been included in it. In this region, therefore, the result of the computation is given simply by the horizontal axis. The distribution curve then rises steeply to the first maximum, to which, as we have seen, the 12 adjacent mercury atoms found in the first co-ordination sphere correspond. It then falls to a minimum. This indicates that there are regions not occupied by atomic centers of gravity, just because of an arrangement resembling close spherical packing. A peak occurs again at about 5.6 Å, and at large distances, the probability that an atom will be found in the volume element considered, no longer depends upon r in any appreciable way.

In a rigid lattice, the sharp lines shown in Fig. 57 replace the broadened maxima of Fig. 56. In this case, the preference for definite distances is a strictly valid law, which eliminates the appearance of intermediate distances. The distribution curve of Fig. 59 gives a quantitative idea of the extent to which the crystal-like structure persists in the liquid in spite of the greater freedom of movement of the atoms. Equation (40) combines analytically the two functions represented in Figs. 59 and 60 and may

TABLE 68

AVERAGE DISTANCES IN LIQUID ALKALI METALS

Substance	Distance in Å calculated from the liquid ring	Width of ring	d_{110} of the solid metal	Shortest atomic distances
Sodium	3.01	6°0′	3.04	3.53
Potassium	3.87	—	3.68	4.38
Rubidium	4.09	4°50′	3.97	4.61
Cesium	4.51	9°30′	4.28	4.93

TABLE 69

AVERAGE PARTICLE DISTANCES IN LIQUEFIED GASES

Substance	Liquid			Solid	
	ϑ_{Cu}	ϑ_{Mo}	d in Å	Lattice constant	d for the most intense lines
Argon	13.5 24.5	6.5	3.22	5.42	3.13
Nitrogen	·	5.67	3.59	5.66	4.01
Oxygen	13.5 23.0	6.25	3.24	a = 5.50 b = 3.82 c = 3.44	1.60 2.58 2.71

well be regarded as a very satisfactory solution of the problem for the case of a monatomic liquid.

Model tests with steel balls, carried out by Debye and Menke and later by other authors, using spheres as well as ellipsoid or rod-shaped bodies, have entirely confirmed the above conception.

Table 68 gives a few relevant data for liquid alkali metals. It is evident that the average lattice plane distances computed from the first peak increase with the position of the metal in the periodic system, just as would be expected from our general knowledge of the atomic radii.

A few data for argon, nitrogen and oxygen are given in Table 69 from

which it is evident that in liquified gases also, the most frequent average distances are of the order of magnitude of 3.5 Å. Columns 5 and 6 show network plane distances for lattices of crystallized A, O_2 and N_2. Comparison with the values in the liquid indicates, as is to be expected, that the identity periods of the unit cells are always greater than the distances of adjacent atoms in the liquid.

b) The Arrangement of the Molecules in Liquid Water

After elucidating conditions in liquids on the assumption of exactly spherical particles, attempts have been made to treat cases in which accurate spherical form and isotropy of the molecular force field are lacking but with deviations from the spherical form not very great and the lattice of the crystalline phase well known. A particularly important substance, whose behavior in the liquid state has long aroused great interest, is water.

TABLE 70

RESULTS OF X-RAY SCATTERING IN WATER

Author	d_1	d_2	d_3	d_4	Temp. in °C.
H. H. Meyer.	3.13	2.11	1.34	0.89	20°
G. W. Stewart.	3.24	2.11	1.13	—	ca. 20°

It has been assumed that because of strong dipole effects proceeding from the individual molecules, a high degree of association prevails in liquid water, so much so that individual molecules in this liquid may not be regarded as in any way independent of one another.

X-ray scattering experiments with water, for which we are indebted chiefly to Stewart[22] and Meyer,[23] and whose results are given in Table 70, have furnished the basis for an exact treatment of this problem. The subject has been pursued recently by Bernal and Fowler[24] in particular, who endeavored to design from the structure of ice (see page 134), from the x-ray diagram of water mentioned above and from the known data for H_2O molecule, a pattern of the molecular arrangement in liquid water the which would represent quantitatively as far as possible all known properties of this substance.

Bernal and Fowler proceeded on the assumption that in ice there is a somewhat distorted tetrahedral arrangement of the water molecules

[22] G. W. Stewart, *Phys. Rev.*, **37**, 9 (1931).
[23] H. H. Meyer, *Ann. Physik*, **5**, 701 (1930).
[24] J. D. Bernal and R. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

and that this prevails in liquid water also to a certain extent. Such a structure, of co-ordination number 4, is very far removed from close spherical packing and is considerably less compact than this (see Fig. 61). In contrast, monatomic liquids or liquids in which the particles possess spherically symmetrical fields of force—as we have seen in the preceding section—are constructed in conformity with the principle of close packing. Were we to arrange water molecules, having the diameter resulting from the known primary valence distances, in the most compact configuration possible, we would obtain a structure with a density of about 1.8; i.e. it would be nearly twice as dense as water.

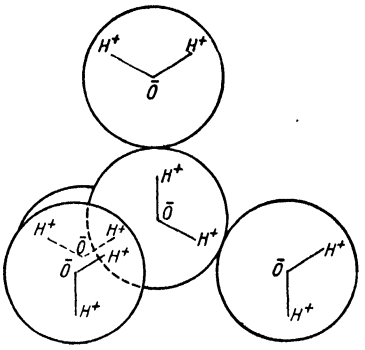


Fig. 61. Tetrahedral arrangement of the H_2O molecules in ice.

To test the validity of the tetrahedral arrangement, Bernal and Fowler have discussed two groupings particularly, one arrangement being quartz-like and the other resembling tridymite. The intensity distribution expected in the x-ray diagram was calculated for both arrangements by assuming an appropriate scattering of the particles and by using equation (40).

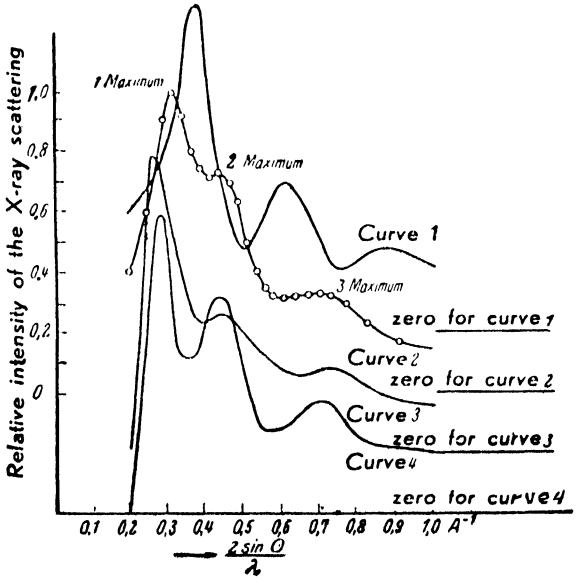


Fig. 62. Comparison of experimental scattering curve for water (circles) with different types of molecular packing.

Fig. 62 gives the results. Curve 1 shows the scattering for a closely packed water in which the molecules have a diameter of 2.76 Å. It is evident that such an arrangement is in entire disagreement with Curve 2 which represents

the experimental result. The first peak in liquid water lies considerably nearer to the point of penetration and corresponds—just because of the looser arrangement of the molecule—to an average minimum distance of 3.24 Å, whereas the first steep and high peak for the closely packed structure lies further out and would hence correspond to a smaller distance of 2.60 Å. Close packing is certainly not the arrangement here. The curves 3 and 4 of Fig. 62 give the theoretical scattering for the two tetrahedral arrangements and evidently show considerably more resemblance to the experimental curve. A more accurate analysis of the conditions led Bernal and Fowler to the conclusion previously mentioned (see p. 134) that in water three arrangements of the molecules are present which are continuously changing into one another.

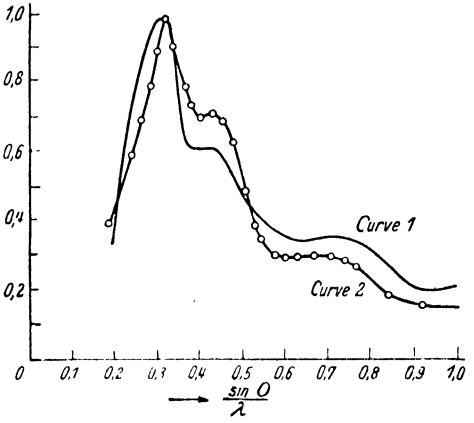


Fig. 63. Curve 2 = scattering curve determined experimentally. Curve 1 = mixture of tetrahedral structure and close packing.

α-water exists preferably below 4° and has a tridymite type of arrangement, which still persists to considerable extent in the structure of solid ice.

β-water is preferred at average temperatures up to about 200° and shows a quartz type of structure and

γ-water approximates to the close spherical packing and is stable at higher temperatures up to the critical point (374°).

These three configuration possibilities do not, of course, pass into one another at sharp transition points, as would be expected in the case of crystalline phases; rather, they resolve into one another gradually with increasing temperature. The fact that the Raman spectrum of water undergoes a very considerable modification with temperature is in harmony with this view. Moreover, a mixture of quartz-like tetrahedral structure and close packing approximates very closely to the scattering curve determined experimentally at 20°, as seen in Fig. 63.

Finally, Bernal and Fowler calculated the heat of sublimation from the model sketched above and found a value of 11.5 calories per mol, whereas the experimental value is 11.81. The attraction is to be attributed essentially to the interaction of the dipoles.

From the angular breadth of the water interferences and their dependence on temperature, and from similar experiments carried out by James[25] on CCl_4, we can deduce in a liquid the average size of the groups which are alternating with one another in space and time. Although no quantitative results are yet available in this direction, we are probably not wrong in assuming an order of 10 for the number of members in such a regional group and a temperature effect such that the groups always become smaller at higher temperature. Just because H_2O is a typical dipole and the dipole forces prevail over the other effects (dispersion, induction) in water, *double* molecules are formed and not polymerisates; the latter would be expected if the induction and dispersion forces were predominant.

c) *Structure of Liquids Containing Elongated Molecules*

Although quantitative mathematical formulations well supported by experiment are not so feasible in these more complicated systems, it is possible to obtain from numerous experiments at least a qualitative working idea of the arrangement in liquids consisting of elliptical molecules.

The liquid paraffins from C_5 to C_{15} were first examined with the aid of x-rays by Sogani[26] and Stewart[27] with the result that the most intense interference occurred at an angle of diffraction corresponding to an average distance of 4.6 Å. The most reasonable explanation of this fact is the assumption that the long chains of these hydrocarbons arrange themselves with their chain axes parallel in consequence of the dispersion forces exerted between them and form small groups or clusters which, although constantly destroyed by thermal motion, reassociate because they represent arrangements of minimum potential energy. The chains in these molecular clusters stiffen through mutual interaction, so that they assume essentially the same zig-zag form which they would possess in the crystal lattice. Because of the relatively high mobility of the individual chains in the liquid, the cross-section of a paraffin hydrocarbon chain is one of rotation symmetry similar to that established by Müller in the high temperature form of the hydrocarbons in the crystalline state (see p. 169).

Recently Katzoff[28] and C. Pierce[29] have examined normal heptane with monochromatic radiation over a temperature range of -50 to $+80°$

[25] R. W. James, *Physik. Z.*, **33**, 737 (1932).

[26] C. M. Sogani, *Indian J. Phys.*, **2**, 97 (1928).

[27] G. W. Stewart, *Phys. Rev.*, **31**, 174 (1928); **32**, 153 (1928).

[28] S. Katzoff, *J. Chem. Phys.*, **2**, 24 (1934); see also D. A. Wilson and E. Ott, *J. Chem. Phys.*, **2**, 231 (1934).

[29] W. C. Pierce, *J. Chem. Phys.*, **3**, 252 (1935); also A. Müller, *Nature*, **129**, 436 (1932).

and subjected the intensity distribution found experimentally to a Fourier analysis. Markedly preferred distances of 1.4, 2.5 and 3.8 Å were indicated. They are to be understood as the intra-molecular distances between an initial carbon atom and its first, second and third neighbors. Then there is a maximum, corresponding to a distance of about 5.2–5.5 Å, displaced at higher temperature to 5.75 Å. In this we have the average distance of individual paraffin chains which are clustered in bundles so that their axes display an arrangement of hexagonal symmetry.

Extensive experiments have been carried out on alcohols by Stewart[30] and Morrow[31] in which the number of carbon atoms varied from 1 to 11. The diagrams show two definite peaks, one in the neighborhood of 4.6 Å, which appears with equal intensity and sharpness in all the substances examined. It is bound up with the average separation of the chain molecules. The second maximum, in contrast, is displaced with increasing number of carbons (see Fig. 64) from 6 to nearly 24 Å. It is less intense and, according to Warren,[32] comes from the end groups of the alcohols, which owing to the dipole attraction existing between them, arrange themselves preferably in definite planes whose distances apart increase with length of chain; hence, this weak interference always moves nearer to the point of penetration with increasing chain length.

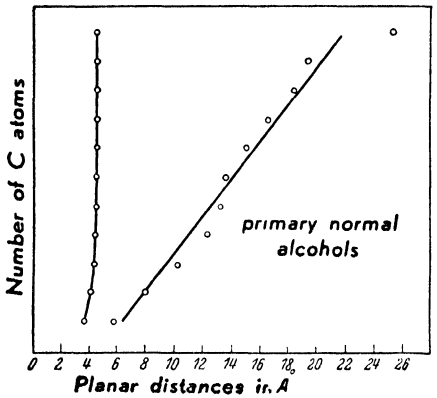


Fig. 64. Relation between d_1 and d_2 and the length of the alcohol molecules. Compare also Table 71.

Normal fatty acids have been studied very carefully in the liquid state, particularly by Katz,[33] Krishnamurti,[34] Morrow,[35] De Smedt,[36] Sogani[37] and others. Table 71 shows an experimental series in which the carbon atoms vary from 1 to 11; it indicates that, just as among the alcohols,

[30] G. W. Stewart, *Phys. Rev.*, **30**, 232 (1927).
[31] R. M. Morrow, *Phys. Rev.*, **31**, 10 (1928).
[32] B. E. Warren, *Phys. Rev.*, **44**, 969 (1933).
[33] J. R. Katz, *Z. Physik*, **45**, 97 (1927); **46**, 392 (1928).
[34] P. Krishnamurti, *Indian J. Phys.*, **2**, 355 (1928); **4**, 449 (1930).
[35] R. M. Morrow, *Phys. Rev.*, **31**, 10 (1928).
[36] J. de Smedt, *Bull. Roy. Soc. Belge*, **10**, 366 (1924).
[37] C. M. Sogani, *Indian J. Phys.*, **2**, 491 (1928).

an internal and feebler interference is observed resulting from interaction between the terminal groups. Here again, with increasing chain length it is found to move toward the primary ray. The second diffraction ring is, on the contrary, independent of the number of carbon atoms of the substance investigated; it leads to an average distance of 4.5 Å and indicates by its sharpness and intensity that these substances in the liquid state also possess relatively well defined bundles of parallel chains.

Other experiments on molecules which depart greatly from the spherical form, especially benzene and other aromatic liquids, have not yet found quantitative theoretical interpretation. There can, however, be no doubt that groups or clusters of elliptical or laminar molecules are formed under the influence of inter-molecular forces, which determine the char-

TABLE 71

TYPICAL LATTICE PLANE DISTANCES OF A FEW FATTY ACIDS

Acid	Number of C-Atoms	d_1 in Å	d_2 in Å
Formic	1	5.2	3.65
Acetic	2	5.9	4.17
Propionic	3	6.0	4.39
Butyric	4	8.5	4.64
Valerianic	5	10.2	4.54
Caproic	6	12.8	4.64
Heptoic	7	14.5	4.54
Caprylic	8	17.0	4.54
Pelargonic	9	18.4	4.54
Capric	10	20.3	4.59
Undecylic	11	22.0	4.54

acter of the interference phenomenon and confirm the view that the individual molecules in a liquid are linked with their immediate environment by a quite definite state of arrangement.

The occurrence of smaller or larger groups of molecules is conditioned by mere space filling by the elliptical particles and is further promoted by forces of attraction prevailing between them. Rehaag and Stuart[88] have demonstrated very strikingly in a two dimensional model the occurrence of groups of elliptical particles which always appear if the packing is sufficiently close that anisotropic space filling can be effected.

If ellipsoidal brass particles in a flat, glass dish are shaken until there is a random arrangement, we obtain for the case in which few particles

[88] H. Rehaag and H. A. Stuart, *Physik. Z.*, **38**, 1027 (1937).

are present no preferred orientation of the separate individuals and also no formation of groups or clusters. The experiment shows that even if 40 per cent of the available volume is filled with particles, shaking results only in a random arrangement of the ellipsoids. But by the time 57 per cent of the space is occupied, quite a marked grouping has set in. Thus, the state of arrangement alters very rapidly within a small density range. In such experiments the cluster formation is due only to pure space filling and would certainly be increased by the forces of attraction existing in actuality.

3. Determination of Size and Form of Very Small Crystals with X-Rays

In the foregoing sections we have discussed the molecular arrangement in crystals and liquids and can appreciate how greatly the use of x-ray diffraction in this field has increased our knowledge; it remains now to show that the interference method is capable of a wider application which has proved very useful in colloid chemistry and particularly so in the domain of high polymers.

This makes it possible to draw conclusions regarding the size and shape of the scattering crystallites from the breadth of the interference fringes in angular measure. If we turn our attention, not, as previously, to the position and intensity of the diffraction phenomena, but to their breadth or lack of sharpness, it is possible to obtain a mathematical relation between the angular breadth of an interference fringe and the number n of the scattering particles responsible for it. The breadth of the interference fringe increases if the number of the interacting network planes within the individual particles of the preparation decreases (see particularly[39]).

The same phenomenon is observed if the particles possess a preferred expansion in a definite direction; in this case few network planes follow one another in one direction and the interference fringes appear broadened, while the diffraction points of the set of network planes running perpendicular to it are of normal sharpness.

The line broadening begins to be observable at $n = 1000$ and can most easily be examined experimentally in the region between $n = 50$ and $n = 200$. Diffraction can also be obtained, however, even with tiny crystals in which only 3 to 5 lattice planes succeed one another in the same direction.

The angular breadth of an interference line, as it appears in powder or fiber diagrams, is determined essentially by two factors: by the influence of

[39] J. T. Randall, *Diffraction of X-rays and Electrons*. London 1934, p. 28 et seq.

the crystallite size and by the thickness of the preparation. Since the former can be controlled by the investigator, there remains the problem of separating the latter in the most exact way possible. In a formula first used by Scherrer,[40] the term governed by the rod-thickness, as a magnitude independent of the reflecting angle, is superimposed by a term governed by the line-width, which depends upon $\cos \theta/2$. This method of calculation is then correct for conditions of completely parallel light and non-absorbing material. In this case, the preparation, regarded as a cylindrical rod, is represented as in Fig. 65 with the same breadth at all angles. If, however, we have parallel light and an absorbing substance, Fig. 66 shows that, because of absorption, the rod always appears to be broader at greater angles; this influence may be well understood mathematically and it has been tested experimentally by an investigation of Brill and Pelzer.[41]

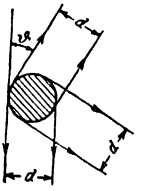


Fig. 65. Cylindrical rod; parallel light; non-absorbing substance.

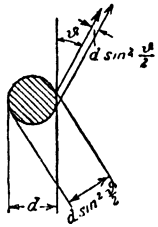


Fig. 66. Cylindrical rod; parallel light; strongly absorbing substance.

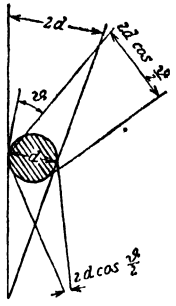


Fig. 67. Cylindrical rod; divergent light; non-absorbing substance.

If we work with divergent light and a non-absorbing substance, as represented in Fig. 67, Bragg's reflection law requires that the rod appear broader at small angles of deviation than at larger, so that the breadth of line, which increases with increasing angle because of interference, counteracts the influence of decreasing breadth of rod. For this case, formulas developed by M. v. Laue[42] are valid and of greater generality than the Scherrer formula mentioned above. Having regard to all these conditions, we are able to obtain fairly reliable data regarding the size and, under some conditions, the form as well, of the crystallites from the half-values of the

[40] P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, **1918**, p. 98; see also R. Zsigmondy, *Kolloidchemie*, 5th ed., Dresden 1925; article by P. Scherrer.

[41] R. Brill and H. Pelzer, *Z. Krist.*, **72**, 398 (1929); **74**, 147 (1930).

[42] M. v. Laue, *Z. Krist.*, **64**, 115 (1926).

x-ray fringe widths, particularly when numerous reflections have been measured. In order to evaluate the accuracy of such data, it is well to bear in mind the assumptions under which the formulas cited have been derived, remembering that the results obtained are invalid otherwise (see Halla-Mark[43]).

We will summarize them briefly and discuss them.

(1) crystallites only of a uniform size are involved;
(2) all particles have exactly the same identity periods;
(3) the lattice is perfect in every individual particle; there are no lattice distortions or defects;
(4) the thermal motion of the atoms causes no measurable broadening of the lines.

By comparing the half-value breadths in x-ray exposures at normal temperature and at the temperature of liquid air, it can readily be established that the influence of temperature is generally negligible. This accords with the requirement of the Debye-Waller theory[44] which, to a first approximation, provides only for a decrease in interference intensity and not for an increase of the half-value breadth.

On the other hand, it is important to discuss the influence arising from points 1, 2 and 3.

Actually, we never meet with exactly uniform particle size, and must always take into consideration a certain distribution curve. A. L. Patterson[45] and J. Hengstenberg[46] have done this for a Maxwell and Gauss distribution curve respectively and found that the deviation of particle size calculated from the Laue formula from the average size given by the distribution curve amounts to about 50%. It is evident, therefore, that condition (1) holds only to the extent that the particle size determination can be expressed only in terms of order of magnitude, i.e. we can decide whether a particle has an edge-length of 100 or 500 Å but not whether it is 100 or 150 Å.

The case is less clear for the other two conditions. There is, as yet, no satisfactory means of separating the broadening of the interference lines due to particle size from the broadening due to lattice defects or to difference in lattice constants. The case in which the lattice itself is perfect in the individual crystallites but the different particles possess different translation periods has been met with in heterogeneous crystal mixtures

[43] See F. Halla and H. Mark, *Röntgenographische Untersuchung von Kristallen.* Leipzig 1937, p. 317.

[44] P. Debye, *Ann. Physik*, **49**, 1 (1914); J. Waller, *Z. Physik*, **17**, 398 (1923).

[45] A. L. Patterson, *Z. Krist.*, **66**, 637 (1928).

[46] J. Hengstenberg, *Z. Krist.*, **69**, 271 (1928).

of metals and need scarcely be considered here; but lattice distortion must be given special notice.

Quantitative determination of lattice defects in high polymeric substances is not feasible with the technique at present available, but it is possible to arrive at an estimate by taking intensity measurements of the radiation due to interference and the diffuse scattered radiation. Every atom displaced from its equilibrium position by lattice distortion intensifies the diffuse radiation and weakens the interference component accumulated in certain directions. In order to obtain an idea of the extent of lattice defects in natural cellulose which has been untreated as far as possible, Hengstenberg measured the breadths of the equatorial interferences and the diatropic reflections from very carefully degummed ramie fibers and estimated simultaneously the monochromatic radiation scattered at the equator and the perpendicular bisector line of the diagram. This scattered radiation lying between the interference lines is quite small and in the planes parallel to the fiber axis is not greater than in the diatropic. The measured half-value breadths of the latter planes show the absence of any considerable lattice defects in them, otherwise a greater breadth would have been found. Since the diffuse radiation at the equator is not much greater than that on the vertical median line of the diagram, the inference is that in these natural materials also, lattice defects perpendicular to the fiber axis cannot essentially falsify the results of the determination. Conditions are very different in preparations which have been strongly treated chemically or mechanically; in this case lattice defects are of undoubted influence, as will be discussed later. It can be said, that the tenacity of rayon is closely connected with the degree of order which can be attained during the coagulation process and there will be much information given about this point in the second volume.

R. Brill has carried out a series of experiments which indicate very clearly the influence of particle size on the sharpness of the Debye-Scherrer lines for iron powder. There is quite a powerful effect, the evaluation of which would be very profitable. Scherrer has already established in the work previously mentioned that the particle sizes of colloidal gold calculated by the use of his formula agree very satisfactorily with those obtained by the Zsigmondy method of direct counting. Later, Brill compared the different relations available for the computation with one another and obtained the data contained in Table 72. This includes a comparison of the relation originally given by Scherrer with the Laue formula modified by Brill and Pelzer. Various preparations of very fine-grained iron, which are of importance in the technique of catalysis in the ammonia process, served as material.

The results are divergent but are of the same order of magnitude.

Table 73 gives similar data for particle size determinations in gold sols and again indicates that the various theoretical equations for interference give values which agree in order of magnitude. The last line in this table giving particle sizes of the same sols determined by Rinde[47] with the ultracentrifuge is of special interest. The data are in general higher than the x-ray data, a fact that should not cause surprise and has to be

TABLE 72

PARTICLE SIZE OF VARIOUS IRON PREPARATIONS

Preparation	Particle size in Å	
	After Scherrer	After Brill, Pelzer and Laue
1. Fe from Fe_2O_3	230	200 210
After heating to 1000° for 10 hours	420	∞ 1000
2. Fe from Carbonyl	77 75	100
Fe from Carbonyl	60	90
Fe from Carbonyl	100	110
Fe from Carbonyl	120	100
3. Electrolytic iron	230	230 210

TABLE 73

PARTICLE SIZES OF VARIOUS GOLD SOLS IN Å

	1	2	3	4	5
After Scherrer	—	—	47	62	81
After Laue	32	38.5	52	65	87
After Brill, Cu-radiation	—	—	47	58	82
After Brill, Fe-radiation	30.5	42	—	—	—
With the ultra centrifuge	40	61	100	149	225

expected in all similar comparisons; it should be remembered that the x-ray method indicates those lattice regions within which coherent scattering of the x-rays occurs, owing to the arrangement prevailing in them. In contrast, the other methods—osmotic pressure, rate of diffusion, etc.—record the structures regarded kinetically as free in the solution, which certainly cannot be smaller than the former and may indeed be greater,

[47] A. Rinde, *Dissertation*. Upsala 1928.

because different circumstances may lead to the aggregation of primary crystals into secondary particles.

In any case, the experiments on inorganic small crystallites described here, to which may be added other works giving the same main result, show that the interferometric determination of size affords essentially accurate results. There has, therefore, been no hesitation in applying these methods to the determination, or at least, to the estimation, of the size and form of micellar dimensions in natural high polymers and in preparations recovered from solution.

Having regard to all previously mentioned experimental precautions, Hengstenberg some time ago calculated the data given in Table 74 for natural ramie fibers. They may not be exact individually but they certainly indicate the right order of magnitude and agree satisfactorily with earlier estimations of R. O. Herzog.

TABLE 74

MICELLE DIMENSIONS IN CELLULOSE

Diameter of preparation	*hkl*	Dimension in Å
0.75 mm.	101	56
0.75 mm.	002	56
0.75 mm.	004	53
1.0 mm.	002	59
0.4 mm.	002	57

More recently the question of the presence of closed lattice-like regions in natural and artificial high polymeric substances has assumed greater proportions. Since x-ray methods play an important part in deciding this problem, and the result is of general significance, it seems justifiable to treat in more detail the questions of distance, size and lattice arrangement in natural high polymers in connection with the structure of crystals, liquids and interferometer measurements of minute crystallites.[48]

4. Observations on Mesophases or Crystalline Liquids

Having described our present knowledge of molecular arrangement in liquids, we shall now discuss a few data on so-called liquid crystals or mesophases. The existence of such systems was discovered by O. Leh-

[48] G. L. Clark, G. J. Ritter and W. A. Sisson, *Ind. Eng. Chem.*, **22**, 481 (1930); W. K. Farr and W. A. Sisson, Contrib. Boyce Thompson Inst., **6**, 315, (1934); W. A. Sisson, Contrib. Boyce Thompson Inst., **8**, 389 (1937); G. L. Clark and E. A. Parker, *J. Phys. Chem.*, **41**, 777 (1937); Cf. also H. Mark, *J. Phys. Chem.*, **44**, 764 (1939). P. H. Hermans has recently made very interesting contributions to this subject; a paper is expected to appear soon. Compare also *Naturwiss.*, **28**, 233 (1940).

mann[49] in the year 1889; their properties have been thoroughly investigated for some years by numerous workers, notably by R. Schenck,[50] D. Vorländer,[51] G. and E. Friedel,[52] and different views have been expressed on the nature of the liquid crystalline state mainly in connection with the optical polarization experiments. In recent years a detailed discussion, instigated by P. P. Ewald, has been published on this subject in a special volume of the *Zeitschrift für Kristallographie*,[53] which should be consulted for greater detail.

It is possible here only to give a few fundamental data on the nature of the observed phenomena, on their probable causes and on the arrangement of the molecules in the mesophases that can be deduced from them.

a) Experimental Results in the Investigation of Mesophases

There are numerous organic chemical substances which show remarkable anomalies on melting. It is particularly striking that the solid crystals of these substances give first a cloudy melt, which displays optical anisotropy with polarized light and clears only on further heating to a quite definite temperature of transition. We have, accordingly, two liquid phases in which obviously different cluster formations of the molecules occur and behave as enantiomorphs of one another, similar to those known for a long time in crystals.

The two liquid phases—the liquid amorphous and the liquid crystalline (occasionally several liquid crystalline phases have been observed)—differ from each other in many respects. While the amorphous is optically isotropic, the crystalline liquid systems always exhibit the behavior of crystals with several optical axes and are also frequently highly pleochroitic (Mauguin, Zocher, Grandjean).

There are numerous experiments on viscosity. Table 75 is taken from R. Schenck and the data indicate that the crystalline liquids can be considerably more viscous than the corresponding amorphous phases of the same chemical composition, but that the reverse is sometimes observed also.

The dielectric properties have been studied, especially by W. Kast,[54] who was able to show that the dielectric constant of these substances changes abruptly at the transition points. Fig. 68 shows this effect in the case of the diethyl ester of ethoxybenzal amino-α-methylcinnamic acid.

[49] O. Schumann cf. the different references in the Vol. 79 of the *Z. Krist.*
[50] R. Schenck, *Z. Krist.*, **79**, 269 (1931).
[51] D. Vorländer, *Z. Krist.*, **79**, 61 (1931).
[52] G. and E. Friedel, *Z. Krist.*, **79**, 1 (1931).
[53] P. P. Ewald, *Sonderband "Fluessige Kristalle,"* Z. Krist., **79**, 299 (1931).
[54] W. Kast, *Z. Krist.*, **79**, 315 (1931).

Magnetic susceptibility changes abruptly at the transition points, according to Foëx and Roger;[55] Fig. 69 gives an idea of this. Of special importance is the fact that, owing to the size of the clusters in the mesophases, it is possible to obtain practically complete arrangement by quite weak magnetic fields. The orientation powers of a magnetic field can in this case be determined very well by measuring the dielectric constant. Fig. 70 shows that with increasing field strength the dielectric constant of crystalline liquid *p*-azoxyphenetol first decreases proportionally and then

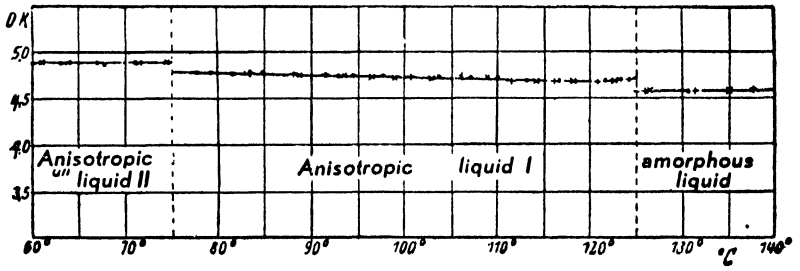


Fig. 68. Change of dielectric constant at the transition points of a crystalline liquid.

TABLE 75

VISCOSITIES OF A FEW CRYSTALLINE LIQUIDS

Substance	1st melting point in degrees Centigrade	2nd melting point in degrees Centigrade	Existence range (difference) in degrees Centigrade	Viscosity (Water = 100)	
				crystalline liquid	amorphous liquid
p-Azoxycinnamicethyl ester	249	141	108	>900	Decomposed
Cholesterolbenzoate	178.5	145.5	33	890-620	420-218
p-Azoxybenzoethyl ester	120	114	6	860-470	350-270
p-Azoxyanisole	134	116	18	141-128	175-135
p-Methoxycinnamic acid	186	170	16	106-91	159-117
p-Azoxyphenetole.	168	137	31	79-66	95-75

approaches a saturation value. Other physical properties, such as conductivity and opacity vary in the same way.

The x-ray diffraction phenomena in crystalline liquids are particularly clear and informative. The investigations of W. Kast and P. W. Glamann,[56] of K. Hermann and A. H. Krummacher[57] and of P. A. Thiessen and his co-workers should be mentioned especially here.

[55] See e.g. G. Foëx, *Z. Krist.*, **79**, 289 (1931).

[56] W. Kast and P. W. Glamann, see l. c. page 210.

[57] K. Hermann and A. H. Krummacher, *Z. Krist.*, **74**, 73 (1930).

The principal experimental result consists of the fact that in liquid crystals the blurred interference rings of which we have learned in the discussion of normal liquids split up in the magnetic field into a pair of crescents, whereas in the amorphous phase the influence of the magnetic field is inappreciable. Diagrams, which show this effect on exposure of the allyl ester of phenetol azoxybenzoic acid in the magnetic field have been taken by Hermann and Krummacher with Cu radiation; a very definite accumulation of the interference intensity in the region of the equator is evident.

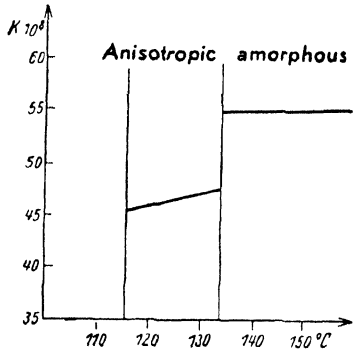


Fig. 69. Change of magnetic susceptibility at the transition points.

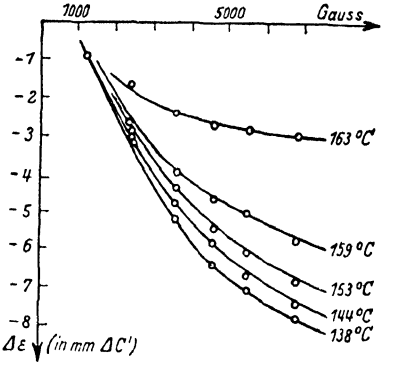


Fig. 70. Influence of the magnetic field strength on dielectric constant.

b) The Molecular Arrangement in the Mesophases

The experimental results mentioned, above all, the optical and x-ray results, demonstrate that the crystalline liquid state is characterized by the fact that there is considerable arrangement of the individual particles intermediate between that prevailing in a crystal and that occurring in a liquid.

Generally speaking, every lattice unit in a crystal lattice is permanently fixed at a given equilibrium position and executes about it more or less high frequency vibrations according to the temperature and lattice forces; it is the mean positions of these vibrations which are fixed, forming a rigid point lattice in space. It has been shown that, in the long chain aliphatic compounds the more or less free motions of large lattice units may be possible in addition to vibrations about the equilibrium position without apparent disturbance of the crystalline state by the movement of the lattice linkage. In these crystals we have a system in which, it is true,

the mean centers of gravity of the individual cells are fixed but in which free rotation about a given axis is possible.

Liquid crystals appear to constitute a further step in the orientation of liquids. Although we are unable today to systematize finally the existing experimental material and the somewhat contradictory views of the authors working in this field, there appear to be two definite arrangements of particularly frequent occurrence, named by G. Friedel: the smectic and the nematic state.

Smectic substances are crystalline-liquid substances in which elongated filament or ribbon-like molecules are arranged in such positions that both ends lie preferably in given planes. Fig. 71 will show a diagrammatic representation of this type of arrangement. Apart, however, from this grouping of the individual particles, they are free to move to a large extent; they can rotate around their axes, and be displaced in such a way that the axes remain parallel and the number of the chains comprised in a bundle, as shown in Fig. 71, can vary; molecules from one set can pass over to another, etc. The only thing fixed is the preference of certain planes which must be separated from one another by a distance characteristic for the substance considered. M. de Broglie and E. Friedel[58] were able to detect interferences in the sodium, potassium and ammonium salts of oleic acid, which, owing to the considerable length of the molecules, were observable as very narrow rings in the immediate vicinity of the point of penetration. From the angle of diffraction, the preferred inter-planar distance in the preparation examined was given as about 43.5 Å; in ethyl azoxybenzoate E. Friedel found an interplanar distance of some 20 Å. Both are in very good agreement with the length of these molecules, if we assume the formation of double molecules, which seems a very plausible assumption on the basis of the information given in chapter D, p. 139.

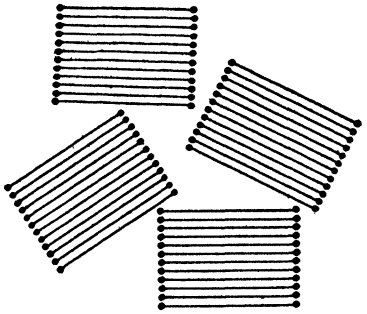


Fig. 71. Diagrammatic representation of the smectic state.

We may now go one step further in the direction of entirely free mobility of the molecular centers of gravity and assume that the preferred arrangement of the ends of the molecule in definite planes no longer holds but that the parallel chain arrangement is preserved. In this way we arrive

[58] Cf. the article of G. and E. Friedel in *Z. Krist.*, **79**, 184–199 (1931).

at an arrangement represented diagrammatically in Fig. 72; the rod or ribbon-shaped molecules can rotate about their long axes, their center of gravity is displaceable in all three directions in space with merely the parallel orientation preserved. Liquids which are found in this state of arrangement are termed nematic in Friedel's nomenclature; as diffracting structures they exhibit a spatial line lattice, in which the individual lines, that is, the extended molecules, still show a scattering, dependent on temperature, with regard to their mutual distances.

C. Hermann,[59] in a detailed investigation of the symmetry groups of amorphous and mesomorphous phases, has devised a systematic treatment of all possible crystalline liquids equivalent to the point lattice concept of crystals and has shown that there are a great many different possibilities for the appearance of the mesophases which behave characteristically in respect to x-ray properties and behavior in polarized light. Everything in nature seems to display essentially the two orientation possibilities named above.

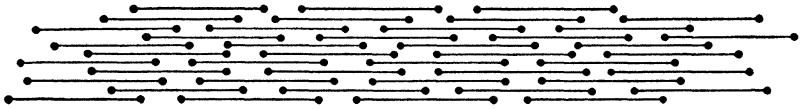


Fig. 72. Diagrammatic representation of the nematic state.

If we confine ourselves to these, we can visualize the transition from solid crystal to amorphous liquid in the following way.

1. Three-dimensional crystal: the centers of gravity of the units are fixed (apart from vibration); rotations are not possible. Examples: hexamethylene tetramine, urea.
2. Crystal with rotating molecules:[60] the centers of gravity of the units are fixed; rotation about one or more axes is possible. Examples: NH_4Cl, sodium stearate at higher temperatures.
3. Smectic state: the centers of gravity of the units are mobile in one direction; rotation about one axis is permitted. Examples: sodium oleate, allyl ester of phenetolazoxybenzoic acid at 72°.
4. Nematic state: the centers of gravity of the units are mobile in two spatial directions; rotation about one axis is permitted. Example: allyl ester of phenetolazoxybenzoic acid at 88°.
5. Amorphous liquids: the centers of gravity of the units are mobile in three directions in space: rotation about three axes perpendicular to one another is possible. Example CCl_4, Hg.

[59] C. Hermann, *Z. Krist.*, **79**, 337 (1931).

[60] W. O. Baker and C. P. Smyth, *J. Am. Chem. Soc.*, **61**, 2798 (1939).

For an informative experiment on the transition from the smectic to the nematic state we are indebted to Hermann and Kupfermacher, who have taken x-ray diagrams of the allyl ester of phenetolazoxybenzoic acid at different temperatures by the use of an orientating magnetic field. Two rings were observed; one in the vicinity of the point of penetration, which is characteristic for the smectic phase (see p. 203), and one at a somewhat greater angle of diffraction which occurs in both phases and shows great intensity; it is related to the thickness of the rod or ribbon-shaped molecules. Table 76 shows the results of x-ray examination of the amorphous, smectic and nematic phase of the substance over a temperature range of 72° to 100°. It is evident that the diameter a of the outer ring is in all cases approximately the same and—evaluated according to Bragg's reflection law—gives a distance apart of the molecular axes ϑ in the region of 4.6 to 5.0 Å, which is in excellent agreement with other knowledge regarding the dimensions of such molecules.

TABLE 76

ALLYL ESTER OF PHENETOLAZOXYBENZOIC ACID, CuK_α

State of the substance	a	$\vartheta/2$	d_a Bragg
100° liquid n. m.	32	8° 47′	5.0 Å
88° nemat. n. m.	34	9° 18′	4.8
79.5° nemat. w. m.	34	9° 18′	4.8
75.5° smec. w. m.	35	9° 33′	4.6
72° smec. w. m..	35	9° 33′	4.6

n. m. = no magnetic field. w. m. = with magnetic field.

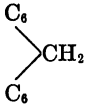
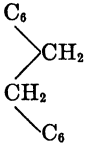
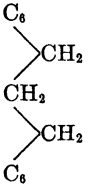
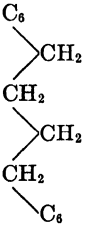
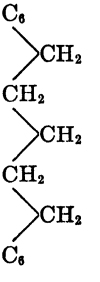
The question of the properties which a molecule must possess to give rise to the phenomenon of liquid crystals is of great interest. In the first place, we have the extensive experimental material collected and sorted by D. Vorländer in systematic researches over a number of years. He summarized his results by stating that the tendency to the formation of mesophases has a geometrical as well as an energy basis.

The spatial effects may be summarized by saying that the molecules shall be extended and rectilinear as far as possible, and a ribbon shape apparently has the advantage over a cylindrical one for this purpose. Internal free rotation is undesirable; stationary or nearly stationary particles are the most suitable. Zig-zagging within the chains and special branching at the ends or in the middle are at once apparent in connection with the formation of crystalline liquid phases. Table 77 from Vorländer is cited as an example and it shows very clearly the influence of a chain inserted between two larger identical molecular components.

To some extent there has been thorough empirical investigation of the strong influence which certain structural units—double bonds, triple bonds, etc.—exert upon the nature of crystalline liquids, thus allowing certain conclusions to be drawn as to the structure of the molecules forming the mesophases from the appearance of these phases.

From the energy standpoint the simultaneous existence of strong dipoles and easily polarizable groups appears to be essential. Further, it is advantageous if the dipole is found on the molecular axis and forms a right angle with it. Easily rotated or otherwise mobile polar groups at the ends of the molecule are of subordinate importance.

TABLE 77

				
non-crystalline liquid	highly crystalline liquid	non-crystalline liquid	average highly crystalline liquid	barely crystalline liquid

If we compare these conditions, determined purely empirically, for the preferred appearance of mesophases with the discussions of p. 98, we obtain the impression that the aggregation of numerous particles over large regions is caused by the attraction of a dipole rigidly fixed on the molecular axis for the readily polarizable parts of another molecule; further, that the dipole of the second attracts a third molecule and so on until a structure results which can be compared to a large number of laths piled on one another, or, in the presence of particles having rotational symmetry, to a bundle of pencils. The arrangement and mobility of the molecules individually depends in a very sensitive way on their form, on the magnitude of the forces acting between them and on the extent of thermal motion.

F. THE BEHAVIOR OF MIXTURES

1. General Remarks on the Investigation of High Polymeric Substances in Solution

The investigation of natural and synthetic high polymeric substances is carried out essentially on two states of these materials. We study them either as they occur in the plant and animal kingdoms as substances of definite form, or as amorphous, resinous or vitreous masses such as result from polymerization reactions. The results of these investigations contribute no evidence, however, for behavior of the isolated elementary units of these substances but merely indicate their properties in the aggregate.

If we desire direct information on the behavior of individual macromolecules, we must disperse the substance under examination in a solvent and consider the properties of the high polymeric substance in solution. The properties of these solutions are so astonishing that they have excited the active interest of research both from the scientific and the technical aspects. The remarkable osmotic phenomena, the phenomena of diffusion and sedimentation, the high viscosity of solutions of high polymers, their ability to yield filaments and films of most diverse properties, their elastic character and their great sensitivity towards mechanical and thermal influences, all are qualitative effects well known and much studied in science and practice and which seem to be typical of the high polymers in the state of fine dispersion. The present status of this field of work is that there exists a great deal of qualitative information, which is not amenable to strict interpretation because the substances investigated have not been characterized with sufficient exactness and because the experimental methods have not been rigorously standardized.

The most important question in the further development of this line of research appears, therefore, to be: In the present state of our knowledge regarding these substances and the experimental methods available, what prospect exists beyond the qualitative treatment hitherto practised successfully, of arriving at satisfactory quantitative laws which will serve not only to express clearly the particular phenomena involved but also to correlate particularly those data which describe the state of the dispersed high polymeric substances? These include the dimensions, or, at least, the average dimensions, of the particles which are free to move in solution,

their form, the extent of the solvent volume affected by these particles, their free motion, the mutual forces between the dispersed particles, etc.

At the outset, we must assume that great difficulties will arise in attempting to discover quantitative relations in this field, for systems are involved which are marked by strong interaction between solvent and solute and between the dissolved (dispersed) particles among themselves, and we know invariably that if the mutual force effect of elementary particles has to be taken into account in addition to the purely statistical consideration, the possibility of theoretical expression of the conditions very soon reaches a limit. Similarly, the derivation of an exact, generally valid equation of state for real gases is highly difficult because we cannot represent mathematically the strong interaction between the molecules in this state; the establishment of an adsorption isotherm for very thick coatings has not been possible with the desired degree of accuracy for the same reason, and the absence of a theory embracing the energy relationships of liquids is to be ascribed to the same difficulty.

We must acknowledge from the first that it will be possible to deduce only laws which have a limited range of validity. In extrapolating beyond the validity limits, we must exercise great caution and must refrain from applying rules obtained for cellulose to rubber or to the proteins.

However, we may adopt the attitude that the study of high polymeric substances in the dissolved or dispersed state has contributed much of great value about the properties of these substances and that it will be possible in future to apply all the previously mentioned effects—osmotic pressure, diffusion, viscosity and elasticity—to the extension of our knowledge of these substances, which are equally of technical and of scientific interest.

In the course of work on the high polymers over the last twenty years, two fundamental opinions have developed regarding how best to describe the physical features of this class of substances and how to fit them into the scope of other chemico-physical knowledge.

One group of research workers expresses the view that the high polymers with all their peculiarities will be comprehensive only if we can discover forces and forms characteristic of these substances alone. Behind the behavior of the high polymers stands some secret which must be learned if we are to obtain a satisfactory, consistent and simple picture of these substances and their reactions. Research in this field must, therefore, be directed, in the first place, to the discovery of this fundamentally new knowledge; the application of previously known laws or force effects would offer but little prospect of success but would be a radically wrong method of elucidating the conditions.

On the other hand, other workers in the field hold the opinion that we must derive the properties and the behavior of the high polymers in a consistent manner from the physics and chemistry of the simpler substances. There are no new previously unknown force effects or forms to be discovered, but we must push knowledge of the low molecular substances sufficiently far in the quantitative direction and apply the results of these researches consistently; in this way the high polymers will be open to an increasing degree to a clear and definite description.

Every advance won by applying exact physical methods to the field of atomic and molecular structure should be made use of immediately in considering the high polymers. The distance rules for primary and secondary valences, the free rotatory power, the dipole properties of molecules, their natural vibrations and their optical behavior, all this is to be drawn on to the last detail in the discussion of high polymers. The experimental methods and also the quantitative results obtained with low molecular substances should be applied to the high polymers.

The secret of these substances and their definite differences in behavior from other substances are not connected with unknown force effects yet to be discovered, but merely with the fact that the known interactions between the atoms and molecules are so complicated, owing to the great accumulation of individual particles, that the impression of new kinds of forces results. It is, therefore, valid to apply the primary valences in their different forms as homopolar, heteropolar or metallic atom linkage and the secondary valences—as dipole, induction and dispersion forces—consistently to the sphere of large molecules and to formulate the question of how new types of hitherto unknown total effects can be produced by the integration of individual effects. It is not a question of seeking new interactions but of studying how such effects can be produced by the combination of the different types of forces investigated in low molecular substances.

It looks as if development in recent years would confirm the accuracy of the second viewpoint and, accordingly, special value has been attached to it in the present treatise. This first introductory volume is devoted to the task of summarizing briefly and, if possible, clearly all the fundamental knowledge of the physical chemistry of material structure which appears necessary to a comprehensive treatment of the high polymers.

In the present sections on the behavior of mixtures, the solutions will occupy the foremost place of interest, because in discussing high polymers, investigations of the different properties of their solutions—osmotic pressure, viscosity, diffusion, etc.—are of principal interest.

It is quite sufficient in the application, for example, of the osmotic laws

to molecular weight determination of ordinary well crystallized organic substances, for the experimentalist working in this field merely to insert the values he obtains for the lowering of vapor pressure, the osmotic pressure, the rise in boiling point or the lowering of the freezing point, in the relevant equation and calculate the desired molecular weight from it. For, generally, in the low molecular domain, the range of validity of these physico-chemical relations—Raoult's Law, Van 't Hoff's Law, etc.— is very large and large deviations or other difficulties are scarcely to be feared. The relations indicated in essentials by the principles of thermodynamics and from the equation of state for perfect gases or dilute solutions can be applied more or less mechanically without much risk.

In the high polymers, however, this is by no means the case. Here it is much more essential to test carefully every relation borrowed from the physical chemistry of ordinary substances for its validity. The significance of such relations must be fully understood and it is certainly no accident that, with regard to the nature of osmotic pressure, very instructive and extended discussion has taken place in the last few years, bearing particularly on the problems of the high polymers. The same is true of viscosity, diffusion and sedimentation.

Accordingly, it seems convenient to utilize the present section on the behavior of liquids mainly for the elucidation of fundamental problems and to discuss the applicability of the results to the high polymers. Space will also be found for a description of the appropriate methods, emphasizing that, although the techniques borrowed from the low molecular region are frequently applicable in the form ordinarily used there, they may require very considerable improvement and refinement. This may be due to the smallness of the effect or to its high sensitivity to temperature variations or to other external influences.

To sum up, we may say that application to high polymers of proved experimental and theoretical methods used in the region of low molecular substances can be successful only if the greatest possible degree of accuracy is employed in carrying out the experiments and every kind of fundamental relation involved is taken into consideration in the theoretical interpretation.

2. Remarks on Processes in the Formation of Binary Mixtures

Before discussing the separate effects which are helpful in the investigation of dispersed high polymeric substances, we may advance a few general remarks on the theory of binary mixtures along the lines of the above information. Opportunity will be taken to derive and discuss fundamental relations to which we shall refer again later.

There are three possible methods of consideration for the evaluation of the experimental data obtained for such systems: the thermodynamic, the kinetic and the statistical.

The first proceeds from direct observations and from a few fundamental laws—the three principal laws supported by general experience—and uses mathematical technique to derive from them additional laws whose consequences are compared with those of experiment. The method combines the advantage of infallibility with the disadvantage that the procedures cannot be materialized through models.

The kinetic method is based on a specific molecular model for each special case; it attempts to follow the individual fates of the separate particles, to interpret their movements theoretically and to deduce, by suitable averaging or summation, the behavior of the directly observable macroscopic system. This method of consideration is demonstrable, it tracks events to their conclusions, but it frequently introduces great mathematical difficulties and depends for success entirely upon the proper and fortunate choice of the model on which the calculation is based.

The statistical method, which was developed last, seeks to combine the certainty of the first method of consideration with the observational character of the second. For this purpose, it is usual to rely on certain generally valid laws which, in contrast to the thermodynamic method, however, relate to the molecular form and to avoid in this way the somewhat difficult and risky choice of a definite model, at the same time making use of general accepted principles and rules for its construction. These principles are applied to the physical state in each special case and we arrive by summation, integration or averaging at relations between magnitudes observable macroscopically. Accurately applied, this method may combine the advantages of the first two; occasionally, of course, it has the disadvantages of both.

With perfect execution all three methods should lead to inherently the same result, although they would naturally express it in different ways and should describe the same phenomena from different aspects. It is accordingly advisable in important cases to use all three methods concurrently and to compare the results before presenting the facts. Only when this comparison gives a conclusive and harmonic picture of the conditions, can we be certain that the elucidation has actually been pursued to the limits of possibility.

We shall now apply all three methods of consideration to the mixing of two substances, with special reference to gas pressure, lowering of vapor pressure and osmotic pressure.

a) Mixing of Two Gases

First let us consider mixing in two gases A and B which are under the same pressure. We imagine the two gases introduced into a constant volume V at constant temperature T, at first separated by a partition and occupying the partial volumes V_1 and V_2. We then remove the wall between them and observe what happens.

We find:

1. There are practically no thermal effects produced; heat is neither evolved nor absorbed; the heat capacity of the system therefore remains constant; there is no change in pressure.
2. The gases mix automatically.

These are experimental facts. To invest them with thermodynamic formulas, we rely on the second law and on the definition of free energy or capacity of the system to perform work. At constant external pressure the following holds:

$$F = H - TS.$$

where F = free energy at constant pressure, H = heat content, S = entropy.

Since mixing takes place automatically, the free energy must have decreased. Its change is given by

$$\Delta F = F_a - F_b = (H_a - H_b) - T(S_a - S_b) \tag{41}$$

The indices b and a may indicate that the magnitudes to which they are annexed relate to the state of the system *before* and *after* mixing.

Since we have proved that no change in the heat content has occurred, ΔH equals zero, so that the whole decrease of the free energy ΔF must have been occasioned by a corresponding increase of the entropy ΔS. We can therefore read equation (41) thus: on admixture, the system's capacity for performing work decreases and its entropy correspondingly increases.

It is not, therefore, molecular forces of attraction which induce the two species of molecules to mix but, in the case of perfect gases, only the increase in entropy, or, what is the same thing, the decrease of free energy F.

From equation (41) it is evident, of course, that the conditions may be very much more complicated if, for example, we do not work at constant pressure, or if, as may be the case in real gases, the internal energy of the system changes during the mixing. The particularly simple conditions chosen are, however, practically fulfilled in many cases by real gases; they correspond to the behavior of ideal gases or ideal gas mixtures.

To determine the entropy gain on mixing, the so-called entropy of

mixing, we have to make use of the equation of state of the ideal gas and of the second law, thus arriving at the expression

$$\Delta S = S_a - S_b = -k(n_1 \ln N_1 + n_2 \ln N_2) \tag{42}$$

$N_1 = \dfrac{n_1}{n_1 + n_2}$ = mol fraction of component one;

$N_2 = \dfrac{n_2}{n_1 + n_2}$ = mol fraction of component two;

k = Boltzmann constant, n_1 and n_2 are the number of mols of the two constituents respectively

the exact derivation of which is to be found in all text books.[1]

So much for the thermodynamic method of consideration; we shall now turn to the kinetic method.

In this case we do not rely on facts observed directly but begin by designing on the basis of reasonable assumptions a *model* of the perfect gas; on the proper choice of this model depends the success of the whole undertaking. We assume that both the gases enclosed in volumes V_1 and V_2 consist respectively of n_1 and n_2 spherical atoms or molecules, of very small total volume as compared with V_1 and V_2 (e.g. $\frac{1}{1000}$), which exert no forces on one another and behave on collision as elastic rigid spheres following the laws of classic mechanics. In each of the partial volumes these particles should execute entirely random motions at velocities w characterized by Maxwell's law of distribution, the average value $\bar{w}$ of which can be calculated simply from the Boyle-Charles equation

$$m\bar{w}^2 = 3kT$$

These are all assumptions regarding the nature of the two gases enclosed in V_1 and V_2, the validity of which will be apparent later from the satisfactory comparison with experimental observations.

Now we remove the separating wall.

A molecule of gas A, which had previously been hindered in its free path by the wall, now flies freely and penetrates volume V_2. It there collides at random with molecules of gas B and recoils. The result can scarcely be other than that the particular molecule in the course of sufficient time will have occupied, during its random, zig-zag motion, all parts of the total volume

$$V = V_1 + V_2.$$

[1] Cf. e.g. G. N. Lewis and M. Randall, *Thermodynamics*, New York 1923.

The same is true for all the other molecules in the two gases. Accordingly, the initial average value of the velocity cannot change, since, according to the law of conservation of energy, such a change could occur only if the system had gained or liberated energy. This, however, is not so, because we have done nothing but removed the dividing wall.

We thus arrive at the conclusion: The total energy of the system remains constant and the two gases mix automatically. This is in complete harmony with observation.

In addition to the thermodynamical consideration, we can now indicate clearly the *reason* for the automatic mixing. It lies in the random motions of the molecules which impel them to occupy all available positions consonant with the experimental conditions prevailing (size of vessel, fields of force, etc.). That the two gases, once they are mixed, cannot separate again is directly evident. It is very improbable that in consequence of the completely random molecular motions, i.e. quite accidentally, all n_1 molecules of the gas A would be found in volume V_1 and all n_2 molecules of gas B in volume V_2. The final state, a mixture of the gases as a result of molecular motion, seems to be more probable than the initial state of separation of the components A and B into the volumes V_1 and V_2 respectively. The entropy difference mentioned above now corresponds to a ratio of probabilities.

To calculate this ratio, we make the simple and plausible assumption that the probability of a particle's being present in a given volume will simply be proportional to the size of this volume; then the ratio of the thermodynamic probabilities that a molecule A will be found in the total volume V instead of in the initial volume V_1 is given by

$$\frac{V}{V_1}$$

For n_1 and n_2 molecules respectively, according to the laws for calculating probabilities and owing to the independence of the molecules of one another, the expressions are

$$\left(\frac{V}{V_1}\right)^{n_1} \quad \text{and} \quad \left(\frac{V}{V_2}\right)^{n_2}.$$

Thus, there corresponds to the entropy increase, which was mentioned above,

$$\Delta S = -kT(n_1 \ln N_1 + n_2 \ln N_2)$$

a probability increment of

$$\Delta W = \left(\frac{V}{V_1}\right)^{n_1} \cdot \left(\frac{V}{V_2}\right)^{n_2}. \tag{43}$$

From the Boltzmann equation

$$S = k \ln W$$

and because V_1 is proportional to n_1 and V_2 to n_2, (from the equation of state), the equivalence of the two equations (42) and (43) is established.

The statistical method of consideration places in the foreground the probability laws as general principles, illustrated here by a very simple case. Again, the method has been vindicated by experience.

Every closed system ever tends towards a state of greatest probability and remains in it if undisturbed by external influences. A general law —that on which we rely in contrast to kinetic considerations—states that the most probable state is reached when, for each species of molecule present in the system, a given probability expression attains a maximum. The problem to be solved in each special case consists in the actual algebraic calculation of this probability expression—the so-called summation of states or phase integral.

In the case of the perfect gas, a very easy calculation shows that the probability is proportional simply to the volume, so that we arrive at once at expression (42) for the increase in entropy on mixing.

We may therefore summarize as follows: under the particularly simple conditions chosen, which are, however, fulfilled in the case of ideal gases, the mixing of the two components is not due to forces of attraction between the different kinds of molecules, for such do not exist, but is simply and solely due to a diffusion tendency induced by the kinetic energy of the individual particles. In the concepts of thermodynamics it is an increase in entropy, according to the statistical concept it is a probability increase which causes the final state to be preferred over the initial one.

b) Mixtures of Liquids

We now pass to the consideration of a mixture of two liquids.[2]

There is naturally no change in the fundamental relations and laws—second law of thermodynamics, Boltzmann equation, etc.—for they are valid for all systems irrespective of their state of aggregation. It is only a question of how far the simplified assumptions earlier found to be true preserve their validity.

[2] Compare particularly J. G. Kirkwood, *Chem. Rev.*, **19**, 275 (1936).

We shall again apply the thermodynamic method first. The change of free energy during the mixing of two liquids of volumes v_1 and v_2, kept at constant temperature T, pressure P and constant total mass, is again given by

$$\Delta F = F_a - F_b = \Delta H - T\Delta S.$$

But, in contrast to the conditions governing ideal gases, experience teaches that on mixing two liquids, the condition $\Delta H = 0$ is practically never strictly satisfied. Constancy of heat content is rigorously true only in the mixing of isotopes and is approximately so in the mixing of very similar substances, e.g. benzene and toluene. Under such circumstances, we can, of course, formally adopt the method of consideration used for gases and the formulas derived for them and state: in the case of an automatic mixing of two liquids of ideal miscibility, the gain in entropy is the only decisive characteristic and there are no force effects between the particles.

Considered statistically, an increase in probability for the mixture as compared with the separated components, corresponds to this gain in entropy. Just as in gases, it is due to the random motions of the molecules and may be determined by the aid of the same formulas. Such mixtures have, accordingly, been termed ideal or perfect solutions.

The quantitative value of the entropy gain in ideal solutions can be found by equally simple expressions as those used for ideal gases (compare equation (42) on page 213 and equation (43) on page 215). This means that there are no other entropy changes besides the ideal entropy of mixing ($-R \ln N_1$ per mol); it corresponds to the fact that the mixture is more probable because the centers of gravity of the particles involved have more possibilities of arrangement in the mixture than they had when separated.

Experience shows, as already stated, that such simple conditions seldom exist in actuality. When two liquids mix, a change of volume and a change of internal energy usually occurs in addition to the gain in entropy and the gain in entropy itself can no longer be described in such a simple way as was used heretofore. The total decrease in free energy is here the negative of

$$\Delta F = \Delta E + P\Delta V - T\Delta S \tag{44}$$

where ΔH has been replaced by $\Delta E + P\Delta V$.
From the thermodynamic standpoint, the total decrease in free energy is now caused by three different terms

a) by a change of internal energy E
b) by a change of volume V
c) by a change of entropy S.

We may now demand from the kinetic-statistical theory a molecular interpretation of the fresh factors which bear upon the mixing of liquids. The answer is: mixing is now influenced by forces which the individual particles exert upon one another and by the possibilities of geometrical packing and arrangement of molecules endowed with different forms and sizes.

Particularly strong forces of attraction between components *A* and *B* and unusually favorable packing conditions between the two kinds of molecule will promote the occurrence of mixing beyond the ideal entropy effect. If, however, the forces between A and A and between B and B are greater than the interaction between A and B, the result is that the free energy of a mixture can be greater than that of the components; the mixed liquids would then automatically separate. The influence of the forces effecting separation would then exceed that of the entropy increase which favors mixing. Finally, the influence of increase or decrease in volume has to be taken into consideration also.

It is evident that the mixing of two liquids can be regarded as simple only in very rare cases; usually it is dominated by three different influences.

In this example, however, we are concerned with the general regularity which is always to be observed in physico-chemical processes and which has to be taken into account very carefully in discussing high polymeric substances.

The behavior of each system is determined essentially by two fundamentally different factors, namely, by the decrease in free energy and by the increase in entropy. The former demonstrates that the forces acting in the system try to effect a minimum of potential energy by displacing the atoms or molecules until further deformations are no longer compatible with the geometrical possibilities of movement; the latter signifies, however, that there is a constant striving towards the most probable state of distribution, as a result of the irregular motions to which the individual particles are subjected.

This position may also be expressed as follows: in any isolated system the total energy is composed of a potential and a kinetic component. Attractive forces between the particles are connected with the decrease of the potential energy while the kinetic energy --in so far as it is present as random molecular motion—results in the increase in entropy and opposes the collective influence of the forces.

If, in the system considered, the forces predominate, a high degree of aggregation and a compact arrangement is generally established, as, for example, in crystals at low temperatures.

If, however, the kinetic energy of the random molecular motions dominates, a condition of minimum density is always established and we arrive at the perfect gases in which forces play no rôle and whose behavior may be interpreted and evaluated successfully on the basis of the purely statistical considerations indicated by the kinetic theory of gases.

In most cases, nevertheless, we have to admit that these two generally opposing influences merge into a somewhat indistinct general picture; on the one hand, the forces try to secure cohesion and arrangement, while the kinetic energy of the random molecular motion is incessantly at work to destroy this arrangement as far as possible and to render the system as diffuse as is permissible under the circumstances prevailing (vessel walls, fields of force, etc.).

In this sense the isothermal mixing of two perfect gases would be regarded as an extreme case in which entropy influence is in complete ascendancy, and the separation of two emulsified liquids as one in which force influences are predominant. In order to explain this contrast as far as possible, this short section on the processes involved in the mixing of two substances has been placed at the beginning of the chapter.

The following remarks will give an idea of the order of the magnitudes concerned. The average kinetic energy per molecule per degree of freedom which is responsible for the entropy effect is

$$E_{\text{kin}} = \tfrac{1}{2}\, k\, T$$

$$k = 1.37 \times 10^{-16} \text{ erg per degree C.}$$

and at room temperature is of the order of magnitude of 10^{-13} to 10^{-14} erg per molecule which gives an amount of 300 cal. per mol for each degree of freedom; hence, for the motion of the center of gravity in the three directions in space, the kinetic energy is about 1000 cal. per mol.

If the opposing force effects prevailing in the system are large, we must expect the existence of a condensed phase; thus for example, the heat of sublimation of rock salt is about 55,000 cal. per mol and that of benzoic acid 20,600, both being values which are quite sufficient to cancel the effect of thermal motion in disrupting the small vibrations about equilibrium positions commanded by the forces.

Conditions are very interesting but extremely complicated if the two effects are of the same order of magnitude and the general behavior depends in a very sensitive way on the question of whether one or the other influence prevails. This is frequently the case, for example, in solutions of high molecular substances and it plays a decisive rôle, particularly, in evaluating experiments on osmotic pressure.

After this short, general discussion, which will have given an idea of the orders of magnitude involved, it is time to pass on to the treatment of vapor pressure and osmotic pressure, their origin and measurement and the interpretation of the results obtained in this field.

3. Lowering of Vapor Pressure in Binary Mixtures

For many years the relation between composition and vapor pressure of a mixture has been a very important and convenient aid in the investigation of solutions and it is consequently not surprising that in examining high polymeric substances, particular attention has been paid to the vapor pressures of their various types of solution. K. H. Meyer and his coworkers[3] in particular, have recently undertaken a systematic experimental investigation in this field with special consideration to chain molecules. By now, there are available the results of a fairly large number of investigations, beginning with systems of simple compounds of low molecular weight, such as benzene and toluene, and ending with substances like rubber and nitrocellulose. It may not be superfluous to recall here the fundamental equations, to explain the phenomenon of vapor pressure lowering and to discuss a few examples from the field of low molecular weight substances, which can throw a significant light upon the problem of high polymers.

In accordance with the accepted concepts and mathematical methods of treatment discussed in the previous section, we must turn our attention particularly to the following question:

How does the fugacity (the tendency to escape) of the various components of a mixture change with the composition? This fugacity f expresses quite generally the tendency to leave the liquid phase and to enter the gaseous one; it is caused by the kinetic energy of the molecules and expresses to what extent the thermal motion has been able to overcome the forces which hold the liquid phase together.[4]

If we confine ourselves to a mixture of two components the theory requires that, in the state of equilibrium,

$$N_1 \left(\frac{\partial \bar{F}_1}{\partial N_1}\right)_{p,T} = N_2 \left(\frac{\partial \bar{F}_2}{\partial N_2}\right)_{p,T}.$$

[3] Compare e.g. K. H. Meyer and A. van der Wyk, *Helv. chim. Acta*, **23**, 488 (1940).

[4] One can find a complete deduction of all fundamental relations in the textbooks of Physical Chemistry, especially in the following ones; G. N. Lewis and M. Randall, *Thermodynamics*, New York 1923; W. Nernst, *Theoretische Chemie*, 15th ed., Stuttgart 1926; H. S. Taylor, *A Treatise on Physical Chemistry*, New York 1924; A. Eucken, *Lehrbuch der chemischen Physik*, 2nd ed., Leipzig 1938.

In this equation N_1 and N_2 denote the mol fractions of the two components, while F_1 and F_2 are the partial molar free energies,

$$\left(\bar{F}_1 = \frac{\partial F}{\partial N_1} = \text{partial molar free energy}\right).$$

If we introduce, instead of the partial molar free energies, $\bar{F}_1$ and $\bar{F}_2$, the fugacities f, we obtain

$$N_1 \frac{\partial \ln f_1}{\partial N_1} = -N_2 \frac{\partial \ln f_2}{\partial N_2}.$$

If, as frequently happens, the vapor existing above the liquid mixture behaves as a perfect gas, we can replace the fugacities or volatilities f by the partial pressures p of the two components in the gas phase and obtain

$$N_1 \frac{\partial \ln p_1}{\partial N_1} = -N_2 \frac{\partial \ln p_2}{\partial N_2}.$$

This expression may be written somewhat differently, having regard to the meaning of ∂ in p, since in a binary mixture $\delta N_1 = -\delta N_2$

$$-\frac{\partial p_1}{\partial N_2} : \frac{\partial p_2}{\partial N_2} = \frac{p_1}{N_1} : \frac{p_2}{N_2}. \tag{45}$$

This indicates that the two curves which represent the effect of the composition on vapor pressure are very closely connected with each other. If, for example, in a given concentration range, the one curve has a linear form the other must have the same form in the same range. Equation (45) was derived by Duhem[5] and Margules[6] and later tested experimentally by Zawidski.[7] Figs. 73a to c give a few examples showing how different mixtures of liquids may behave in regard to the effect of composition on partial pressure. Already this different behavior shows very clearly that binary mixtures of liquids are affected by various influences and that the opposing effects of potential and kinetic energy give rise to a wide variety of combinations.

Conditions are particularly simple in the mixture propylene bromide-ethylene bromide, because there the partial pressures are simply proportional to the mol fractions. One could say that the molecules of the first kind are indifferent to those of the second kind and behave as if the latter were not present at all. Mixtures in which this independence holds over the whole concentration range and atall temperatures, have been termed

[5] Duhem, *Compt. rend.*, **102**, 1440 (1886).
[6] Margules, *Sitz. ber. Akad. Wiss. Wien*, **104**, 1283 (1895).
[7] Zawidski, *Z. physik. Chem.*, **35**, 129 (1900).

ideal or perfect mixtures. In them it is obviously possible for the molecules of substance 1 to be replaced by those of substance 2 without the occurrence of any changes either of an energetic or a geometrical nature. Both types of molecule present are effective only in proportion to their number.

In this case we can write

$$f_1 = f_1^0 N_1; \qquad p_1 = p_1^0 N_1$$

in which f_1^0 and p_1^0 represent the volatility and partial pressure of the pure component one; or, if we revert to the partial molar free energy:

$$d\bar{F}_1 = RT\, d \ln f_1$$

$$\frac{\partial \bar{F}_1}{\partial N_1} = \frac{RT}{N_1}$$

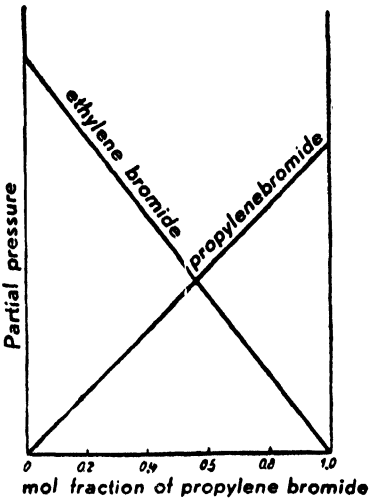


Fig. 73a. Partial pressure diagram of an ideal mixture; the partial pressures are proportional to the mol fractions.

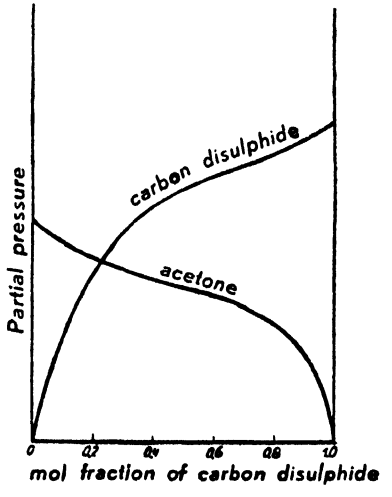


Fig. 73b

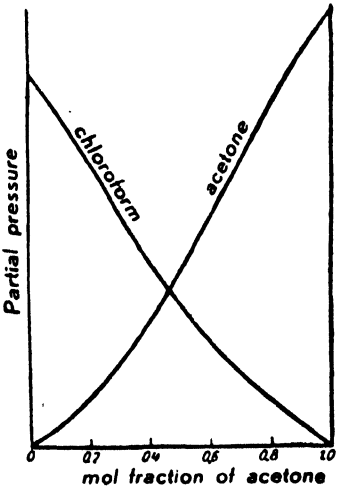


Fig. 73c

Fig. 73b. The partial pressures of the components of this system are not proportional to the mol fractions.

Fig. 73c. Departures from ideal behavior are not very great here.

There are few mixtures which satisfy this condition accurately over the whole range of concentration, unless one would take into account mixtures of isotopes, which behave as strictly ideal. But there are others, however, in which the above relation is fulfilled in quite good approximation and which may be designated practically "ideal" solutions. In addition to the pair of substances represented in Fig. 73a systems[8] such as

methanol—ethanol

benzene—toluene

chlorobenzene—bromobenzene

$SnCl_4$—CCl_4

may be cited.

In such cases, mixing of the two species of molecule is effected without the influence of any kind of force effects and no geometrical packing possibilities play any rôle. Mixing is here merely a result of the ideal entropy increase, which has its basis in the increased possibilities of interchange of molecules 1 and 2 with each other.

The majority of substances and particularly the low and high molecular weight substances composed of long chain molecules, exhibit an entirely different behavior which departs significantly from that of an ideal or perfect mixture. The problem arises therefore, first to determine by experiment the nature of these deviations as accurately as possible and then to ascertain by the application of the equations derived above how these deviations can be interpreted from the point of view of molecular behavior.

For ideal mixtures the following holds:

$$\Delta \bar{F} = \bar{F}_1 - F_1^0 = RT \ln N_1 \tag{46}$$

$$\bar{H}_1 - H_1^0 = 0$$

$$\bar{S}_1 - S_1^0 = -R \ln N_1$$

There are no changes in heat content and the change in entropy corresponds to the simple principle of the interchange of one and two.

The following deviations are recognized as possible:

$$\bar{H}_1 - H_1^0 \neq 0; \qquad \bar{S}_1 - S_1^0 = -R \ln N_1 \tag{a}$$

Here we have a heat of mixing differing from zero, while the entropy of mixing retains as before the ideal value. Such mixtures which are realizable in great number in the domain of low molecular weight substances, Hildebrand[9] has termed regular solutions.

[8] Cf. G. C. Schmidt, *Z. physik. Chem.*, (A) **121**, 246 (1926).

[9] J. H. Hildebrand, *Solubility of Non-Electrolytes*, 2nd Ed., New York 1936.

It has been shown experimentally by G. C. Schmidt[10] that, in fact, many systems of low molecular weight compounds behave according to equation (a) and Scatchard[11] has observed that in the systems $C_6H_6 \cdots CBr_4$ and $(CH_3)_2O \cdots (CH_3)_2CO$ the entropy of mixing has the ideal value. The total change of free energy during mixing of such substances is given by the addition of the ideal entropy change, $-R \ln N_1$ and the heat of mixings $\Delta\bar{H}_1$. Usually the sign and magnitude of the latter are decisive, whether the two liquids mix or not.

$$\bar{H}_1 - H_1^0 = 0; \qquad \bar{S}_1 - S_1^0 \neq -R \ln N_1. \tag{b}$$

In this case no interactions involving energy take place in the sense of excess attractions or repulsions between 1 and 2 but the entropy change differs materially from the ideal. This is best understood by saying that the molecules of 1 are somehow restrained or assisted in their movements in the vicinity of molecules 2, so that any interchange of the centers of gravity of the two kinds of molecules produces an additional effect upon the randomness of the arrangement. Mixtures or solutions of this kind have been termed *athermal* by K. H. Meyer, owing to the absence of thermal effects.

Among compounds of low molecular weight and similar size athermal mixtures or solutions usually show an entropy of mixing amounting to $-R \ln N_1$; they behave like ideal solutions. This means, apparently, that in the absence of forces between the molecules of the two species, there are also no additional entropy effects.

If, however, one component is large compared with the other, and especially if chain-like molecules are involved, athermal solutions can show anomalous entropies of mixing in the sense that the change of entropy is always more negative than $-R \ln N_1$, regardless of whether $\Delta\bar{H}_1$ is less or more than zero.[12]

$$\bar{H}_1 - H_1^0 \neq 0; \qquad \bar{S}_1 - S_1^0 \neq -R \ln N_1. \tag{c}$$

In this most general case we have to take into account energy as well as entropy effects; we are concerned with an *irregular* mixture.

Experiments show that solutions of chain substances, even if they are not true high polymers, always introduce anomalies in the sense that

$$(\bar{F}_1 - F_1^0)\ chain < (\bar{F}_1 - F_1^0)\ normal$$

holds.

[10] G. C. Schmidt, *Z. physik. Chem.*, (A) **101**, 286 (1922); **121**, 221 (1926).
[11] G. Scatchard, *Chem. Rev.*, **8**, 321 (1931).
[12] Cf. K. H. Meyer and A. v. d. Wyk, *Helv. chim. Acta*, **23**, 488 (1940).

The question arises whether these anomalies are due solely to energy interactions between the two kinds of molecules which have been mixed together (regular behavior) or to entropy effects alone (athermal behavior) or to both simultaneously (irregular behavior).

The most important work in the low molecular weight field is that of Brönsted and Colmant,[13] Meyer and Lühdemann[14] and Boissonas, who have made important contributions to this question by very careful measurements of the vapor pressures of binary systems containing chain molecules.

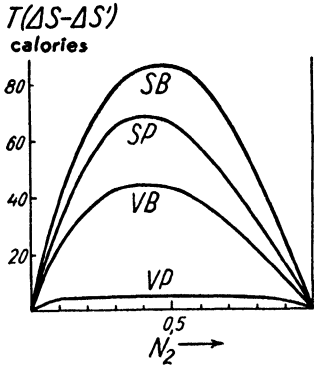


Fig. 74

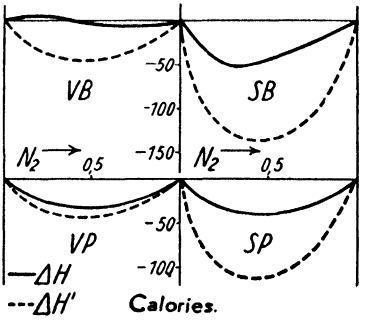


Fig. 75

Fig. 74. ΔS = observed entropy increase per mol solution. $\Delta S'$ = entropy increase per mol ideal solution.

Fig. 75. ΔH = observed heats of solution per mol solution. $\Delta H'$ = heats of solution for a "regular" solution calculated from ΔS.

The following substances were investigated:

Butyl valerate	in benzene . . . . . *VB*	Fig. 74 and 75.
" "	in propyl bromide. . . . . *VP*	
Butyl sebacate	in benzene. . . . . *SB*	
" "	in propyl bromide . . *SP*	
Oleic acid oleyl ester	in cyclohexane	
" " " "	in *n*-hexane	
" " " "	in carbon tetrachloride	
" " " "	in chloroform	
Thapsic acid dioleyl ester	in cyclohexane. 1b	Fig. 76.
" " " "	in *n*-hexane. 2b	
" " " "	in carbon tetrachloride. . 3b	
" " " "	in chloroform. 4b	

[13] J. N. Brönsted and P. Colmant, *Z. physik. Chem.*, **168**, 381 (1934).

[14] K. H. Meyer and R. Lühdemann, *Helv. chim. Acta*, **18**, 307 (1935).

Recently Boissonas has also investigated the system octadecane, with benzene, hexane and carbon tetrachloride.[15]

Brönsted and Colmant determined at 18° the vapor pressure in relation to the mol fraction in the butyl esters of valerianic and sebacic acid respectively. They found in all cases

$$f_1 < N_1 .$$

To discover the origin of the departures, Boissonas determined the heats of solution of these systems by a direct calorimetric method and

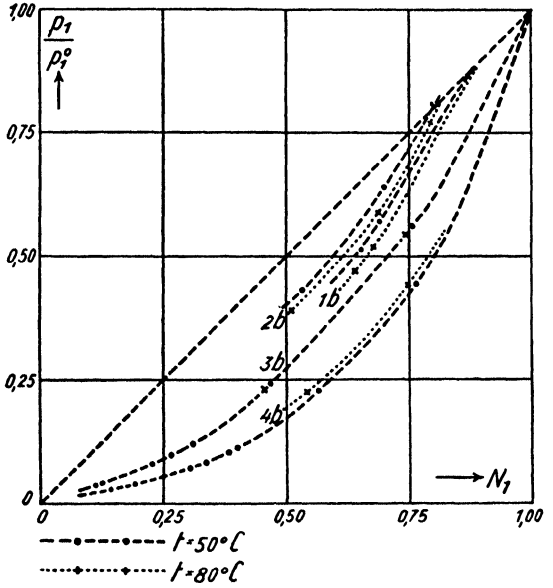


Fig. 76. Vapor pressure of solutions of thapsic acid dioleyl ester; the curves obtained all lie below the straight line.

compared them with the vapor pressure measurements of Brönsted and Colmant. The result is that the heat effects observed are not sufficient to explain the amount of departure from the behavior of an ideal solution which has actually been found. We are, accordingly, concerned not with regular mixtures in which there are no additional entropy effects but with fairly complicated systems. In every case the entropy gain is considerably greater than that corresponding to a perfect solution. The system butyl valerate-propyl bromide alone approaches ideal behavior. The deviations,

[15] Ch. G. Boissonnas, *Helv. chim. Acta*, **20**, 768 (1937).

as is evident from Fig. 74 and 75, are greater, the greater the difference between the molecular weights of the two components.

Meyer and Lühdemann[14, 16] arrived at similar results for the substances of higher molecular weight (532 and 787) investigated by them. By measuring the vapor pressure over the whole range of mixing at several temperatures, it was found that deviations from the ideal behavior could not be explained by heat of solution alone but that, in addition to the energy interactions between the different kinds of molecule, entropy effects appear which are considerably greater than the entropy of mixing in a regular solution.[17]

Fig. 76, which gives the vapor pressure of thapsic acid dioleyl ester in different solvents, may be taken as an example. It is evident that in all cases the measured pressure is considerably lower than that corresponding to an ideal solution. A comparison with the heats of mixing indicates that here again we are not concerned with regular or athermal mixtures but with an irregular solution in which the gain in entropy on association of the two components is very much greater than the pure entropy of mixing.

It may perhaps be observed here that the entropies of fusion and evaporation of chain substances sometimes assume abnormally high values, probably because the long and mobile molecules found in the gas and in the fused mass can better utilize the inherent free mobility in the form of rotations or vibrations of larger molecular parts than was feasible in the crystalline state.

This effect has already been discussed by Haller[18] and by Fowler and Guggenheim.[19] Recently K. H. Meyer[20] has proposed a statistical treatment, which elucidates the whole situation very clearly. If one wants to attempt a quantitative examination of the deviations observed by Brönsted and Colmant, Boissonas, and Meyer and Lühdemann, it is necessary to calculate the entropy gain connected with the curling up of a long chain molecule.

Let us, as an example, calculate the approximate entropy gain which occurs if one ground mol (14 g.) of the paraffin $C_{60}H_{122}$ passes from the state of extended chains into the state in which the chains have their greatest probability.

[16] Cf. K. H. Meyer and A. v. d. Wyk, *Helv. chim. Acta*, **23**, 488 (1940).

[17] Cf. Wo. Ostwald, *Kolloid Z.*, **46**, 259 (1928); cf. also W. Haller, *Kolloid Z.*, **56**, 257 (1931).

[18] W. Haller, *Kolloid Z.*, **56**, 257 (1931).

[19] E. A. Guggenheim, *Trans. Faraday Soc.*, **33**, 151 (1937); R. H. Fowler and G. S. Rushbrooke, *Trans. Faraday Soc.*, **33**, 1272 (1937).

[20] K. H. Meyer, *Z. physik. Chem.*, (B) **44**, 383 (1939).

The force of contraction of such a chain is given by equation (18) on page 75; it runs

$$\sigma = \frac{3kT}{nl_\alpha^2} \times \Delta l$$

and, therefore, the work during contraction from the extended to the most probable state will be

$$a = \frac{3kT}{2nl_\alpha^2} \times \Delta l^2.$$

If we have $\frac{N}{p}$ chains per ground mol

N = Loschmidt number

p = degree of polymerization,

the corresponding work per ground mol will be

$$A = \frac{3RT}{n \times p \times l_\alpha^2} \cdot \Delta l^2.$$

This is obviously equal to $T\Delta s$, so that the entropy gain owing to contraction is given by

$$\Delta s = 3R \frac{\Delta l^2}{p \times n \times l_\alpha^2}$$

In this equation we have:

p = degree of polymerization; in this case, equal to 60
n = number of independently and freely mobile links of the chain; in this case about 8.
l = length of the independently mobile link; in this case about 8 Å.
Δl = difference between the length of the extended (70 Å) and curled chain (10 Å).

Hence we get approximately

$$\Delta s = \frac{3 \times 2 \times 36 \times 10^{-14}}{6 \times 8 \times 64 \times 10^{-15}} \sim 0.7 \text{ cal.} \quad (l \text{ converted into cm.})$$

which gives the right order of magnitude for the "curling entropy." A. Wassermann[20a] found a similar entropy effect in investigating the equilibrium of the formation of larger organic molecules, which he attributed to the existence of slow vibrations in the two molecules combining with each other. It has been shown also in the theory of reaction kinetics that

[20a] A. Wassermann, *Trans. Faraday Soc.*, **33**, 128 (1937).

if large molecules with many vibrational degrees of freedom are involved, the entropy changes caused by the internal mobility of these large structures must always be taken into consideration, because they influence decisively the steric factor in these reactions.

It should be pointed out that, here again, an effect is present which is of less importance in the treatment of systems composed of small molecules. In that case the interchangeability of the single independent particles of the mixture is the main point; the two components can replace one another, they can occupy, to the order of magnitude, the same space and also possess the same internal mobility. The entropy gain on mixing is due merely to the fact that, in the mixture, more places are available to each of the participants.

If, however, one part of the mixture consists of very large molecules with high internal mobility and the other of normal molecules, which may reasonably be regarded as rigid spheres, the conditions of simple replaceability no longer hold and we obtain the above mentioned additional entropy effect.

4. Osmotic Phenomena

a) The Origin of Osmotic Pressure

If a sugar crystal is placed in water, it dissolves automatically. This is a case in which the diffusion tendency of the sugar molecules in conjunction with the forces of attraction of the water molecules on the sugar overcomes the cohesive forces of the crystal. The heat of fusion of a cane sugar crystal has not been measured directly but it would be of the order of magnitude of 15000 cal. per mol, indicating that an energy of 10^{-12} erg is necessary to remove a sucrose molecule from the crystal. We see that this is very much greater than the value of $\frac{3}{2} kT$ at room temperature ($\sim 6 \times 10^{-14}$ erg) and infer from this that cane sugar is a stable crystal, which is true.

If, however, it is put in water, solvent molecules penetrate the fine fissures and cracks of the crystal surface, interact with the hydroxyl groups of the glucose or fructose residues and thereby interfere with the cohesion of the crystal to such an extent that the average kinetic energy is sufficient to detach the individual $C_{12}H_{22}O_{11}$ molecules from the solid phase and drive them into the liquid. There, combined with a few water molecules, they execute molecular motion under the influence of random impacts, which push them hither and thither and make them victims of chance. In a short time the solid sugar crystal disappears with the automatic formation of a homogenous solution.

On thermodynamic principles the cause will be attributed to the increase in entropy consequent on solution, while the statistical-kinetic mode of consideration will recognize as decisive the predominance of the random molecular motion over the acting forces.

We shall now assume that the solution is very dilute and that the sugar molecules constitute only a few per thousand of the water molecules present. If there is a wall which allows the molecules of the solvent to pass but is impermeable to the particles of the solute (semi-permeable), energy will be imparted to the wall by the dissolved particles and their pressure—the osmotic pressure—is observable by direct experiment.

Let us imagine now a dilute sugar solution brought in contact with the pure solvent through a semi-permeable membrane and inquire what happens.

We give the answer first by thermodynamic principles and then by statistical-kinetic considerations.

Let equilibrium be established in an osmotic cell; an excess pressure then prevails in the solution equal to the osmotic pressure P. If the capacity of the cell is sufficiently large, one molecule of the solvent may be forced through the membrane into the solution without altering the concentration of the solution appreciably. If this process is conducted reversibly, the performance of work is

$$P\bar{V}_1 = -\Delta\bar{F}_1 \tag{47}$$

and if the solution is an ideal one, we have seen that

$$\Delta\bar{F}_1 = -T\Delta\bar{S}_1 = RT \ln N_1.$$

Since further $N_1 = (1 - N_2)$, the following holds for ideal solutions:

$$P = -\frac{RT}{V_1} \ln (1 - N_2). \tag{48}$$

The equation merely indicates that—thermodynamically considered—osmotic pressure is produced only by the gain in entropy on dilution.

For comparison let us consider the corresponding formula for the pressure p of an ideal gas; it runs, for n mols,

$$p\,dV = n \cdot T\,dS = nRT\,d \ln V \tag{49}$$

from which

$$pV = nRT, \tag{50}$$

if n moles are present in volume V. Here also the left hand side of (49) measures the work which the gas can perform when, under the pressure p, it expands by the volume dV, whereas the right hand side is nothing other

than the gain in entropy on mixing n moles of an ideal gas with the empty space of volume dV.

Both laws hold over regions of mixing and pressure respectively in which the conditions requiring the absence of any interfering forces are fulfilled; they have different mathematical form, as is evident from comparison of equations (48) and (50); the osmotic pressure of ideal solutions obeys a logarithmic law according to the molar concentration n/V. In both cases the entropy gain by the volume increase is decisive for the pressure on the wall; this increase in entropy is, however, expressed each time by a different mathematical function of the variables involved.

If, moreover, the ideal solution is dilute $\left(\frac{N_2}{V_1} \ll N_1\right)$, the *partial* molar volume of the solvent $\bar{V}_1$, differs only slightly from the molar volume V_1 of the solvent, and approaches also the molar volume V of the solution. By series expansion of the logarithm, we arrive at

$$P = \frac{RT}{V}\left(N_2 + \frac{N_2^2}{2!} + \frac{N_2^3}{3!} + \frac{N_2^4}{4!} + \cdots\right).$$

If N_2 is very small, the higher powers disappear as compared with the first term; to a first approximation $N_1 = 1$ and $N_2/V = c_m$ the concentration of the dilute solution in mol/liter. We thus obtain the limiting value of the osmotic pressure for ideal solutions at high dilution:

$$P = RTc_m, \tag{51}$$

which expression is known as van 't Hoff's law.

Unfortunately, we frequently find in the literature and especially in the textbooks, the loose expression, that, according to van 't Hoff, osmotic pressure equals gas pressure, without sufficient indication of the rather restricted conditions under which this statement is accurate.

According to statistical-kinetic conceptions, osmotic pressure and gas pressure have the same origin, namely the random molecular motion of the gas molecules on the one hand and of the dissolved particles on the other. The difference in the two cases lies, as mentioned before, in the different way in which the total volume of the system is made up. The gas, on expansion into a vacuum, has access to free space, whereas the new places required for the calculation of probability, according to the theory of the mixing process, are offered to the molecules of the solute only by interchange with the particles of the solvent.

The manner in which the suction exerted on the pure solvent by molecular motion is actually developed in the immediate surroundings of the membrane is a difficult question to answer in view of the lack of an equa-

tion of state for liquids, and the comprehensive treatment in K. Jellinek's *Text Book of Physical Chemistry* is recommended for reference. A detailed discussion of the relationships here would lead us too far afield; for the present it is only necessary to know that:

1. The osmotic pressure of a solution is produced by the thermal impacts of the dissolved particles on the semi-permeable membrane, just as gas pressure results from thermal impacts on the vessel walls. The difference between the two phenomena lies not in the mode of origin but in the fact that the gas molecules move in a vacuum, whereas the particles of the solute move in a liquid consisting of molecules which occupy space.

2. The osmotic pressure of ideal solutions is given by

$$P = -\frac{RT}{V_1} \ln (1 - N_2),$$

so that, for low concentrations, after expansion of the logarithm,

$$P = \frac{RT}{V_1} N_2 = \frac{RT}{V_1} \cdot \frac{n_2}{n_1} = RTc_2$$

results.

b) Experimental Results of Osmotic Measurements

The van 't Hoff equation has been carefully tested experimentally from two aspects. One requirement is that the osmotic pressure of dilute solutions is proportional to the temperature. Data by Morse[21] on cane sugar solutions show that the relationship holds in very dilute solutions, so that the purely statistical character of the phenomenon is evident.

The second requirement of van 't Hoff's equation, that osmotic pressure is proportional to concentration, is also well satisfied by dilute cane sugar solutions.

This indicates that practically ideal dilute solutions are involved in these systems, so that it is possible to derive the molecular weight from osmotic pressure measurements just as from vapor density determinations in gases. The osmotic pressure is seldom determined directly on low molecular weight substances, because there are no readily prepared and easily manipulated semi-permeable membranes except for a few crystalline substances. The indirect method is generally chosen, i.e. by determination of lowering of vapor pressure, increase of boiling point or lowering of freezing point. The experimental technique and evaluation of the results are so well known that they need not be described here. They can be found in all text books of physical chemistry.

[21] J. H. Morse, *J. Am. Chem. Soc.*, **34**, 1 (1905).

In contrast, a little may be said regarding osmotic measurements in the realm of high molecular weight substances.[22] The Beckmann method of freezing point lowering and boiling point rise is applicable only to measurements of molecular weights up to 4000 or 5000, because of the minuteness of the effects. In favorable instances, and by observing special precautions, it may be possible to go a little higher, as Staudinger[23] has shown in the course of his numerous experiments on the structure of high polymeric substances. However, even these measurements do not extend into the true high polymeric or eucolloidal range but only to its lower limits.

Direct measurements of the lowering of vapor pressure by isothermal distillation or similar methods present not inconsiderable difficulties. Numerous experiments of Hess, his co-workers[24] and others[25] have shown that osmotic measurements by these methods are attended with great difficulties and must be carried out very carefully if they are to give trustworthy results.

In the high polymer domain there remains, therefore, only the direct method of using semi-permeable membranes, which has actually been developed successfully by Herzog and Spurlin and a number of observers in recent years.[26] In this way we may use either the *static elevation method*, in which equilibrium between osmotic and hydrostatic pressure serves as the criterion, or a dynamic method which was first designed by Van Campen[27] and later developed by C. G. Boissonnas, Obogi and Broda,[28] and K. H. Meyer. In the latter the osmotic pressure, which causes a streaming of the pure solvent through the semi-permeable membrane is compensated by a suitable counter-pressure in such a way that the motion of the liquid practically ceases.

The chief difficulty in both cases is always the suitable choice of the

[22] More detailed data will be found in another volume of this series. Cf. also M. Ulmann, *Die Molekülgrössenbestimmung hochpolymerer Naturstoffe*, Dresden 1936.

[23] See H. Staudinger, *Die hochmolekularen organischen Naturstoffe*, Berlin 1932. A review of recent literature e.g. by G. V. Schulz, *Z. physik. Chem.*, (A) **180**, 1 (1937).

[24] E.g. K. Hess and M. Ulmann, *Ber.*, **66**, 495 (1933); **67**, 2131 (1934).

[25] See especially the book of M. Ulmann and his following papers, *Z. physik. Chem.*, (A) **156**, 419 (1931); **164**, 318 (1933); (B) **68**, 134, 1217 (1934).

[26] Cf. R. O. Herzog and H. M. Spurlin, *Z. phys. Chem. Bodenstein Festband*, p. 239 (1931); A. Dobry, *J. Chem. Phys.*, **32**, 50 (1935); Ch. G. Boissonas and K. H. Meyer, *Helv. chim. Acta*, **20**, 783 (1937); G. V. Schulz, *Z. Phys. Chem.* (A)**180**, 1 (1937); O. Kratky and H. Mark, *Fortschr. Chem. Org. Naturst.*, **1**, 255 (1938).

[27] Van Campen, *Rec. Trav. chim.*, **50**, 915 (1931).

[28] Ch. G. Boissonnas, *Helv. chim. Acta*, **20**, 779 (1937); R. Obogi and E. Broda, *Kolloid-Z.*, **69**, 172 (1934).

semi-permeable membrane, the preparation and careful treatment of which is highly essential for the performance of osmotic measurements in the high molecular field. The systematic and extensive investigations of Manegold[29] have furnished important information on the general systematic production of such membranes. It is nearly always possible to select and prepare suitable membranes for aqueous solutions in the range of true high polymers. Difficulties arise on the one hand in dealing with smaller particles, because the membrane is then permeable to the solute and, on the other hand, in changing to non-aqueous solvents. For the first difficulty, O. Kratky[30] has recently developed a method in which the amount of the dissolved substance passing through can be determined analytically and the influence of this counter-effect deducted. By this method one can start with truly high polymeric substances and go downward to the limit below which cryoscopic or ebullioscopic measurements are effective. For aqueous solutions the experimental determination of molecular weight by osmotic methods is possible, therefore, over the whole range from the smallest to the largest structural units.

Conditions are rather less favorable in non-aqueous solutions, because suitable membranes are more difficult to obtain. It is necessary to employ special methods of preparation for every individual case, particularly those suggested in the numerous original papers of Adair, Boissonas, Broda, Büchner, Dobry, Fent, Herz, Obogi, Wo. Ostwald, Pauli, Schulz and Sörensen.[31]

The results of all these experiments will be discussed fully in another volume of this series and it will merely be stated here that at sufficient dilution van 't Hoff's law in its simple form as a limiting law is satisfied also by solutions of the high polymers.

The requirement that the osmotic pressure be proportional to the temperature has also been tested in the field of high polymers and found to be confirmed at sufficiently low concentrations. It must, of course, be pointed out that the range of applicability of the van 't Hoff law is considerably smaller in preparations consisting of filamentary molecules and that deviations soon appear in the sense that the osmotic pressure increases considerably more rapidly than linearly with concentration and that its dependence on temperature is of quite a different kind.

Since there is every reason to hope that we shall be able to derive from this behavior important information regarding the state of high polymeric

[29] See f.i. the review in *Kolloid-Z.*, **61**, 140 (1932).

[30] See the comprehensive paper by O. Kratky and H. Mark cited on p. 232.

[31] The literature is cited on page 232, and 234 et sequ.

substances in solution, this relationship has been repeatedly examined in recent times. It appears convenient to pass on to discuss it.

c) *Osmotic Behavior at Higher Concentrations*

The rise of the osmotic pressure with the amount of substance dissolved at higher concentration ranges has been the subject of many experiments. The osmotic behavior of moderately concentrated solutions has been examined experimentally, in proteins by Adair,[32] Pauli and Fent[33] and Sörensen,[34] in cellulose derivatives by Büchner,[35] Dobry,[36] Herz,[37] Duclaux,[38] Obogi and Broda[39] and in rubber by Caspari[40] and an excessive increase in osmotic pressure with concentration invariably found.

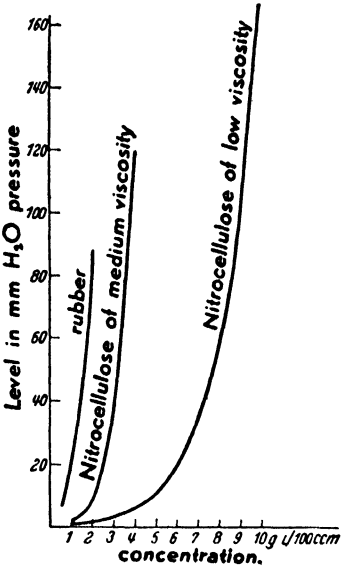


Fig. 77. Rise of osmotic pressure with concentration in a few high polymeric substances.

A series of data obtained in these investigations is recorded in Fig. 77 to give an idea of the experimental effect. In all cases a steeply ascending curve expresses the relation between osmotic pressure and concentration and the question arises, whether this relation can be evaluated to get additional information on the state of high polymers in solution. If we expand the osmotic pressure as a function of concentration into a series in powers of c_2, we get

$$P = Ac_2 + Bc_2^2 + Cc_2^3 + \cdots \qquad (52)$$

At extremely low concentrations, all terms containing higher powers of c_2 than

[32] G. S. Adair, *Proc. Roy. Soc. London*, (A) **108** 627 (1925); **109**, 292 (1925); **120**, 573 (1929); **126**, 16 (1929).

[33] Wo. Pauli and R. Fent, *Kolloid-Z.*, **67**, 288 (1934).

[34] S. P. L. Sörensen, *Z. physiol. Chem.*, **103**, 15 (1918); **106**, 1 (1919); *Kolloid-Z.*, **53**, 102, 170, 306 (1936).

[35] E. H. Büchner, *Trans. Faraday Soc.*, **29**, 32 (1933).

[36] A. Dobry, *J. chim. phys.*, **31**, 568 (1934); **32**, 50 (1935); *Bull. soc. chim.*, (5) **2**, 1882 (1935).

[37] W. Herz, *Cellulosechem.*, **16**, 56 (1935).

[38] J. Duclaux, *J. chim. phys.*, **28**, 537 (1931).

[39] R. Obogi and E. Broda, *Kolloid-Z.*, **69**, 172 (1934).

[40] W. A. Caspari, *J. Chem. Soc.*, **105**, 1239 (1914).

one will be small compared with the first term and we obtain, as a limiting law, the equation

$$P = Ac_2$$

The interpretation of the first coefficient, A, of the series in equation (52) is unambiguous; it is directly connected with the number of particles which move independently in the solution and, since the total weight of dissolved material is known, is also connected directly with the molecular weight, M_2, of the dispersed substance.

In sufficiently dilute solutions, it will always be possible to calculate the weight M_2 of the kinetically independent particles in the solution from

$$\lim_{c_2 \to 0} \frac{P}{c_2} = \frac{RT}{M_2}$$

This has been emphasized particularly by Wo. Ostwald.[41]

The question now arises, whether and how the second coefficient of the series (52) can be interpreted kinetically. As A already represents the pure gain in entropy for the ideal mixing, the higher coefficients, B, C, etc., will describe either additional entropy terms or the action of forces between solvent and solute particles and between the solute particles themselves.

Several attempts have been made to interpret the coefficient B. Wo. Ostwald, in his well-known investigations of high polymers, has shown that osmotic pressure may be expressed to a fair approximation by the equation

$$P = ac_2 + bc_2^n \tag{53}$$

in which the constant n generally has a value around 2. c_2 equals concentration by weight.

Ostwald has emphasized that, by applying this equation to osmotic measurements, it is possible to determine conclusively the weight M_2 of the particles of high polymeric substances by means of the limiting value

$$\lim_{c_2 \to 0} \frac{P}{c_2} = \frac{RT}{M_2}$$

In practice all osmotic measurements on hemi- and eu-colloidal high polymeric substances obtained by this means have given plausible values for the size of the particles free to move in the solution, which values are in good agreement with those obtained in other ways.

[41] Wo. Ostwald, *Kolloid-Z.*, **49**, 60 (1929); see also W. Haller, *Kolloid-Z.*, **56**, 257 (1931); *Z. physik. Chem.*, (A) **159**, 375 (1932). Comp. furthermore a series of articles by Wo. Ostwald; e.g. *Kolloid-Z.*, **36**, 99 (1925); **46**, 259 (1928); **51**, 273, 361 (1930); **67**, 211 (1934).

The relevant data arranged according to substance will be tabulated in detail in another volume of this series and discussed with respect to their agreement with other data and their importance to the structure of high molecular substances.

The second term of equation (53) led Ostwald back to the phenomenon of sol swelling in which he assumed that the swelling pressure corresponding to the interaction between solvent and solute should simply be added in the form of a swelling function, due to Freundlich, to the osmotic pressure given by the first term. This would interpret B completely as due to the forces between solvent and dissolved particles and would attribute the second term in (52) entirely to solvation.

Several authors, e.g. Adair,[42] Burk and Greenberg,[43] and Stamberger,[44] have adopted a similar view and have tried to explain the deviations from van 't Hoff's law in accordance with the van der Waals theory of real gases by introducing a co-volume b, caused by solvation. They have proposed to use, instead of van 't Hoff's law, an equation of the form

$$P = \frac{RT}{M_2} \cdot \frac{1}{V - b} = RT \left(\frac{c_2}{M_2} + b c_2^2 \right). \tag{54}$$

G. V. Schulz[45] in particular has developed this idea and has applied the Budde formula previously used by Sackur[46] by assuming a functional connection between the specific co-volumes, i.e. between the actual space-filling of the dissolved particles and the osmotic pressure.

The solvation equilibrium established by interaction between the solute and the solvent would be reached as soon as the solvation pressure defined in analogy to the swelling pressure, became equal to the osmotic pressure of the solution. The agreement with experimental measurements attained by G. V. Schulz on the basis of this assumption is very remarkable.

With the aid of the activity theory of binary mixtures of liquids, Kratky and Musil[47] have recently discussed the rise in osmotic pressure with concentration in the range apart from very dilute solutions and we shall shortly describe their results.

If, as before, (see p. 223) we wish to demonstrate that energy effects may operate in addition to simple entropy effects, we obtain, within the

[42] G. J. Adair, l.c. on page 234.
[43] N. E. Burk and D. M. Greenberg, *J. Biol. Chem.*, **87**, 237 (1930); **98**, 353 (1932).
[44] P. Stamberger, *J. Chem. Soc.*, (A) **1928**, 2318; *Kolloid-Z.*, **53**, 90 (1930).
[45] G. V. Schulz, *Z. physik. Chem.*, (A) **158**, 237; **159**, 347; **160**, 409 (1932).
[46] O. Sackur, *Z. physik. Chem.*, **70**, 477 (1910).
[47] O. Kratky and A. Musil, *Z. Elektrochem.*, **43**, 326 (1937) and **43**, 686 (1937).

meaning of the general activity theory of binary mixtures of liquids, the following equation for the osmotic pressure

$$PV_1 = \Delta H_1 - T\Delta S_1 \tag{55}$$

In the equation, H_1, V_1 and S_1 are molar values at constant pressure for heat content, for volume and for entropy. The letters bearing index 1 as usual relate to the solvent. The sign Δ indicates that the difference between the molar values for the solution and for the pure solvent is to be inserted in the equation.

In this sense we may read (55) in the following way. The work performed by the osmotic pressure if one mol of solvent is sucked through the semi-permeable wall into the solution, the latter being thereby diluted through the addition of one mol of the liquid, may be represented by two quantities: a) by the entropy difference between the original solution and the diluted solution multiplied by T, and b) by the decrease of the energy content at constant pressure.

We shall now employ the expression for the entropy used by Laar[48] in the thermodynamics of liquid mixtures and obtain

$$PV_1 = \underbrace{-RT \ln (1 - N_2)}_{1} + \underbrace{RT\Delta f(b_1)}_{2} + \underbrace{\Delta C_{v_1} T \ln T}_{3} + \underbrace{\Delta i_1}_{4} \underbrace{-\Delta H_1}_{5}$$

Entropy-of-mixing term — Additional-Entropy terms — Energy term

In addition to the terms explained above, N_2 represents the mol fraction of the solute, b_1 the co-volume of the solvent, C_{v_1} the heat capacity and i_1 an entropy constant for a given normal state, both relating to the solvent.

The entropy term denoted by 1 has already been discussed. It enters in alone if no interactions occur between the solvent and the solute; it has been previously termed (see p. 213) the ideal mixing entropy. The terms 2, 3 and 4 are additional entropy differences based on the fact that the volume, the heat capacity and the chemical constant of a molecule when surrounded by its own species assume values different from those it would assume if incorporated in solution in a medium of molecules of different kinds. Finally, 5 represents the energy term, which owes its existence to the difference in the play of forces between similar and dissimilar molecules.[49]

[48] J. J. van Laar, *Z. anorg. allgem. Chem.*, **145**, 39 (1925); *Z. physik. Chem.*, (A) **134**, 311 (1928); **137**, 421 (1928). See also R. Lorenz, *Das Gesetz der chemischen Massenwirkung*, Leipzig 1927, p. 67.

[49] The ideal expression for the mixing entropy is, of course, valid only if the two

Generally, therefore, these additional functions are connected with the departures from additivity shown by the volume V, the heat capacity C_v, and the chemical constant i and the enthalpy H on dilution of the solution. They find their tangible expression in volume contractions, heat effects and anomalous behavior of specific heats. Physically they should be attributed to an excess or deficiency in attraction between the molecules of solvent and solute over the cohesion of identical molecules. Hildebrand[50] has termed solutions in which additional entropy terms such as 2, 3 and 4 are missing, *regular* solutions (see p. 222). In them the excess and deficiency attractions may be related quantitatively to the heat of dilution, since in the insertion of molecules of one component between those of the other, a heat effect other than zero results because the energy necessary for the separation of identical molecules differs from that obtained in bringing together dissimilar particles.

In the following discussion we shall adopt the phrase *interaction term*, used by Kratky and Musil to express all the functions to be added to the pure mixing term and examine briefly the extent to which they describe the increase in osmotic pressure with concentration. For this purpose we first take out the factor RT from all functions, expand the logarithm, arrange according to powers of N_2 and obtain

$$PV_1 = RT[N_2 + \tfrac{1}{2}N_2^2 + \tfrac{1}{3}N_2^3] + RT\{k'N_2^2 + k''N_2^3\}. \qquad (56)$$

In this equation, the functions derived from the mixing term alone are included in a square bracket, those arising from the interaction terms by a double bracket; k' and k'' are characteristic constants.

Powers of N_2 are present within both brackets: in the former, the first power, from which we conclude that this is characteristic for the ideal mixing term. Actually, we know from van 't Hoff's law that when P and N_2 are proportional, the mixing entropy is alone in evidence and the interaction terms have no influence on the phenomenon. If, however, we wish

---

kinds of molecules mixed do not differ very greatly in size; so that, on exchange, a molecule A takes the place set free by a molecule B. If this is not so, the mixing component of the entropy will assume another form. See e.g. E. A. Guggenheim, *Proc. Roy. Soc. London*, (A) **135**, 181 (1932); **148**, 304 (1937); **169**, 134 (1938); furthermore E. A. Guggenheim, *J. Phys. Chem.*, **34**, 1751 (1930) and *Trans. Faraday Soc.*, **33**, 151 (1937).

[50] J. H. Hildebrand, *J. Am. Chem. Soc.*, **51**, 66 (1929); further E. A. Guggenheim, *Proc. Roy. Soc. London*, (A) **135**, 181 (1932); J. H. Hildebrand, *J. Am. Chem. Soc.*, **57**, 866 (1935); J. J. van Laar, *Z. physik. Chem.*, (A) **137**, 421 (1928); W. Heitler, *Ann. Physik*, (4) **80**, 630 (1928); E. A. Guggenheim, *Proc. Roy. Soc. London*, (A) **148**, 304 (1935); J. G. Kirkwood, *J. Chem. Phys.*, **3**, 300 (1935).

to pursue mathematically the effect of concentration on osmotic pressure, we must bear in mind that the coefficient of the quadratic term, for example, may depend partly on the mixing term of the entropy but partly also on the interaction terms, and can arise both from entropy and energy. A clear distinction is not possible here but comparison of the formula with experiment will allow of deductions regarding the coefficients of the different terms in N.

We, therefore, compound the two effects by combining the same powers of N_2 in (56) and arrive at

$$PV_1 = RT \cdot N_2 + RT(\tfrac{1}{2} + k')N_2^2 + RT(\tfrac{1}{3} + k'')N_2^3. \qquad (57)$$

It is clear from this equation that, in the coefficients of the quadratic term, for example, the part due to mixing is expressed by $\frac{1}{2}$ and the part due to the total of all the interaction terms by k'. Whether the influence of the ideal mixing entropy is still appreciable in the higher terms of the expression depends, as we see, on the magnitudes of the two factors k' and k''. We shall find later that k'' generally exhibits fairly high values in solutions of high molecular weight substances in common solvents, so that the $\frac{1}{3}$ can be neglected. This is not so, however, with k', where both effects are of about the same order of magnitude and must therefore be considered explicitly.

For testing this method of consideration, Kratky and Musil have employed the assumption advanced and proved by Boissonas[51] that the energy and additional entropy interaction terms of a long valence chain are made up of increments of the individual structural units in which the increments themselves have magnitudes independent of the length of the chain and depend only on the total concentration. This hypothesis relies on the circumstance that in homologous and polymeric homologous series we have frequently experienced good results from additive rules and the more so the longer are the chains involved. As a matter of fact K. H. Meyer and M. Dunkel[52] some years ago assumed very successfully that molecular cohesion in high polymeric substances is made up additively from given increments of individual groups of molecules, a subject discussed previously in this book, and Staudinger[53] has used the same method very successfully in the quantitative treatment of viscosity problems, a work which will be reported upon later (see page 287).

[51] Ch. G. Boissonnas, *C. R. Soc. phys. Geneve*, **53**, 40 (1936); see also J. N. Brönsted and P. Colmant, *Z. physik. Chem.*, (A) **168**, 38 (1934).

[52] K. H. Meyer and M. Dunkel, *Z. physik. Chem.*, (A) **138**, 42 (1928).

[53] H. Staudinger in his book *Die hochmolekularen organ. Verbindungen*, Berlin 1932.

Very long chain molecules in which the chemically divergent end groups are not of major importance and which, therefore, consist of practically identical members, should exhibit interaction with the solvent proportional to the degree of polymerization and therefore to the molecular weight. Thus the amount of interaction is the same per unit quantity.

For the mathematical treatment of the conditions, we may adapt equation (57) to the usual method of representing the experimental results and insert the concentration by weight c_2; we then obtain

$$\frac{P}{c_2} = \underbrace{\frac{RT}{M_2}}_{1} + \underbrace{Bc_2 + Cc_2^2}_{2}, \tag{58}$$

This is nothing else but equation (53). The comparison shows that the second coefficient B always contains a small share of ideal mixing entropy, expressed by the term $\frac{1}{2}$; whether or not it can be neglected in comparison with k', depends upon the magnitude of that constant.

In considering such systems, one may distinguish the four following types:

a) *ideal* solutions, in which the effect of concentration upon the osmotic pressure is given by the term $\frac{1}{2}$ only, k' being zero;
b) *regular* solutions, in which the effect of concentration upon the osmotic pressure is given by $k' + \frac{1}{2}$, k' being due to the action of forces only;
c) *athermal* solutions in which the influence of concentration upon osmotic pressure is given by $\frac{1}{2} + k'$, k' being due only to additional entropy effects;
d) irregular solutions, k' being due to solvation and entropy effects.

The existing experimental evidence points to the likelihood that all four possibilities are realized in low molecular weight systems but that only c) and d) are effective if long chain molecules are dissolved in solvents which consist of small particles, such as acetone, hexane, toluene, etc.

Measurements of Büchner and Steutel[54] and of G. V. Schulz[55] prove that B is independent of the molecular weight of the dissolved substance. Figure 78 shows the P/c_2 values for a series of nitrocelluloses in acetone plotted against c_2. Straight lines are obtained up to a concentration of about 4% and the angle of inclination with the horizontal axis is independent of molecular weight. In the experiments depicted by Figure 78 the molecular weight varied from 20,000 to 100,000.

[54] E. H. Büchner and H. E. Steutel, *Proc. Acad. Sci. Amsterdam*, **36**, 2 (1933).
[55] G. V. Schulz, *Z. physik. Chem.*, (A) **176**, 317 (1936).

Similar observations have been made on rubber solutions by Caspari.[56] Recently the four systems,

nitrocellulose-cyclohexanone[57]
rubber-toluene[58]
guttapercha-toluene[59]
cellulose triacetate-tetrachloroethane[60]

have been investigated by K. H. Meyer and his collaborators. In all cases the molecular weight was determined from the limiting value at low concentrations; it was 70,000, 270,000, 30,000 and 42,000 respectively, where direct proportionality of the osmotic pressure was maintained. It turned out again that B does not depend upon M_2.

In order to find out to what extent B (or k') is influenced by energy or entropy terms, the free energy of solution must, itself, be measured. In the above-mentioned systems this was done by measuring the osmotic pressure at different temperatures.

Accordingly, we shall pass next to a description of the influence of temperature upon osmotic pressure.

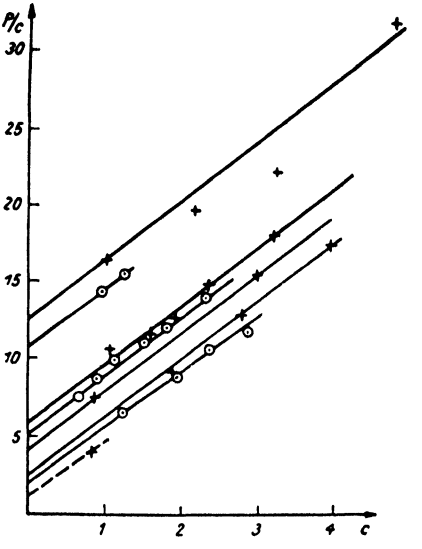


Fig. 78. P/c plotted against c for a few nitrocelluloses of different molecular weights.

d) Effect of Temperature on Osmotic Pressure

The energy interaction between solvent and solution is expressed by the term $\Delta\bar{H}_1$, i.e. the amount of heat absorbed or evolved when one mol of solvent is added to a large quantity of solution; it is the smaller the more dilute the solution.

To obtain this value, one has to measure the temperature dependence of the partial molar free energy of solution, which is equal to the product $P_{os}\bar{V}_1$. It is conceivable that both P_{os} and $\bar{V}_1$ are magnitudes dependent on

[56] W. A. Caspari, *J. Chem. Soc.*, **105**, 1239 (1914).
[57] C. G. Boissonnas and K. H. Meyer, *Helv. chim. Acta*, **20**, 783 (1937).
[58] K. H. Meyer, E. Wolff and C. H. Boissonnas, *Helv. chim. Acta*, **23**, 430 (1940).
[59] E. Wolff, *Helv. chim. Acta*, **23**, 439 (1940).
[60] O. Hagger and A. J. A. v. d. Wyk, *Helv. chim. Acta*, **23**, 484 (1940).

temperature and, therefore, it is necessary to determine the change in both factors and not to confine the measurements merely to the effect of temperature on osmotic pressure.[61]

From a knowledge of the free energy and its temperature coefficient it is possible to establish the entropy gain during mixing:

$$\Delta\bar{F}_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1$$
$$\Delta\bar{F}_1 = \bar{F}_1 - F_1^0 = P_{os}\bar{V}_1$$
$$(P_{os} = \text{osmotic pressure})$$
$$\Delta\bar{H}_1 = \bar{H}_1 - H_1^0$$
$$\Delta\bar{S}_1 = \bar{S}_1 - S_1^0$$

We shall turn first to the calculation of the partial molar entropy of dilution. From

$$\left(\frac{\partial\bar{F}_1}{\partial T}\right)_P = -\bar{S}_1 \text{ where } \bar{F}_1 = \left(\frac{\partial F}{\partial n_1}\right)_{n_2} \tag{59}$$

we obtain the equation

$$\left(\frac{\partial\bar{F}_1 - F_1^0}{\partial T}\right)_{Pn_2\cdots} = -(\bar{S}_1 - S_1^0) \tag{60}$$

which is the basis for calculation of the entropy.

Further

$$\left(\frac{\partial\bar{F}_1}{\partial P}\right)_{T,n\cdots} = \bar{V}_1. \tag{61}$$

At osmotic equilibrium

$$\bar{F}_{1(P)} = F^0_{1(P^0)}, \tag{62}$$

where P denotes the pressure on the solution and P^0 the pressure on the solvent (component 1). From (61) it follows that:

$$\bar{F}_{1(P)} - \bar{F}_{1(P^0)} = \int_{P^0}^{P} \bar{V}_1\, dP. \tag{63}$$

By replacing $F_{1(P)}$ in (63) by $F^0_{1(P^0)}$, we obtain

$$F^0_{1(P^0)} - \bar{F}_{1(P^0)} = -(\bar{F}_1 - F_1^0)_{P^0} = \int_{P^0}^{P} \bar{V}_1\, dP. \tag{64}$$

We differentiate (64) with respect to T, to obtain the entropy for dilution by equation (60).

$$\left[\frac{(\partial\bar{F}_1 - F_1^0)}{\partial T}\right]_{P^0} = -\left[\frac{\partial}{\partial T}\int_{P^0}^{P} \bar{V}_1\, dP\right]_{P^0} = -(\bar{S}_1 - S_1^0)_{P_0}. \tag{65}$$

[61] Ch. G. Boissonnas and Kurt H. Meyer, *Z. physik. Chem.*, (B) **40**, 108 (1938).

In practice it is sufficient to measure the osmotic pressure at two temperatures, represented by the following equation:

$$\frac{(\bar{F}_1 - F_1^0)_T - (\bar{F}_1 - F_1^0)_{T'}}{T - T'} = -\frac{\left[\int_{P_0}^{P} \bar{V}_1\, dP\right]_T - \left[\int_{P^0}^{P} \bar{V}_1\, dP\right]_T}{T - T'} = -(\bar{S}_1 - S_1^0) \quad (66)$$

We thus obtain the entropy of dilution at a temperature lying between T and T'.

The heat of dilution $\bar{H}_1 - H_1^0$ may be obtained in a similar way. From the equation:

$$\left[\frac{\partial(F/T)}{\partial(1/T)}\right]_P = H \quad (67)$$

we obtain instead of (65):

$$\left[\frac{\partial\left(\frac{\bar{F}_1 - F_1^0}{T}\right)}{\partial(1/T)}\right]_{P^0} = \left[\frac{\partial\left(\frac{\int_{P^0}^{P} \bar{V}_1\, dP}{T}\right)}{\partial(1/T)}\right]_{P^0} = \bar{H}_1 - H_1^0 \quad (68)$$

or, if we are content with measurements at two different temperatures:

$$\bar{H}_1 - H_1^0 = \frac{\frac{\left[\int_{P^0}^{P} \bar{V}_1\, dP\right]_T}{T} - \frac{\left[\int_{P^0}^{P} \bar{V}_1\, dP\right]_{T'}}{T}}{1/T - 1/T'}. \quad (69)$$

For the calculation we must know the effect of pressure, temperature and concentration on the partial molar volume of component 1. We have therefore to investigate these three factors.

The effect of pressure on $\bar{V}_1$ is small and can always be neglected: the effect of concentration should be determined experimentally; in many cases however the volume changes during mixing are so small as to be negligible; then $\bar{V}_1 = V_1^0$.

The effect of temperature on the other hand is not negligible.

On the basis of the foregoing discussion, we may write equation (60) in the following form:

$$\bar{S}_1 - S_1^0 \approx \frac{[(\bar{V}_1(P - P^0)]_T - [\bar{V}_1(P - P_0)]_{T'}}{T - T'} \quad (70)$$

and equation (69) in the form:

$$\bar{H}_1 - H_1^0 \approx \frac{\frac{[\bar{V}_1(P - P^0)]_T}{T} - \frac{[\bar{V}_1(P - P^0)]_{T'}}{T'}}{1/T - 1/T'}. \quad (71)$$

For the case in which $\bar{V}_1 = V_1^0$, we may put:

$$\bar{S}_1 - S_1^0 \approx \frac{[\bar{V}_1^0(P - P^0)_T - [\bar{V}_1^0(P - P^0)]_{T'}}{T - T'} \tag{72}$$

$$H_1 - H_1^0 \approx \frac{\dfrac{[V_1^0(P - P^0)]_T}{T} - \dfrac{[V_1^0(P - P^0)]_{T'}}{T}}{1/T - 1/T'}. \tag{73}$$

Using the above derivations, particularly the equations (72) and (73), K. H. Meyer and his collaborators[62] have determined experimentally the entropy of mixing for different systems containing long chain molecules. The result was that in all these cases the entropy gain during mixing exceeded quite considerably the ideal value of the mixing entropy, $-R\ln N_2$. This holds, regardless of whether the solution is endothermic or exothermic and is, apparently, an effect which is characteristic for the presence of long chain molecules, which exhibit a certain amount of internal mobility.

When discussing the vapor pressure of mixtures, we found the same situation and it is reasonable to adopt the same explanation for it now.

Taking a kinetic point of view, it is obvious that long, flexible, chain molecules possess a considerable degree of internal Brownian movement, with the consequence that such molecules will perform sinuous or worm-like motions in solution. Haller[63] has discussed this type of motion and has shown that it results in certain additional collisions between the molecules, and that these extra collisions produce an additional term in the osmotic pressure; he gets

$$P = \frac{RT}{M_2} \cdot c_2 + RT \cdot s \cdot c_2^2. \tag{74}$$

In this equation the constant B of (58) is interpreted fully by the entropy effect $RT \cdot s$, where s is a quantity describing the internal Brownian movement of the chains.

Kuhn[64] later worked out a more detailed theory of the internal (or micro-) Brownian movement and combined it with the intra-molecular statistics. He found that the entropy gain if one extended chain with n links curls up in its most probable condition is given by

$$\Delta S = \tfrac{1}{2}k\left(\frac{L - L_0}{L_0}\right)^2 \tag{75}$$

L_0 = length of the chain in the contracted state

L = length of the chain in the extended state.

---

[62] Cf. K. H. Meyer, *Z. physik. Chem.*, (B) **44**, 383 (1939).

[63] W. Haller, *Kolloid-Z.*, **56**, 257 (1931).

[64] W. Kuhn, *Kolloid-Z.*, **76**, 258 (1936).

If we assume that, in the pure, crystallized (long chain) substance, all molecules are straight, whereas they have the opportunity to curl up to one-fourth of their maximum length if dissolved, we get an additional entropy gain per molecule of about

$$\Delta S = 30k.$$

This corresponds to the equation (17) on page 74 and shows that rather considerable entropy gains are to be expected if long chain molecules, after being frozen in a lattice-like arrangement, are liberated and acquire their full internal mobility.

K. H. Meyer[62] has recently given a simple, statistical picture of the mixing of large and small molecules, which shows that small molecules do not interchange place statistically with macro-molecules, but only with certain fractions of the latter. Considering the system rubber-toluene, he was able to show that a chain of about six isoprene residues, with a molecular weight of about 400, behaves like a free particle. A rubber chain containing 1200 isoprene residues would, therefore, be characterized by an n-value of 200 (compare the discussion on page 227).

Summarizing, we may say: Vapor pressure and osmotic measurements both point to the probability that long chain molecules, under certain conditions, have a high internal mobility in solution and certainly do not behave as stiff rods.

c) A Few General Data on Solubility with Particular Regard to Chain Molecules

The question of what solvent to employ and to what extent a given substance is soluble in it is one of the greatest importance to the chemist who has to experiment with the particular substance. The problem is as old as the science of chemistry itself and was answered by the alchemists before the scientific era of chemistry in the following terms: "Similia similibus solvuntur."

Physical chemistry allows us, in conjunction with our present knowledge of molecular structure, to give a more precise expression to this old empirical law and to make quantitative assertions, at least in a few favorable cases, regarding solubility and its dependence on the molecular structure of the participating systems.

Since conditions among the true high polymeric substances will receive detailed treatment in another volume of this series, we shall confine ourselves here to a discussion of the solubility of low molecular weight substances and concentrate on the behavior of chain molecules with the idea of applying the results later to the high polymers.

We shall first examine the way in which a single molecule of the solute can pass from the association of the condensed phase (liquid or crystal lattice) to the state of a dilute solution.

a) The molecule must be set free from the association in the condensed phase; for this the heat of vaporization (or in crystals the heat of sublimation) W_1 is necessary.

b) A place must be made available for receiving the dissolved molecule inside the liquid. For this an expenditure of potential energy is necessary against the forces of cohesion, the quantity of which we shall denote by W_2. W_1 and W_2 are two amounts of energy expended and have, therefore, the same sign.

c) We now place the liberated molecule in the space made available for it. Attraction will occur between it and the surrounding solvent particles, corresponding to an amount of energy W_3, but this is energy gained, and it will have the opposite sign to W_1 and W_2.

During the whole course of the solution process we have, therefore, to reckon with an amount of energy

$$W = W_1 + W_2 - W_3,$$

which must either be absorbed or liberated according as $W_1 + W_2$ is greater or less than W_3.

To a rough approximation, substances may be divided into two groups: the apolar and the polar. Substances which belong to one group are generally soluble in one another and frequently completely miscible, but not the substances of one group in those of the other.

Let us take as an example the solution of toluene in benzene. Both are typical apolar substances; the molar energy of interaction between toluene molecules among themselves is of the same order of magnitude as that between benzene molecules among themselves and between benzene molecules and toluene molecules. W will therefore be unable to assume any very high value, whether positive or negative. Because the forces within and between the two components have the same character as dispersion forces, they are removed essentially from the whole process. It is, so-to-speak, immaterial to the toluene molecule whether it is surrounded by other toluene molecules or by benzene molecules; the diffusion tendency (entropy gain) alone enforces the miscibility (solubility) of the two substances.

A second example is furnished by glycol and water. The conditions are

entirely similar; the internal cohesion of the liquid glycol, that of the water, and the attraction between glycol and water molecules, go back to the dipole effect of the OH-groups. Here also the total force effects will adjust themselves to a potential energy not differing greatly from zero; and again the miscibility will be determined by the diffusion tendency of the one substance into the other.

Let us consider also an opposite case to illustrate the conditions; we shall try to dissolve toluene in water. W_1, referring to toluene again, is no greater than before but W_2, referring to water, is large and W_3 is considerably smaller. It is easy to liberate one toluene molecule from the liquid phase, because the heat of evaporation, W_1, is small. But it is difficult to make a hole inside the liquid water for the toluene molecule, because the forces between the water molecules are much larger; W_2 is large. The interaction between one water molecule and one toluene molecule is small, hence W_3 is equally small and W will assume a large positive value. This value is so large that no solution can occur, even though the entropy gain would favor it.

This discussion may be regarded as a certain qualitative foundation for the statement: "Similia similibus solvuntur."

Quantitative relations concerning solubility cannot be derived by the aid of such a rough method of consideration as the above. Since we have imagined the case of a single molecule, the change in the vapor pressure over the solution, for example, compared with the vapor pressure of the pure solute has not been taken into account, yet this particular difference is frequently decisive for the quantitative relationships. Accordingly, we must go back to the exact, but less demonstrable, methods of thermodynamics.

The solubility of any substance Two in any solvent One is characterized by the saturation concentration (expressed in mol fraction) N_2^s. This is reached if the pure substance Two is in equilibrium with the (saturated) solution. The partial molar free energy of substance Two must then be identical in both phases, or, expressed differently: In the reversible transference of one mol of Two from the pure phase into the saturated solution, the partial molar free energy of solution is exactly equal to zero: $\Delta\bar{F}_2 = 0$ and since generally $F = H - TS$, it follows that

$$\Delta\bar{H}_2 - T\Delta\bar{S}_2 = 0.$$

If we confine ourselves to low molecular weight substances, experience teaches that their solutions often behave approximately as "regular solutions" in Hildebrand's meaning, i.e.

$$\Delta\bar{S}_2 = -R \ln N_2$$

and consequently, because

$$N_2 = N_2^s:$$

$$\Delta\bar{H}_2 \approx -RT \ln N_2^s.$$

The equation states that the solubility in this case is determined quantitatively by the partial molar heat of solution.

Let us now consider a crystalline substance, e.g. naphthalene, which will dissolve in benzene. We can then resolve the partial molar heat of solution $\Delta\bar{H}_2$ of the naphthalene into the heat of fusion plus the heat of solution of the fused naphthalene on dissolving in the saturated solution. Experience shows that, during the mixing of two apolar liquids, the heat of solution is generally very small, at any rate in comparison with the heats of fusion of these substances. The numerical value of $\Delta\bar{H}_2$ is, therefore, determined practically entirely by the heat of fusion since the additional heat of dilution may be ignored in a first approximation.

In such simple cases the solubility is, therefore, a function of the heat of fusion ΔH_2^f only so that

$$-\Delta H_2^f = RT \ln N_2^s. \tag{75}$$

Since heat is always absorbed on fusion ($\Delta H_2^f > 0$), a greater heat of fusion stipulates a much lower solubility:

$$N_2^s \approx e^{-\frac{\Delta H_2^f}{RT}}.$$

If we now turn to apolar liquids, it is evident from the above that, owing to the smallness of $\Delta\bar{H}_2$, the solubility is generally very high. If, as is often the case, the heat of dilution is zero, or a small but negative value, equation (75) could never be complied with, for, by definition, $N_2^s < 1$ and therefore $\ln N_2^s$ must be negative. In this case equilibrium can never exist between a pure phase and even a concentrated solution; the two substances are miscible in all proportions.

Conditions are often more complicated in systems of two polar liquid substances. The heats of dilution are then frequently not negligibly small. Partial miscibility is found in these systems, e.g. ether/water or nicotine/water.

Finally, if the substance to be dissolved is crystalline at the experimental temperature, experience shows that the heats of fusion of polar compounds are usually rather high. In this case the heat of fusion determines the solubility. Accordingly, the differing solubility of galactose and glucose in water or of silite and inosite in the same solvent must be due to the

different heats of fusion of the two isomers, which allows of interesting deductions regarding the structure of the two types of crystals and ultimately of the constitution of these substances.

The above ideas have been considerably improved upon by K. H. Meyer and van der Wyk[65] using chain molecules; they have used them for making quantitative predictions on the solubility of such substances, which are in remarkable agreement with experience.

The solution of a high paraffin in a lower member of the same series was first considered. In this case the heat of dilution, according to experience, is very small; this is understandable because any given molecule of the paraffin undergoing solution is surrounded by CH_2 groups regardless of whether it is in the state of a pure substance or in that of dilute solution. If the solvent (say C_6H_{14}) is mixed with the substance to be dissolved (say $C_{20}H_{42}$), if the latter is already molten, there is practically no thermal effect attending the mixing. The total magnitude of ΔH is, therefore, to be attributed in this case to the heat of fusion of the long chain paraffin. King and Garner[66] have proved empirically that the heat of fusion Q of normal paraffins increases proportionally to the number Z of the links and that for each CH_2 group, this heat gets an increment q, amounting to about 610 cal. per mol. We may therefore state

$$-\Delta\bar{H} = Q = Z \cdot q.$$

According to experience, the melting point increases with increasing chain length, following the empirical relation

$$\frac{1}{T_f} = a + \frac{b}{Z},$$

in which the constants a and b have the following values in normal paraffins

$$a = 2.395 \times 10^{-3}$$

$$b = 17.1 \times 10^{-3}.$$

Table 78 shows how well this relation represents the melting points in the region from C_{12} upwards. By applying the Gibbs-Helmholtz equation to the solution process, we obtain

$$\frac{\partial \ln N_2}{\partial \frac{1}{T}} = -\frac{\Delta\bar{H}}{R}$$

[65] K. H. Meyer and A. J. A. van der Wyk, *Helv. chim. Acta*, **20**, 1321 (1937).
[66] A. M. King and W. E. Garner, *J. Chem. Soc.*, **1936**, 1372.

or, by integrating between two temperatures lying close together,

$$\ln N_2'/N_2'' = \frac{Z \cdot q}{R}\left(\frac{1}{T'} - \frac{1}{T''}\right).$$

Taking the experimental temperature T as the lower limit of the integration and the melting temperature T_f as the upper limit, we obtain

$$-\ln N_2 = \frac{Z \cdot q}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right).$$

If the expression $(a + b/Z)$ is inserted for $1/T_f$, we obtain

$$-\ln N_2 = \frac{Z \cdot q}{R}\left(a + \frac{b}{Z} - \frac{1}{T}\right)$$

Now, taking the antilogarithm,

$$N_2 = Ae^{-BZ}$$

$$\text{with} \begin{cases} A = e^{\frac{bq}{R}} & \text{and} \\ B = -\frac{q}{R}\left(a - \frac{1}{T}\right). \end{cases}$$

TABLE 78

MELTING POINTS OF NORMAL PARAFFINS

C_nH_{2n+2} Melting point (Abs.)			C_nH_{2n+2} Melting point (Abs.)		
n	$T_{obs.}$	$T_{calc.}$	n	$T_{obs.}$	$T_{calc.}$
12	262°	262.5°	27	332°	330°
13	267°	269.5°	30	339°	337°
15	283°	283°	31	341°	340°
19	305°	304°	32	342°	342°
20	310°	308°	35	348°	347°
24	324°	322°	60	374°	374°

Table 79 gives a comparison with experimental data; it records the measured and calculated solubilities of two higher hydrocarbons in decalin (mol. wt. = 138). The agreement is quite remarkable and supports the assumptions on which the theory is based; w stands for the saturation concentration in weight per cent. It is evident from equation (75) how quickly the solubility of chain substances, on the basis of this theory, must decrease with increasing chain length, an effect which is entirely confirmed by experience.

We see in the present case that the experimentally observed increase in heat of fusion with chain length is alone sufficient to explain the rapid decline in solubility to a first approximation.

It may be pointed out, however, that, with increasing chain length, an additional entropy effect may enter in. As already mentioned (cf. page 71), there is a considerable gain in entropy when long chains are liberated from a crystal lattice, where their internal motion was highly limited, to enter the liquid state where they can exhibit free internal mobility. This entropy gain would lower the melting point and increase the solubility of long chain compounds, and it may be that the higher values of $w_{obs.}$ compared with $w_{calc.}$ in Table 79 are connected with this effect.

TABLE 79

t(°C)	$N_{2calc.}$	$w_{calc.}$	$w_{obs.}$
	$C_{34}H_{70}$		
25	8.49×10^{-3}	2.88%	—
35.5	2.79×10^{-2}	8.8%	7.14%
40	4.56×10^{-2}	14.15%	14.9%
46	8.69×10^{-2}	24.7%	26%
	$C_{60}H_{122}$		
25	4.05×10^{-6}	0.0025%	>0.01%
40	7.66×10^{-5}	0.05%	0.04%
64.5	1.03×10^{-4}	3.3%	4.09%
68.5	1.26×10^{-2}	7.3%	8.19%
75	2.84×10^{-2}	15.2%	23.4%

The opposite influence has been observed recently. Baker and Smyth[67] have pointed out that a relatively high mobility—rotational or vibrational—in the crystalline phase of a substance reduces the entropy gain during the melting or dissolving processes and, hence, raises the melting point and lowers the solubility of the substance. In the cases of tetra-, penta- and hexa- substituted benzenes, this influence could be traced very clearly and most interesting results were obtained regarding the interactions of the different substituents.[68]

[67] W.O.Baker and C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 1229 (1938); **61**, 1695, 2063, 2798 (1939); *J. Chem. Phys.*, **7**, 574 (1939).

[68] C. P. Smyth and G. L. Lewis, *J. Am. Chem. Soc.*, **62**, 721, 949 (1940).

f) The Distribution of Chain Molecules in the Dissolved State

K. H. Meyer and van der Wyk[69] have attempted to explain the formation of aggregates in aqueous solutions of soaps, higher fatty acids and the like, by a theory bearing a certain resemblance to the above method of consideration which was applied successfully to the solubility of chain molecules. They select for the purpose the equilibrium existing between isolated molecules of number n_1 and between associates of two particles of the number n_2 and so on and apply the law of mass action. Since the addition of a further particle to a group having v particles involves no different process than the addition to a group containing $(v + 1)$ particles, it may be assumed that the decrease in free energy is independent of v, so that the following must hold

$$\cdots \frac{n_{v+2}}{n_1 \cdot n_{v+1}} = \frac{n_{v+1}}{n_1 \cdot n_v} = \frac{n_v}{n_1 \cdot n_{v-1}} = \cdots \frac{n_3}{n_1 \cdot n_2} = \frac{n_2}{n_1^2} = K. \tag{76}$$

Besides isolated molecules, there are in equilibrium, simultaneously, aggregates of $2, 3 \ldots, (v - 1), v, (v + 1)$ and so on molecules.

From (75) it follows directly

$$\begin{aligned} n_2 &= n_1^2 \cdot K \\ n_3 &= n_1^3 \cdot K^2 \\ n_v &= n_1^v \cdot K^{v-1} \end{aligned} \tag{77}$$

If we consider one liter of such a solution, the total molar concentration in relation to the molecular weight of the isolated molecule may be represented by

$$S_m = \sum_{v=1}^{v=\infty} v \cdot n_v = \frac{n_1}{(1 - n_1 K)^2} \text{ (mol per liter).}$$

At a suggested concentration S_m and association constant K, it is, therefore, possible to calculate, by the aid of this equation, the concentration of the individual molecules and, therefore, using the previous equations to find the concentrations of the particles of different size. Figs. 79 and 80 are distribution curves for an association equilibrium of this type assuming different values for K and a constant concentration $S_m = 0.5$. For low values of K ($K = 0.1$), nearly all particles are dissolved monomolecularly and only very few are in aggregates of two or three;

[69] K. H. Meyer and A. J. A. van der Wyk, *Helv. chim. Acta*, **20**, 1321 (1937).

high K values (K = 10000), on the other hand, show a fairly flat distribution curve which tells us that in this type of solution, having a strong tendency toward association—for K is a measure of this—micellae of several hundreds of single molecules are present side by side with small

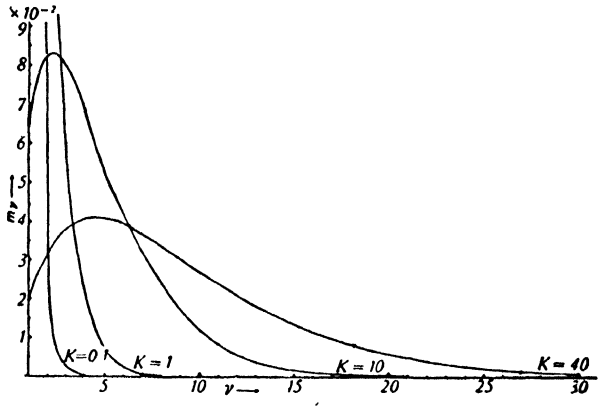


Fig. 79. Mass fractions m_ν for different degrees of association ν at a total concentration of 0.5 mol per liter (K from 0.1 to 40).

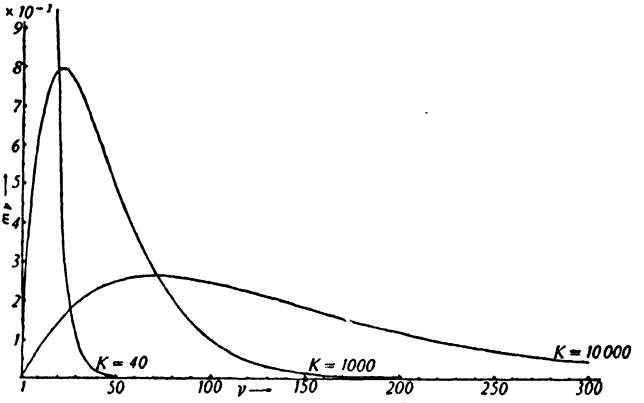


Fig. 80. Mass fractions m_ν for different degrees of association at a total concentration of 0.5 mol per liter (K from 40 to 10000).

particles even in dilute solution. For average K values there are more or less sharp peaks which show that a certain proportion of the solute is in the form of micellae of definite size, simulating to some extent conditions of homogeneity in such a solution.

The apparent degree of association Z of such solutions, as is evident, for example, from cryoscopic measurements, is given by

$$Z(Z - 1) = K \cdot S_m \tag{78}$$

The well known experiments of McBain and his co-workers[70] on the micellar nature of solutions of higher fatty acids can be interpreted by the aid of this theory.

Another method of treatment has been employed by Hartley[71] who assumed that only micellae of a definite size v are present together with isolated molecules, and took no account of aggregates lying between the two. If we accept this, we arrive at the result that the formation of the micellae would depend very strongly upon concentration, for the law of mass action would in this case take the form

$$\frac{n_v}{n_1^v} = K \tag{79}$$

Micellae development would then be very sensitive toward n_1 and would be determined by something like a critical concentration.

g) Theories Regarding Interaction between Solvent and Solute

In conjunction with the preceding sections, in which experimental evidence on the effect of concentration and temperature upon vapor and osmotic pressure has been described, it seems fitting to discuss the ideas which have been evolved as to the molecular mechanism of interaction between dissolved chain-like particles and solvent. Although we are at present still far distant from the stage of quantitative and detailed data, a few fundamental principles are already making their appearance.

It seems legitimate to consider two separate possibilities in the interaction between solvent and solute.

a) Certain portions of the solvent are attached by intermolecular forces to definite places on the dissolved particles where they execute slow vibrations and set up an equilibrium with the free solvent; this equilibrium may be compared with either a vapor pressure or an adsorption equilibrium. The forces are localized at quite definite points of the dissolved macromolecule, which may, accordingly, be termed points of adhesion. The magnitude of the forces may vary from 1000 to 10,000 cal. per mol of adsorbed substance, according to the groups responsible for them. The cause of these forces may lie in permanent dipoles possessed by the dis-

[70] E.g. J. W. H. McBain and Betz, *J. Am. Chem. Soc.*, **57**, 1909 (1935).

[71] G. S. Hartley, *Aqueous Solutions of Paraffin Chain Salts*, Paris 1936, p. 23ff.

solved particles, which either interact with the dipoles of the solvent or attract easily polarizable liquid molecules after inducing a moment in them.

There is, of course, the further possibility that strongly polar solvent molecules seek out easily polarizable points on the dissolved particles and remain fixed there because of strong interaction. Finally, the dispersion effect may be regarded as still a third reason for this attraction.

In the case of large, compact particles, these force effects usually lead to the formation of monomolecular adsorption layers but they are also able to form, in certain circumstances, adsorption films of several layers. In these films the binding strength of the individual solvent particle declines continuously from the surface of the adsorbent outwards, so that, in these cases, a variable adsorption or solvation potential has to be taken into account.

If we attempt to express the number of solvent molecules directly bound to the dissolved particles by van der Waals forces, it is best to employ the formula for the saturation range of an adsorption isotherm. The bound molecules are now present in large excess and the temperature is, in general, sufficiently low for saturation to exist.

If n/V dispersed particles are present in the unit volume of the solution whose volume is V, the number N_1 of the solvent molecules bound by them will be given by an expression of the form

$$N_1 = Z \cdot \varphi \cdot e^{\frac{\epsilon}{RT}} \cdot \frac{n}{V}. \tag{80}$$

In this, φ stands for the phase volume available to the adsorbed molecules, Z for the number of points of adhesion of each separate dissolved particle and ϵ for the energy of adsorption in cal. per mol of solvent. All these values are naturally to be regarded as average values, since, as mentioned above, the points of adhesion differ in nature and in the exact number possessed by each dissolved particle.

b) Very often dispersed colloidal particles have a hollow or sponge-like structure. The diffusion pressure of the molecules of the liquid causes them to penetrate, in course of time, all the interstices between the dissolved particles, although they are not fixed there by special forces. On purely mechanical grounds, the solvent molecules may be retained in the interstices for a long time.

Mathematically, this part can be expressed only incompletely; for it is clear that it depends to a high degree on the abundance of cavities or on the spongy texture of the dissolved particles. The number N_2 of the solvent molecules bound in this way is always, however, proportional

to the concentration n/V of the dissolved particles. We may therefore write

$$N_2 = a\frac{n}{V}, \tag{81}$$

where α is a function of the size and form of the dissolved particles; α will be small for small or compact particles but large for large and ragged ones.

The two cases discussed above occur at infinite dilution, that is, by considering only the interaction of a single isolated particle with the solvent. But it is necessary to recognize that, even in quite dilute solutions involving laminar or chain particles, some, at least of these bodies will come together. To some extent, therefore, it will happen in such solutions that the solvent particles will orient themselves between the surfaces of slightly separated solute particles and suffer distortion of their own structure. The resulting immobilization of solvent will be more extensive the more polar are the solvent molecules and the greater the number of orienting groups carried by the suspended particles. This type of interaction also depends greatly on temperature; it is adversely affected by rising temperature on two counts. First, the rate of diffusion of the dissolved particles increases, so that the duration of the positions favorable to stratification will be shortened, and second, the development of an oriented layer will be hindered by the kinetic motion of the solvent molecules.

Mathematically the number of the molecules N_3 of solvent immobilized per cm^3 in this way may be expressed by

$$N_3 = \beta\left(\frac{n}{V}\right)^2, \tag{82}$$

where β splits up into two parts; one corresponds to a frequency-of-collision factor and embraces, therefore, the effective cross-section and the average velocity of the dissolved particles; the second corresponds to a numerical factor which indicates how many molecules of liquid can be fixed by two particles favorably situated and opposite each other. Naturally, it can only be represented in broad outline since it depends, as previously mentioned, on the polar properties of the solvent and of the dissolved particles and also to a great extent on the shape and the internal mobility of the latter. In order of magnitude, however, the experimental material seems to indicate that, under suitable conditions, it should be possible to bind in this way a quantity of liquid whose volume may constitute up to 20–50 times the dry volume of the solute particles or even more.

If we combine the three effects discussed above, we reach the following

result: solvent can be fixed at the surface of the particles by forces, it can penetrate by diffusion into the interstices of the particles and there be immobilized and join in their kinetic motion and it can be bound between two particles by *layer orientation.*

If we denote the total volume of solution by V, the total number of liquid molecules by N and the volume of any one of these by v_0, and take n as the total number of dissolved particles and V the dry volume of each of these, V may be expressed by

$$V = N \cdot v_0 + n \cdot v.$$

Whereas in normal crystalloidal solutions, the two terms of the sum in this equation relate to spatially distinct regions of volume, it is not so in the present case. Rather, a certain number N_g of the N molecules of liquid present are more closely bound to the dissolved particles and therefore are actually to be included with the latter.

There remain only N_f

$$N_f = N - N_g = N - (N_1 + N_2 + N_3)$$

as truly free molecules of liquid. Accordingly, the free volume is not $N \cdot v_0$ but $N_f \cdot v_0$. In accordance with our data

$$N_f \cdot v_0 = [N - (N_1 + N_2 + N_3)]v_0.$$

The expressions derived above may be inserted for N_1, N_2 and N_3. They indicate the effect of temperature and concentration and also the absolute order of magnitude of the individual components contributing to N_g. If, as has happened repeatedly,[72] the train of thought of the van der Waals theory is applied to solutions of this kind, we should insert the expression $N_f v_0$ in the volume correction. The term $(v - b)$ generally used can be regarded as a first, but too strictly ideal, approximation. A better approximation is the swelling equation by G. V. Schulz,[73] who replaced the co-volume b by an expression dependent upon the concentration.

It must, of course, be emphasized that, in reality—as the swelling isotherms have shown—the three types of binding outlined above are continually overlapping and it means that certain liberties are taken in our definitions of the boundary; they are, however, in line with the experimental methods available. If we wish to proceed more formally, we might speak simply of a part of the bound quantity of liquid greatly dependent on temperature and a part independent of temperature, so that the tempera-

[72] Cf. e.g. Wo. Ostwald l.c. on page 235.

[73] G. V. Schulz, *Z. physik. Chem.*, (A) **158**, 237 (1932).

ture-dependent part would appear under 1 and 3 and the temperature-independent part under 2; division into 1 and 3 would result only in taking the effect of concentration into account in such a way that 1 indicates proportionality to concentration but 3 proportionality to the square of concentration. In order to obtain a complete description of the behavior of suspended particles in a solvent, we must now consider, in addition to the force action between solute and solvent, the possibility of gains in entropy. It may be declared quite generally that the degree of dispersion will be preferred to as great an extent as the degree of randomness resulting from its production. If large, chain-like or net-like molecules can thus display internal vibrational or rotational motions which were absent before, or, if an orientation which existed before is destroyed by the process of dispersion, the entropy term will favor solution.

It will not be easy to put this influence into quantitative form in a given case, but it must be taken into account in a general sense; throughout the present chapter we have endeavored to emphasize this effect.

5. The Viscosity of Liquids and Solutions

One of the most striking properties of solutions of high molecular weight substances is their high *viscosity*; this has aroused interest both in research and in industry.

In industry, the peculiar viscosity of solutions of high polymers has played an important role in the fashioning of films, filaments and varnished articles of every kind, and it may be said that in many cases viscosity may constitute one of the most essential criteria of quality for the solutions used industrially. For many years viscosity has been applied as an empirical but useful guide to the quality of many materials, so that a whole series of standard technical methods for its measurement have been devised.[74]

The remarkable phenomena of high viscosity have also aroused scientific interest and E. Berl,[75] W. Biltz,[76] J. Duclaux,[77] Wo. Ostwald[78] and O. Sackur[79] began experimental investigations in this field over twenty years ago. The aim was not only to obtain an empirical insight into viscosity,

[74] See: E. C. Bingham, *Fluidity and Plasticity*, New York 1922. E. Hatschek, *The Viscosity of Liquids*, London 1928. G. Barr, *Viscosimetry*, London 1931. *First and Second Report on Viscosity*, Amsterdam 1935 (1939) and 1938. Cf. also the monograph on "Viscosity" in this series.

[75] E. Berl, *Z. ges. Schiess-u. Sprengstoffw.*, **5**, 82 (1910).

[76] W. Biltz, *Z. physik. Chem.*, **73**, 481 (1910); **83**, 625, 683 (1913); **91**, 705 (1916).

[77] J. Duclaux, *Compt. rend.*, **152**, 1590 (1911).

[78] Wo. Ostwald, *Kolloid-Z.*, **24**, 7 (1919); **43**, 190 (1927); **49**, 60 (1929).

[79] O. Sackur, *Z. physik. Chem.*, **70**, 477 (1910).

but largely to establish a connection between this conveniently measurable quantity and the molecular state of the solution, i.e. size, form and internal mobility of the dissolved particles. Berl and Biltz recognized quite early, through experiments on starch and on cellulose derivatives, that the viscosity of solutions of the same concentration increased with increasing particle size, although without attempting to establish a quantitative relation between the two properties. In recent years this question has entered a new stage, particularly through the extensive researches of H. Staudinger,[80] in that he has devised an equation connecting viscosity and molecular weight quantitatively. Tests of the Staudinger equation have led to the accumulation of a large amount of experimental data and to considerable theoretical understanding of the conditions. Quite apart from the question of the exact validity of this equation, we have in any case to acknowledge its great influence on the development of the viscosity problem.

In the course of this development, systematic experiments with test models by F. Eirich and his collaborators[81] and the closely related theoretical studies of E. Guth and R. Simha,[82] begun at the suggestion of the author, have contributed to the elucidation of the problem. The studies and calculations of M. L. Huggins[83] and W. Kuhn[84] have cleared up many essential points.

It will be the purpose of the following section to describe the present status of our ability to connect viscosity with molecular structure by applying physico-chemical methods to high molecular weight substances. It seems fitting, as in the treatment of vapor pressure lowering and of osmotic pressure, to go further into the principles underlying viscosity of solutions and to discuss first the measurement and theoretical significance of the viscosity of pure liquids.

a) The Normal Viscosity of Pure Liquids

Apart from surface forces and compressibility, observations and measurements show that the differential equations of hydrodynamics in their

[80] See particularly the book *Die hochmolekularen organischen Verbindungen*, Berlin 1932, p. 56, 489 etc. Also more recently: *Kolloid-Z.*, **82**, 129 (1938).

[81] Cf. e.g. F. Eirich and H. Mark, *Ergeb. exakt. Naturw.*, **15**, 1 (1936): F. Eirich, H. Margaretha and M. Bunzl, *Kolloid-Z.*, **75**, 20 (1936); F. Eirich and J. Sverak, *Kolloid-Z.*, **85**, 16 (1938). F. Eirich and R. Simha, *J. Chem. Phys.*, **7**, 116 (1939).

[82] See e.g. E. Guth and R. Simha, *Kolloid-Z.*, **79**, 266 (1936).

[83] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1938); *J. Applied Phys.*, **10**, 700 (1939).

[84] W. Kuhn, *Z. physik. Chem.*, (A) **161**, 1 (1932).

simplest form are not sufficient to describe the conditions which prevail in real liquids. There exists always a considerable amount of internal friction and it is, therefore, important to consider the interactions which exist between two liquid planes moving in relation to each other. These interactions are caused by the van der Waals forces between the separate, rather closely packed molecules of the liquid. These forces, which macroscopically are compensated fairly accurately in the stationary liquid, induce frictional effects in the flowing, self-deforming phrase; the kinetic energy of a flowing liquid, left to itself, is converted gradually into heat. The more viscous the liquid, the more rapid is this process: viscosity and internal friction can be regarded as equal to each other.

Newton was the first to realize that the force corresponding to this performance of work against internal friction behaves entirely differently from that operating in external friction; he assumed that the shearing force of internal friction τ is proportional to the surface f, and to the relative velocity u of the liquid planes in relative motion. By conversion to the limiting value for infinitely thin planes, he was able to write

$$\tau = \eta \cdot \frac{du}{ds} \cdot f \tag{83}$$

The proportionality constant η in this Newtonian Law bears the name viscosity; its dimensions are

$$[\eta] = m \cdot l^{-1} \cdot t^{-1}.$$

The *unit viscosity* in absolute (cgs) units—one poise—is possessed by any liquid in which the force of 1 dyne is necessary to maintain a velocity gradient of 1 cm per sec per cm perpendicular to a surface of one cm^2. In this case also the power expended is 1 erg per sec.

It is evident from the above that a certain shearing stress must prevail between the planes of a liquid in stream-line flow in order to maintain the motion. In internal friction (as well as in external friction) a work transference into heat takes place.

To give an idea of the magnitude of this work transference in moving liquids in a few important cases, attention is directed to Table 80 which gives some coefficients of viscosity at different temperatures in absolute units. From them it may be deduced that in water two planes, distant one cm from each other, with one stationary while the other moves forward at a velocity of one cm per second, can transfer the force of one mg to a surface of about 100 cm^2. In a one per cent solution of nitrocellulose in acetone, this capacity for force transfer is about 700 times greater.

We may proceed in various ways to measure the coefficient of viscosity.

Three methods, however, have proved very simple and they, only, will be described here. For the many other ways of determining viscosity by direct or indirect means the original literature should be consulted.[85]

The classical methods of determining the viscosity of liquids are the following:

a) Flow of a liquid through a cylindrical tube.
b) Motion of a solid body, generally a sphere, in a liquid.
c) Observation of the behavior of a liquid between two concentric cylinders of which one is stationary and the other in rotation.

TABLE 80

VISCOSITIES OF SOME IMPORTANT LIQUIDS

Substance	Temperature in degrees Centigrade	η in [g cm^{-1} sec^{-1}]
Water	0	0.0175
Water	20	0.0100
Water	80	0.0035
Alcohol	20	0.0121
Benzene	20	0.0064
Aniline	20	0.0447
Glycerine	21	7.78
Nitrocellulose 1% in Acetone	20	6.75
Acetyl cellulose 1% in CH_2Cl_2	20	4.88
Alkali cellulose 1% in Schweizer's Reagent	20	5.53

a) If the fundamental equations of hydrodynamics for viscous liquids are considered from the point of view of finding simple relations for determining η, it is evident that one must necessarily realize conditions in which stream-line flow occurs, as far as possible, so that the effects of inertia may be neglected. These effects are always active in the case of turbulence but practically cease in the case of purely laminar flow, which is characterized by the fact that all the particles of the liquid possess parallel velocity vectors. Such an approximation results in such great simplification of the hydrodynamic equations for viscous liquids that it permits integration in an elementary way which need not be discussed here. It gives directly the velocity distribution in the system considered as well as the amount of liquid flowing in a given time through the tube and other data relevant

[85] E.g. C. Engler, *Z. angew. Chem.*, **5**, 725 (1892); **20**, 832 (1907); B. Redwood, *J. Soc. Chem. Ind. Japan*, **5**, 121 (1886); S. Erk, *Chem. Fabrik*, **1**, 715 (1928); E. Grüneisen, *First Report on Viscosity*, 2nd ed., Amsterdam 1939, p. 112ff.; C. J. van Nieuwenburg, *Second Report on Viscosity*, Amsterdam 1938, p. 241ff.

to the determination. Thus, the following equation is obtained for the velocity distribution in a tube of radius a and length l:

$$u = \frac{1}{4\eta} \cdot \frac{\Delta p}{l} \cdot (a^2 - r^2) \tag{84}$$

It is immediately evident that the rate of flow u must be proportional to the pressure gradient Δp, and inversely proportional to the length of the tube and to the coefficient of viscosity η. The distribution of the velocity over the cross-section of the tube is parabolic; at the wall

$$r = \alpha$$

there is zero velocity, while on the axis of the tube u assumes its maximum value

$$u_{\max} = \frac{a^2}{4\eta} \cdot \frac{\Delta p}{l} .$$

The velocity gradient, considered over the cross-section, is not constant but is dependent on r according to

$$\frac{du}{dr} = -\frac{1}{2\eta} \cdot \frac{\Delta p}{l} \cdot r$$

and reaches its highest value at the wall. The conditions are illustrated in Fig. 81.

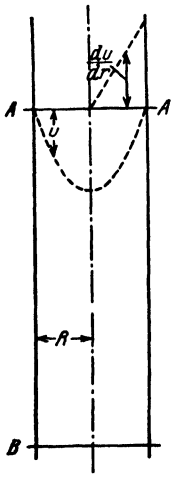


Fig. 81. Flow section of a viscous liquid in a cylindrical tube.

The total volume of liquid V flowing through the tube in unit time is obtained by a simple integration; it is

$$V = \frac{\pi}{8\eta} \cdot \frac{\Delta p}{l} \cdot a^4. \tag{85}$$

This equation was first derived by Hagen and Poiseuille and constitutes the principal law of flow. It offers a very suitable means of determining η experimentally, since the four quantities V, a, l and Δp are all easily measurable.

The following are special provisos for the validity of the above equations (84) and (85):

a) Newton's law connecting shear stress and velocity gradient must hold and

b) there must be no turbulence in the flowing liquid.

The first condition depends on the nature of

the liquid or solution and may not always be capable of realization, although approximately true in the majority of cases. On the other hand turbulence can be controlled by sufficiently decreasing the velocity of flow.

b) At low velocities and with dimensions of the apparatus which are large compared with molecular dimensions, the movement of a solid body in a viscous liquid can be expressed mathematically so simply that the corresponding differential equation may be integrated. In this case, however, the calculation is not strictly accurate but a near approximation, because it is impossible to exclude turbulence entirely. The limits within which the following equations may be applied must be carefully checked experimentally in each case or tested on theoretical principles.

If a sphere of radius a, which must be large compared with molecular dimensions, attains a velocity u in a viscous liquid, a force K is required whose magnitude is given by the equation of Stokes:

$$K = 6\pi\eta a \cdot u \tag{86}$$

In falling ball experiments in liquids, the rate at which a sufficiently large sphere sinks slowly in a viscous medium will be given by

$$u = \frac{m \cdot g}{6\pi\eta a}; \; m = V(\rho_1 - \rho_2) \tag{87}$$

g = acceleration of gravity
V = volume of the sphere
ρ_1 and ρ_2 = density of the ball and density of the liquid, respectively.

Since, in equation (87) the acceleration due to gravity g is known and the rate u, the radius a and the apparent mass m can easily be measured, it affords a simple means of determining the coefficient of viscosity. When the movement of the sphere is very slow, the container sufficiently wide and the sphere sufficiently large, values of η are obtained in excellent agreement with those determined by other methods.

Oseen[86] has suggested a more exact formula in which, owing to the fact that the inertia effect never entirely disappears, the quadratic term in the velocity u is taken into account. The force for attaining a given rate u is then greater because inertia must be overcome as well as the internal friction of the liquid.

c) The third—perhaps the most reliable—method for determining the coefficient of viscosity is that of Couette.[87] Two concentric cylinders of radii r_1 and r_2 are so arranged that one is stationary while the other is

[86] C. W. Oseen, *Ark. Mat. Astron. Fysik*, **6**, 29 (1910); **9**, 16 (1913).
[87] J. Couette, *J. physique radium*, **9**, 566 (1891).

rotated with the angular velocity U. The space between is filled with the viscous liquid of viscosity η. The velocity distribution is given by

$$u = U \frac{r_2^2}{r_2^2 - r_1^2} \cdot \frac{r^2 - r_1^2}{r^2}$$

a relation which is easy to check, since for

$$r = r_2$$

the rate of the liquid is equal to that of the rotating cylinder, while for

$$r = r_1$$

it disappears, as it must do, if the inner cylinder is to remain at rest.

If both cylinders have the same height h, the turning moment μ necessary to maintain continuous motion is given by

$$\mu = 2\pi\eta U h \frac{r_1^2}{r_2^2 - r_1^2} \tag{88}$$

or, for a small thickness δ of the layer of liquid between the two cylinders,

$$\delta = r_2 - r_1 \ll r_1$$

by

$$\mu = 2\pi\eta U h \frac{r_1}{\delta};$$

since the values μ, U, h, δ and r_1 can be readily measured by a suitable experimental arrangement, this method affords a possibility of determining the coefficient of viscosity, which is frequently of special importance because, by suitable choice of the velocity of the rotating cylinder, it is possible to work with quite small shear stresses and to study the behavior of the liquid under quite small forces. It is usual to suspend the stationary cylinder on a torsion wire, and to determine directly by means of a mirror reading the torsional force to which it is subjected by the liquid.

Under the conditions prescribed, the methods outlined above always give identical values for the coefficients of viscosity of pure liquids assuming that turbulence does not exist and that Newton's law connecting velocity gradient and shear stress truly represents the conditions. This is actually the case, as is known from experience, for the majority of pure liquids, but there are exceptions, which appear important for our purpose because they concern liquids made up of long chain substances; as we shall see later, these play an important part in the realm of high polymer solutions. It has been proved impossible in many cases to describe the me-

chanical behavior of a liquid by a simple coefficient of viscosity. The relationships are often complicated and more constants are required for expressing completely the response of the particular system to a mechanical stress. Before going further into these flow anomalies we shall discuss briefly some recent attempts to explain the coefficient of viscosity of pure liquids.

b) Theories Regarding the Viscosity of Pure Liquids

In connection with the researches into the structure of liquids mentioned above, a series of very interesting attempts has been made to investigate the internal friction of pure liquids from the standpoint of molecular theory.[88]

Van der Waals, Jr.[89] derived an equation for the coefficient of viscosity based on the idea that internal friction arises as it does in a gas, where the momentum is transmitted from molecule to molecule by collisions. He obtains for η the expression

$$\eta = 0.335 n^2 d^4 m a \frac{v}{v-b} exp\left(-\frac{\epsilon}{RT}\right)$$

n, d and m = number, diameter and mass of the molecules

$$a = \sqrt{\frac{2kT}{m}}$$

ϵ = energy difference between the average energy of a molecule and the energy at the moment of collision

b = co-volume

Andrade[90] has proceeded on entirely different principles to obtain the following expression for η

$$\eta = 1{\cdot}33 \times \nu \frac{m}{d}.$$

---

[88] See especially *First and Second Report on Viscosity and Plasticity*, Amsterdam-New York, 1935 and 1938; furthermore E. C. Bingham and S. D. Stookey, *J. Am. Chem. Soc.*, **61**, 1625 (1939) and E. P. Irany, *J. Am. Chem. Soc.*, **60**, 2106 (1938); **61**, 1734 (1939).

[89] See especially: *Second Report on Viscosity and Plasticity*, Amsterdam-New York, 1938, p. 38 et seq. and J. D. van der Waals, Jr., *Proc. Acad. Amsterdam*, **21**, 743 (1918).

[90] E. N. da C. Andrade, *Phil. Mag.*, **17**, 497 (1934). See also *Second Report* loc. cit. Chapt. II, p. 5-20.

The value of ν is best determined from the Lindemann melting point formula and is given by

$$\nu = const\left[\frac{T_s}{MV_M^{\frac{2}{3}}}\right]^{\frac{1}{2}}.$$

T_s = melting temperature
M = molecular weight
V_M = molecular volume.

We then obtain for the viscosity of a liquid at the melting point T_s, the expression

$$\eta_s = 5{\cdot}1 \times 10^{-4} M^{\frac{1}{2}} (V_M^{\frac{2}{3}}) T_s^{\frac{1}{2}}. \tag{89}$$

This very simple formula enables the viscosity of liquid metals to be expressed with very satisfactory accuracy as a function of their melting point, as is seen from Table 81.

TABLE 81

Substance	η observed	η calculated according to (00)
Hg	0.021	0.021
Tl	0.028	0.025
Sn	0.020	0.019
Cu	0.038	0.039
Sb	0.024	0.015
Bi	0.023	0.023

From the very numerous formulas advanced, we shall choose only that of Herzog and Kudar;[91] it is closely related to the expression of van der Waals, Jr. and its principal aim is to rationalize, with the aid of molecular theory the empirical equation of Batschinski[92]

$$\eta = 7{\cdot}90 \times 10^{-5} \frac{T_s^{\frac{1}{2}} \cdot v_s^{\frac{1}{3}}}{M^{\frac{1}{2}} (v - b)},$$

v = specific volume at the melting point

which is in harmony with experiment. Herzog and Kudar obtained an expression of the form

$$\eta = 3{\cdot}55 \times 10^{-5} \frac{T_s^{\frac{1}{2}} \cdot v_s^{\frac{1}{3}}}{M^{\frac{1}{2}} (v - b)}.$$

It is evident that there is satisfactory relationship between the two expressions up to a factor of the order of magnitude 2.

[91] R. O. Herzog and H. C. Kudar, *Z. Physik*, **80**, 217 (1933); **83**, 28 (1933).
[92] A. J. Batschinski, *Z. physik. Chem.*, **84**, 643 (1913).

All current theories show that the viscosity of liquids is mainly due to their dense packing which is a consequence of the forces between the molecules. The characteristic lowering of viscosity with rising temperature depends essentially on the effect which temperature has upon specific volume, a point still awaiting final elucidation.[92a]

An interesting method of treating viscosity of binary mixtures theoretically has been devised by van der Wyk[93] and will be discussed on page 000.

c) *Anomalies in the Flow Properties of Pure Liquids*

According to the Hagen-Poiseuille law, the volume of a liquid V, which flows through a capillary of radius a in time t is given by the expression

$$V = \frac{\pi}{8\eta} \cdot \frac{\Delta p}{l} \cdot t \cdot a^4 .$$

The amount is thus proportional to the product of pressure difference and time of flow. Small pressure differences give, for equal cross-sections, long periods of flow; large pressure differences give correspondingly shorter periods. In many liquids, e.g. glycerin, lactic acid, and in numerous solutions, such as cane sugar, this proportionality between the total amount of liquid flowing through the viscosimeter and the product $\Delta p \cdot t$ is, in fact, well satisfied over large pressure ranges. Frequently, however, we come across exceptional deviations, for example, in lubricating oils and, particularly, in solutions of high polymers.

Considering the Hagen-Poiseuille formula we find that the departures from the behavior expected from Newton's law can be represented, if we substitute for the Newtonian expression a more general relation between velocity gradient and shear stress. Many workers have endeavored to find an expression which would satisfy experimental facts.[94] Rabinowitsch,[95] Reiner[96] and Weissenberg,[97] particularly, have interested themselves recently in the anomalous behavior of viscous liquids.

In the first instance, Bingham[98] suggested a substitute for the New-

[92a] See e. g. H. Eyring, *J. Chem. Phys.* **4**, 283 (1936); R. Simha; ibid. **7**, 202 (1939); compare also H. Eyring's contribution at the Gibson Island Conference of the AAAS in July, 1940.

[93] A. J. A. van der Wyk, *Nature*, **138**, 845 (1936).

[94] See e.g. Literature references in H. Mark, *Physik und Chemie der Cellulose*, Berlin 1932, p. 74; also especially R. Houwink, *Second Report*, Amsterdam, 1938, p. 185 et. seq.

[95] B. Rabinowitsch, *Z. physik. Chem.*, (A) **145**, 1 (1929).

[96] M. Reiner, *Kolloid Z.*, **50**, 199 (1930); *J. Rheol.*, **2**, 337 (1931).

[97] K. Weissenberg, *Kolloid Z.*, **46**, 277 (1928).

[98] E. C. Bingham, l.c.p.

tonian equation which was adopted by Freundlich and his co-workers[99] and was tested experimentally and discussed in detail by Reiner.[100]

We may consider the following concept: In the theory of elasticity of solid bodies, the shearing stress is proportional to the elastic displacements which the separate particles of the body undergo during deformation. In the theory of normal frictional liquids, these are directly proportional to the velocity at which the liquid planes glide over one another; they disappear if the velocity and, therefore, the velocity gradient, is zero. If we assume that a liquid possesses something of the properties of an elastic solid, it is easy to imagine that it may withstand definite shearing forces without flowing and that it possesses therefore a kind of flow limit. Sufficiently small shearing stresses would produce no motion in the liquid, but would merely store up a certain amount of elastic energy of tension.

This is the behavior envisaged if the expression

$$\tau = \vartheta + \eta \frac{du}{ds} \tag{90}$$

is substituted for the Newtonian law, from which it is clear that the shearing stress τ on the left hand side corresponds to the sum of the two terms on the right hand side:

1. The movement of liquid, characterized by

$$\eta \frac{du}{ds} \quad \text{and}$$

2. the elasticity, designated by ϑ.

In this case, ϑ evidently performs the function of a flow limit for the liquid exhibiting anomaly and constitutes a second constant necessary for defining the rather more complex conditions now prevailing. So long as the shearing stresses are smaller than this flow limit, it will only be a matter of energy being stored in the liquid and there will be no movement. Only when the shearing stress exceeds the flow limit, will a velocity gradient be produced in the observed system.

It is possible to calculate the behavior of an anomalous liquid in the three cases discussed—capillary flow, falling sphere and Couette flow—by substituting the Bingham expression for the Newtonian law and obtaining different equations for the amount of liquid passing through the capillary, the times of fall, etc.

Szegvari[101] has shown that the behavior of many inorganic sols, e.g.

[99] H. Freundlich, *Z. physik. Chem.*, **108**, 153, 175 (1924).
[100] M. Reiner, *Kolloid Z.*, **50**, 199 (1930).
[101] A. Szegvari, *Z. physik. Chem.*, (A) **145**, 1 (1929).

V_2O_5, Al_2O_3, CeO_2, Fe_2O_3, and also of some dyestuff suspensions—benzopurpurin, cotton yellow, etc.—can be described by the simple law (90) in good agreement with experiment. On the other hand, high polymeric substances in particular cannot be treated satisfactorily in this way. Numerous experiments on the viscosity of starch, gelatin, rubber and cellulose derivatives show that we must assume a more general relation between the shearing stress τ and the velocity gradient

$$\frac{du}{ds}$$

if the flow properties of these complicated systems are to be formulated.

In discussing these relationships, it is convenient to replace the viscosity η by the fluidity φ according to the equation

$$\eta \cdot \varphi = 1.$$

Newton's law is then written

$$\frac{du}{ds} = \varphi \cdot \tau,$$

and Bingham's

$$\frac{du}{ds} = \varphi \cdot \tau - \vartheta.$$

In the first, the velocity gradient is directly proportional to the shearing stress. Rabinowitsch and Weissenberg,[102] to whom we are indebted for a comprehensive treatment of the phenomena in question, have shown that an indeterminate function

$$\frac{du}{ds} = f(\tau)$$

may be introduced in the calculation of Poiseuille flow, so that it enters into the final result and can be determined by comparison of this result with experiment. It is thus possible to determine empirically in this way the function replacing the Newtonian law, a process which has been carried out on a series of liquids and solutions by the authors mentioned.

The fact emerges that glycerin, castor oil and honey exhibit no departures from the Hagen-Poiseuille law and are to be classed as normal viscous liquids. In contrast, solutions of acetyl cellulose and nitrocellulose in acetone and of rubber in benzene depart materially. Combined investigations of the effect of pressure, time and capillary dimensions

[102] B. Rabinowitsch and K. Weissenberg, *Kolloid Z.*, **39**, 80 (1926).

on the flow of the liquid enable the modified theory to be tested thoroughly and a suitable expression for the systems mentioned to be found. This has the form

$$\frac{du}{ds} = 8a\tau + 10b\tau^2; \tag{91}$$

in this

$$\tau = \frac{r}{2}\frac{\Delta p}{l}$$

r = capillary diameter
Δp = pressure difference
l = length of capillary

a and b are two constants of the liquid which have, however, no direct and clear physical meaning.

The new law contains a quadratic term in τ, instead of the supplementary term of zero order which has the physical significance of a flow limit. The theory of elasticity of solids obviously does not fit the solutions named. In the limiting case of quite small velocity gradients, the Newtonian law holds and not Hooke's law, which is characteristic of elastic bodies. A liquid defined by the law begins to flow only at infinitely small shearing stresses, in which initially the behavior approaches that of a Newtonian liquid, owing to the subordinate importance of the squared term. If the shearing stress is increased, the quadratic term becomes appreciable and the velocity gradient increases out of proportion to the shearing force. A liquid of this type is, in respect to its properties under mechanical stress, further removed from an elastic solid than the normal.

M. Reiner,[103] in connection with measurements of Herschel and Bulkly[104] on benzene solutions of rubber, has proposed a law of the form

$$\frac{du}{ds} = a\tau + b\tau^2 - c\tau^3 \tag{92}$$

which, as is evident, may be regarded as a development of those derived by Rabinowitsch and Weissenberg mentioned above.

To sum up, we may say that two types of departures from the normal behavior of a viscous liquid have been observed experimentally and discussed theoretically. Neither relate, as a rule, to pure liquids, which exhibit Newtonian behavior predominately, but to solutions or sols. The departures may be described as follows:

[103] M. Reiner, *Kolloid Z.*, **39**, 80 (1926); **50**, 199 (1930); *J. Rheol.*, **1**, 14 (1929).
[104] W. H. Herschel and R. Bulkly, *Kolloid Z.*, **39**, 291 (1926); *J. Rheol.*, **1**, 506 (1930).

a) The solution resembles a solid, it has elastic properties and its hydrodynamics are governed by a relation of form (90), which is substituted for the Newtonian law in the principal equation of hydrodynamics. Such solutions exhibit elasticity or rigidity. In addition to the coefficient of viscosity, a coefficient of elasticity is necessary for their definition. Examples of such systems are sols of Al_2O_3, Fe_2O_3, CeO_2, V_2O_5, benzopurpurin, etc.

b) To express the hydrodynamics of a solution of high polymers, it appears necessary to employ, instead of the Newtonian expression, one of the form

$$\frac{du}{ds} = a\tau + b\tau^2 + c\tau^3 \cdots \tag{93}$$

This indicates a departure in the opposite sense from the earlier one, i.e. in the direction that, at infinitely small shearing forces the Newtonian behavior appears as the limiting value, while the solution becomes increasingly more fluid and mobile with increasing τ. Here, also, the coefficient of viscosity, calculated formally from the Hagen-Poiseuille law, decreases with increasing shearing stress but in an entirely different way from that in elastic liquids.

Fig. 82 will illustrate the conditions; in this the coefficient of viscosity indicated by Poiseuille's law is plotted against shearing stress. A normal liquid is characterized by a constant η and appears in the diagram as a horizontal line. Elastic fluids, or solutions, have a larger η at small τ values, which decreases slowly to the Newtonian value. Super-fluid solutions, on the other hand, show normal behavior under the smallest shearing forces and progressively lower values for η with increasing τ.

In the two anomalous cases, the coefficient of viscosity decreases with increasing shearing stress, the one in the direction of Newton-Poiseuille behavior and the other away from it.

This must be interpreted by the fact that changes in structure arise from the mechanical strain in the solution. In the first case it may be assumed that any structure which has been produced by the interaction of dissolved particles in the liquid is destroyed by shearing stress. Direct observation of sol elasticity by Freundlich and Seifriz[105] supports this view.

On the other hand, the behavior appears to be entirely different in sols of high molecular weight substances. Here, also, the fluidity increases with increasing shearing stress but, obviously, not because an existing structure is destroyed; probably it is because orientation of the particles

[105] H. Freundlich and F. Seifriz, *Z. physik. Chem.*, **104**, 233 (1923).

takes place during the flow of such systems, or, if flexible primary valence chains are dispersed, they may be stretched and flattened out by the flow. Both effects naturally reduce frictional resistance and induce the behavior represented in Fig. 82, curve 3.

After this brief discussion of the viscosity of pure liquids, it is time to pass to the question: Is it possible to draw deductions from measurements of the viscosity of solutions, regarding the magnitude, form and internal mobility of the dissolved or dispersed particles and the energy interactions between them?

We are still a long way from a satisfactory answer to this question, but experiments directed to the problem have made important contributions to the knowledge of solutions of high polymeric substances and at the same time many theoretical points of view have been brought up.

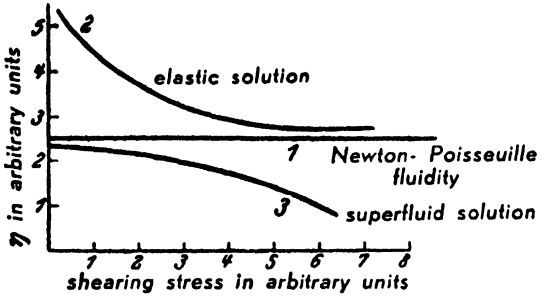


Fig. 82. Departure of viscosity from normal behavior.

In the following section we shall first review briefly the theoretical ideas developed to describe and explain the viscosity of solutions. Then we shall enumerate some relations connecting directly measurable viscosity with data on size, form and properties of the dissolved particles, which are of particular interest to us. In this connection we shall review the existing experimental material and discuss particularly the model experiments of Eirich[106] and his co-workers. A closing section will deal with general results relating to high polymers, while details in regard to the different high molecular weight substances previously investigated will be reserved for another volume.

d) Viscosity of Solutions

The number of papers concerning the viscosity of binary mixtures of solutions of low molecular weight substances is considerable. In spite

[106] F. Eirich, *Kolloid Z.*, **74**, 276 (1936); **75**, 20 (1936); **81**, 7 (1937); **83**, 108 (1938).

of the abundant experimental material, theoretical treatment is difficult because a satisfactory theory of pure liquids did not exist until quite recently.

We are better provided for in regard to the viscosity of suspensions, and, since solutions of high polymers represent transition stages between solutions and suspensions, we shall first discuss solutions of low molecular weight substances, then suspensions and, finally, high polymers.

Van der Wyk[107] has advanced a theory of viscosity of binary mixtures based on Andrade's theory of the viscosity of pure liquids referred to above. He tried to find an explanation first for the processes in normal binary mixtures. The formulas current for these mixtures, which represent viscosity as dependent on the concentration of the constituents, are, however, without exception, empirical laws. Attempts have certainly been made to give theoretical support to the laws but they usually turn out to be not quite successful. Therefore Kendall,[108] in a series of extremely careful experiments, has suggested that the practical usefulness of these interpolation formulas is slight as soon as the viscosities of the two components of the mixture exhibit large differences.

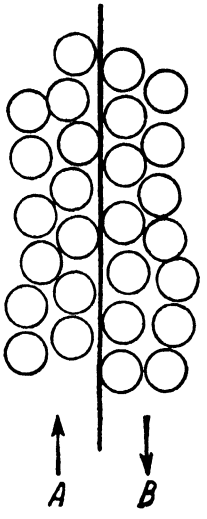


Fig. 83. Laminar flow in a liquid.

Accordingly, for treating solutions, it is necessary to start from pure liquids. Relinquishing hydrodynamic concepts, the liquid is conceived as a closely packed molecular discontinuum. If a stationary laminar flow prevails in such a structure, liquid planes (flat or curved) are displaced parallel to one another in the direction of flow. Let us consider a section including the direction of flow and the velocity gradient, e.g. a section along the axis of a capillary through which the liquid is forced (Fig. 83).

To maintain the flow, a suitable and continuous amount of work must be performed. The plane moving fastest continually loses kinetic energy. Hence, the molecules in this layer will lose a part of their forward momentum by transfer of kinetic energy in a direction perpendicular to that of flow. This liberation of kinetic energy does not constitute an equivalent gain to the adjacent plane; rather it causes a temperature increase, because friction converts the mechanical energy into heat.

[107] A. J. A. van der Wyk, *Nature*, **138**, 845 (1936).

[108] See, e.g., J. Kendall, *J. Am. Chem. Soc.*, **39**, 1785 (1917).

The friction between the two planes is, however, not to be regarded as directly analogous to external friction, because the internal friction of liquids is practically independent of pressure, as Coulomb showed long ago.

On the other hand, the process may not be directly compared with the internal friction of gases. In the latter the transmission of momentum is caused by an interchange of molecules between the planes or by extinction of momentum through a collision between a molecule in one plane with a molecule in another. If this process determined the friction of liquids, the friction would increase with rising temperature (at constant volume), as in gases. The internal friction of liquids, however, usually decreases greatly with increasing temperature. Accordingly, it is reasonable to assume that the transmission of molecular momentum (diffusion of energy perpendicular to the direction of motion) in liquids is caused by intermolecular forces and not by elastic collisions. The fact that the viscosity of liquids with high molecular cohesion is high, is in good harmony with this.

It is possible to express statistically the force effect between two neighboring molecules in a condensed system by imagining that the two molecules adhere to each other for a given instant of time and remain apart and independent for the rest of the time. Andrade[109] visualizes a definite oscillation state or even a momentary association as a condition of adherence. Sheppard's[110] view of a mutual orientation of the two molecules is equally acceptable. Apart from these differences of outlook, it is clear that the transmission of momentum is bound up with a definite state of the two molecules. This means that transference of momentum takes place always and only if this state exists between two molecules considered. The state may be characterized by the energy ϵ corresponding to it.

According to Boltzmann, the fraction $\frac{\Delta N}{N}$ of the molecules which possess a definite state of energy ϵ is given at any instant by an expression of the form

$$\frac{\Delta N}{N} \sim exp\left(-\frac{\epsilon}{kT}\right). \tag{94}$$

On the other hand, however, the number of transferences is proportional to the loss of kinetic energy of flow of a plane, i.e. is also proportional to the internal friction or viscosity. Thus the following holds

$$\eta \sim \frac{\Delta N}{N} \tag{95}$$

[109] E. N. da C. Andrade, l.c.

[110] S. E. Sheppard, *Nature*, **125**, 489 (1930).

This formula enables us to express with reasonable accuracy the dependence of the viscosity of simple liquids on temperature.[111]

By analogy to the pure liquid, we shall describe a binary mixture as a closely packed discontinuum of similarly sized molecules of components 1 and 2 which are distributed regularly throughout the material. This description is to some extent opposed to the hydrodynamic concept, in which one component is regarded as the continuum and the other as a discrete particle group.

Streamline flow in such a medium can be expressed as in a pure liquid. We first imagine a given molecule of component 1, which may lie in plane A, (Fig. 83) at the instant at which this molecule assumes the energy state ϵ characteristic for the transmission of its momentum *mu*. The partner in plane B to which the momentum is given up is either a molecule of the same kind 1 or, possibly, a molecule of component 2. If N_1 and N_2 are the mol fractions of the two components, the probability of the former case is proportional to N_1 and of the latter to N_2.

The state of transmission is not characterized by the same energy ϵ in both cases. If ϵ_1 is the energy corresponding to the transference for the first case and ϵ_{12} the energy corresponding to the transmission of momentum to a molecule of the second kind, the interaction between the given molecule in plane A and all the molecules in plane B is proportional to the expression $N_1\epsilon_1 + N_2\epsilon_{12}$.

The interaction of all the molecules of the component 1 in plane A and the whole plane B is then proportional to

$$N_1(N_1\epsilon_1 + N_{12}\epsilon_2)$$

Exactly the same holds for the molecules of component 2 in plane A; these contribute

$$N_2(N_1\epsilon_{12} + N_2\epsilon_{12}).$$

The total interaction ϵ between the liquid planes is therefore

$$\epsilon \sim N_1(N_1\epsilon_1 + N_1\epsilon_{12}) + N_2(N_1\epsilon_{12} + N_2\epsilon_2) = N_1^2\epsilon_1 + 2N_1N_2\epsilon_{12} + N_2^2\epsilon_2.$$

According to (94) and (95) $\ln \eta$ is proportional to the value ϵ at constant temperature. By insertion in the above expression and recalling that $N_1 + N_2 = 1$, we obtain

$$\ln \eta = N_1^2 \ln \frac{\eta_1\eta_2}{\eta_{12}^2} + 2N_1 \ln \frac{\eta_{12}}{\eta_2} + \ln \eta_2. \tag{96}$$

---

[111] Compare H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936); R. H. Ewell and H. Eyring, ibidem, **5**, 726 (1937); F. Eirich and R. Simha, ibidem, **7**, 116 (1939). R. Simha, ibidem, **7**, 202 (1939), where similar expressions are discussed from different points of view.

The application of this formula to quasi-ideal mixtures is in very good agreement with experiment; Table 82 gives a few examples.

From the above derivation it is evident that the relation between a simple function of viscosity and concentration is not linear but parabolic. Moreover, a new value η_{12} appears, termed "binary viscosity," which describes the interaction and with it the friction between two different kinds of molecules.[112] It appears impossible in the absence of these two conditions to establish a well-founded interpolation formula.

TABLE 82

THE VISCOSITY OF QUASI-IDEAL MIXTURES (IN CENTIPOISES)

hexane (1)—carbontetrachloride (2)			benzylbenzoate (1)—toluene (2)		
$N_1 \cdot 10^2$	$\eta_{obs.}$	$\eta_{calc.}$	$N_1 \cdot 10^2$	$\eta_{obs.}$	$\eta_{calc.}$
0	0.97	0.97	0	0.55_2	0.552
9.88	0.85_1	0.852	23.7	1.18_3	1.15
20.37	0.74_2	0.752	42.6	2.01_5	2.01
43.4	0.58_5	0.582	65.0	3.61_4	3.64
69.7	0.46_2	0.456	78.9	5.08_0	5.15
84.3	0.40_3	0.405	90.0	6.66_0	6.67
100.0	0.36_4	0.36_4	100.0	8.45_0	8.45
η_{12} (calculated) = 0.506 cp.			η_{12} (calculated) = 2.75 cp.		

With the aid of the foregoing, it is easy to understand the reasons for the failure of the interpolation formulas previously proposed. These expressions can be brought to a common algebraic form, namely,

$$f(\eta) = c_1 f(\eta_1) + c_2 f(\eta_2).$$

It is evident from this form that we have implicitly assumed that $f(\eta)$ is an additive function of the concentration c. This condition does not, however, hold as we have seen above.

In dilute solutions, i.e. if $N_2 \ll N_1$ and N_1 nearly equal one we may replace (96) by

$$\ln \frac{\eta}{\eta_1} = 2N_2 \ln \frac{\eta_{12}}{\eta_1}. \tag{97}$$

At the same time

$$N_2 = w \frac{M_1}{M_2},$$

[112] A. J. A. van der Wyk, *Compt. rend. soc. phys. hist. nat. Genève*, **54**, 133 (1937)

where w is the concentration by weight of the (dissolved) substance 2, and M_1 and M_2 are the molecular weights of solvent and solute, respectively.

Using a definition which has been introduced by Staudinger, we define the specific viscosity η_{sp} by

$$\eta_{sp} = \frac{\eta}{\eta_1} - 1.$$

Hence the following equation results from (99)

$$\ln (1 + \eta_{spec}) = w \frac{2M_1}{M_2} \ln \frac{\eta_{12}}{\eta_1}.$$

At adequate dilution we always obtain $\eta_{sp} \ll 1$ and (99) can be written

$$\eta_{sp} = w \frac{2M_1}{M_2} \ln \frac{\eta_{12}}{\eta_1}. \tag{98}$$

For any given mixture the following holds at high dilution

$$\eta_{sp} = \text{const} \cdot w.$$

Since most liquids in a high state of dilution approach the state of perfect solutions, the last equation is applicable in nearly all cases. Actually it agrees as regards form both with the empirical Staudinger law and with the formula of Einstein derived by hydrodynamic theory.

In solutions of high polymers in normal solvents, it is only in the range of highest dilution that we can be sure that $\eta_{sp} \ll 1$.

Although it is readily evident that the given derivation is not valid for molecules of very different sizes, it is possible to secure good agreement with experiment if we ignore the exact physical meaning of the constant and form equation (98) as follows:

$$\ln (1 + \eta_{sp}) = \ln \eta_{rel} = \text{const} \cdot w.$$

$$\eta_{rel} = \frac{\eta}{\eta_1} = ke^w \tag{99}$$

This is nothing but another way of writing the equation proposed by Arrhenius, which also holds only in regions of dilution ($N_1 \gg N_2$). The utility of this equation for this particular case has long been recognized empirically. (Compare page 294.)

e) The Origin of Viscosity in Suspensions

A. Einstein[113] performed a mathematical analysis in 1906 on the origin of viscosity in suspensions, which may be described today as the classical

[113] A. Einstein, *Ann. Physik*, (4) **19**, 289 (1906); **34**, 591 (1911).

foundation of all researches directed to this problem. His calculations relate to the behavior of very dilute suspensions of spherical particles and will have to be supplemented and expanded in many respects to enable them to express suitably the conditions actually indicated by experiments in the domain of high polymers.

First, it was necessary to consider the viscosity of suspensions of spherical particles at somewhat higher concentrations, for which purpose the Einstein calculation had to be repeated, taking into account the terms with higher powers of c. It was then found to be particularly important to examine the behavior of non-spherical suspensions, i.e. of rod-shaped or laminar particles. In the theories which had to be devised, the necessity of distinguishing between coarse and fine particle suspensions was soon recognized, because Brownian motion is absent in the former but appreciable in the latter case. Finally, it was desirable to consider the region of higher concentrations of non-spherical particle suspensions also, so that, in all, a great number of relations had to be worked out to pave the way for a quantitative possibility of answering the questions arising.

Table 83 summarizes the equations derived hitherto for the specific viscosity of solutions and the names of the authors who devised them. It may be pointed out that only problems relating to spherical particle suspensions have been satisfactorily solved. All other expressions are valid only within certain limitations and cannot be formulated with accuracy.

In connection with the table, the origin of the different formulas will be discussed briefly and the most important conditions governing their validity indicated.

The Einstein calculation is based on the following assumptions:

1. The molecules of the dissolved substance are large in comparison with the free path of the molecules of the solvent, but small in comparison with the dimensions of the apparatus. The solvent is assumed to be incompressible.
2. The suspended particles are rigid spheres to which the solvent liquid adheres completely.
3. The concentration of the solution is so low that any mutual disturbance of the particles may be ignored.
4. The flow should be so gradual that turbulence is excluded and effects of inertia are negligible.[114, 115]

[114] In regard to removal of these limitations see F. Eirich and O. Goldschmidt, *Kolloid Z.*, **81**, 7 (1937) and F. Eirich and R. Simha, *Monatsh.*, **71**, 67 (1937).

[115] Einstein's formula, according to its derivation, holds only for Couette flow. Its usefulness for capillary viscosimeters and the probability of its general validity was proved by R. Simha, *Kolloid Z.*, **76**, 16 (1936).

TABLE 83

DIFFERENT EXPRESSIONS FOR THE SPECIFIC VISCOSITY OF SOLUTIONS AND SUSPENSIONS

Type of suspension or solution		At extreme dilution			At moderate concentrations
		Without the influence of Brownian movement	With complete Brownian movement		Without Brownian movement
Rigid spheres		Einstein, Simha $2.5\,c$			Gold, Guth and Simha $2.5c + 14.1c^2$
Liquid (soft) spheres		Taylor $r.c$; with r varying from 2.5 down to 1.			———
Rigid rod-like particles	minimum value	Jeffery $2.0\,c$	Guth, Huggins, Jeffery $2.0\,c$	Simha $\left[\frac{f^2}{15(\ln 2f - \frac{3}{2})} + \frac{f^2}{5(\ln 2f - \frac{1}{2})} + \frac{14}{15}\right] c$	———
	maximum value	Jeffery $\left[\frac{f}{2\ln 2f - 3} + 2\right] c$ Eisenschitz $\frac{1.15\,f}{11\ln 2f}\cdot c$	Huggins, Kuhn $\left(2.5 + \frac{f^2}{16}\right) c$ Eisenschitz $\frac{f^2}{15\ln 2f - \frac{45}{2}}\cdot c$		Gold and Guth $\left[\frac{f}{2\ln 2f - 3} + 2\right] c + \frac{kf^3}{(2\ln 2f - 3)^2}\cdot c^2$
Rigid discs	minimum value	Jeffery $2.06\,c$	Guth $\frac{5}{12}\cdot\frac{f}{\tan^{-1} f}\cdot c$	$\frac{16}{15}\cdot\frac{f}{\tan^{-1} f}\cdot c$	———
	maximum value	Jeffery $\frac{4f}{3\tan^{-1} f}\cdot c$	Guth, Jeffery $\left[\frac{4f}{3\tan^{-1} f}\right]^2\cdot c$		

In this table, c denotes the volume concentration of the dispersed phase, f the axis ratio of the suspended particles and k a constant of the order of magnitude 1 (see page 284).

5. The undisturbed flow is represented by a Couette streaming.

On the validity of these assumptions, the following gives the viscosity of suspensions:

$$\eta_c = \eta_o\left(1 + 2.5\frac{\varphi}{V}\right) = \eta_o(1 + 2.5c) \tag{100}$$

η_c = viscosity at concentration c
η_o = viscosity of the pure solvent
φ = total volume of the dispersed phase
V = total volume of solution
c = volume concentration of the solution in $cm^3/100\ cm^3$.

In using this formula it is customary to employ the *relative viscosity*

$$\eta_r = \frac{\eta_c}{\eta_o} = 1 + 2.5c$$

or the *specific viscosity* following a proposal of Staudinger

$$\eta_{sp} = \eta_r - 1 = 2.5c$$

or finally the *intrinsic viscosity* of Kraemer

$$\eta_i = \frac{\eta_{sp}}{c} = 2.5$$

The latter gives the relative increase in internal friction due to the presence of the dispersed particles at unit volume concentration.

Einstein's viscosity law may therefore be expressed thus: If a few rigid spheres are distributed in a liquid, the coefficient of viscosity increases by a fraction which corresponds to 2.5 times the total volume of the suspended spheres.

It is noticeable that the increase of viscosity is connected only with the total volume required by the solute, and is independent of whether this is occupied by many small or few larger particles, provided, of course, that the conditions outlined above are fulfilled. This law cannot, therefore, be used for determining particle size, because neither the number nor the size of the particles appears explicitly in it. These results are valid, moreover, for the flow in a capillary tube, as shown by R. Simha.[116]

The results of the Einstein calculation have been variously tested experimentally and confirmed. Bancelin[117] and Sven Oden[118] early demonstrated with spherical sols of gamboge and sulphur that propor-

[116] R. Simha, *Kolloid Z.*, **76**, 16 (1936).

[117] J. Bancelin, *Compt. rend.*, **152**, 1582 (1911).

[118] Sven Oden, *Nova Acta Regiae Soc. Sci. Upsaliensis*, (4) **3** (1913); for further literature see e.g. H. Freundlich, *Kapillarchemie*, Leipzig 1932. Vol. 2.

tionality exists between specific viscosity and concentration if the sols are sufficiently dilute. Fig. 84 shows one of their results. Later, F. Eirich[119] subjected the Einstein relation to test in two extensive researches. Glass spheres of radii varying from 0.0075 to 0.02 cm. and spores of fungi, 4–5 μ in diameter were used. Photomicrographs of such spheres show that they comply quite faithfully with the demands of sphericity and uniformity. These model sols were measured in different viscosimeters, using special precautions, and the effects of the concentration and the dispersion of the solute were tested for small and large spheres. Table 84 shows a few results obtained by Eirich and his co-workers.

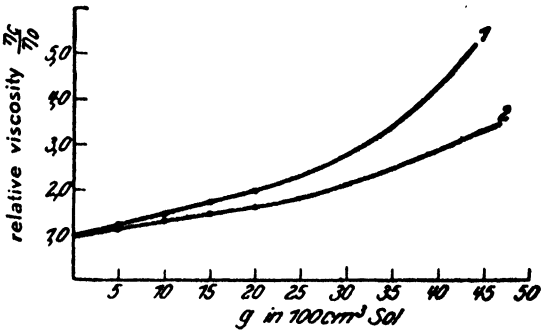


Fig. 84. Proportionality between η_{rel} and c in spherical sols.

TABLE 84

TEST OF EINSTEIN'S VISCOSITY EQUATION

Viscosimeter	Radius of spheres in cm $\times 10^{-4}$	η_{sp}/c	$\frac{\eta_{sp}-2.5c}{c^2}$
Rotating cylinder method (Couette)	3	2.5 (± 0.2)	9.0 (± 2.0)
	80	2.5 (± 0.2)	12 (± 4.0)
	160	2.5 (± 0.2)	13 (± 2.0)
Capillary tube method (Ostwald)	3	2.7 (± 0.3)	6 (± 3.0)
	80	1.8 (± 0.3)	—
	160	2.0 (± 0.3)	—
Falling ball method (Stokes)	80	2.4 (± 0.5)	—

They may be summarized roughly as follows:

1. Specific viscosity is directly proportional to concentration.
2. The proportionality factor approximates to 2.5; the lower values obtained in capillaries can be ascribed, presumably to inertia effects,

[119] F. Eirich, *Kolloid Z.*, **74**, 276 (1936); **81**, 7 (1937).

according to the experiments of F. Eirich and O. Goldschmidt together with some preliminary calculations of R. Simha.[120]

3. It is immaterial whether there are many small or few large spheres present, if the necessary conditions for the validity of the Einstein equation are satisfied.

The fundamental viscosity equation of Einstein is fully confirmed by this investigation, which affords considerable support to all the formulas derived in this field by the aid of hydrodynamic theory.

It is evident from Fig. 84 that the range of validity of the linear relation between specific viscosity and concentration is relatively small. It seemed important, therefore, to examine the dependence of internal friction upon concentration at higher concentrations. This was done for spherical suspensions, to a first approximation by Guth, Gold and Simha,[121] using a method indicated by M. v. Smoluchowski. Under the same conditions as before, but now permitting turbulent flow, there was obtained, on ignoring all terms with cubic or higher powers of c, the equation

$$\eta_c = \eta_0 (1 + 2.5c + 14.1c^2). \tag{101}$$

In addition to the linear term with the factor 2.5, there is a quadratic term with the factor 14.1. In this approximation, also, the increase in friction is independent of the absolute dimensions of the spheres, not, of course, quite strictly, because in the process of calculation it has been necessary to dispense with certain terms related to the dimensions of the dissolved particles.

The experimental testing of equation (101) is again due to Eirich and his collaborators (loc. cit.). As we have seen in the relation between osmotic pressure and concentration, it is best to plot the value of η_{sp}/c against c, whereupon, provided equation (101) is valid, a straight line is to be expected, whose ordinate intercept must be 2.5, while its slope towards the c axis corresponds to the factor 14.1.

Table 84 also shows the result of Eirich's experiments. As mentioned, the ordinate reading is quite accurate, but the mutual interaction of the spheres, which is expressed in the angle of inclination of the curve, is not indicated with the same exactitude. However, in view of the difficulties of the experiment, the approximation may be regarded as satisfactory.

If we consider the nature of the influence between the suspended spheres,

[120] F. Eirich and O. Goldschmidt, *Kolloid Z.*, **81**, 7 (1937); F. Eirich and R. Simha, *Monatsh.*, **71**, 67 (1937).

[121] E. Guth and R. Simha, *Kolloid Z.*, **74**, 266 (1936); O. Gold, *Dissertation*, Vienna 1937.

we see that disturbances arise which are caused, not by direct forces of interaction between the particles—for at the highest concentrations involved their average distance is still too great—but by the additional currents caused by the presence of the spheres in the liquid—currents which mutually disturb one another. Occasionally the opinion has been expressed that viscosity depends on concentration in a way suggesting that far-reaching forces are active between the dissolved particles. Actually it is not a question of such forces but of the mutual influence on the flow of liquid as modified by the particles.[122]

It is considerably more difficult to calculate the rise in viscosity of a liquid if rod-shaped, instead of spherical particles are suspended in it. Jeffery[123] was the first to work on this problem and, by applying hydrodynamic principles, he extended the Einstein theory to ellipsoids. Here the essential conditions for the Einstein concept—very dilute solution, rigidity of particles and gradual flow—are preserved. The calculation process also is analogous but two new complications arise:

a) Under the influence of flow, the suspended particles execute a spinning motion which leads to uncertainty in the results, to the extent that the final state of the planar distribution of the particles is dependent on the non-definable initial state and the relative viscosity is considerably affected.

b) Owing to the effect on orientation, Brownian molecular motion enters into the process and influences the end result. If, for example, the suspended particles are so large that the Brownian motion exerts no appreciable effect on them, then there is the uncertainty mentioned under (a) and discussed by Jeffery, Eisenschitz,[124] Kuhn,[125] Huggins[126] and by Guth[127] and Simha.[128] If, however, the particles are small, the directional

[122] Concerning the causes of the two other principal mechanisms of interaction, solvent immobilization and anisotropic particle form, see e.g. B. E. Hatschek, *Kolloid Z.*, **9**, 280 (1912); H. Fikentscher and H. Mark, *Kolloid Z.*, **49**, 185 (1929); F. Eirich and H. Mark, *Ergeb. exakt. Naturwiss.*, **15**, 1 (1936); R. Burgers, *First Report of Viscosity and Plasticity*, Amsterdam, New York 1935.

[123] G. B. Jeffery, *Proc. Roy. Soc. London*, (A) **102**, 163 (1923).

[124] R. Eisenschitz, *Z. physik. Chem.*, (A) **163**, 133 (1933).

[125] W. Kuhn, *Kolloid Z.*, **62**, 269 (1933).

[126] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

[127] E. Guth, *Kolloid Z.*, **74**, 147 (1936); **75**, 15 (1936); R. Simha, *J. Phys. Chem.*, **44**, 25 (1940). Compare also A. Peterlin, *Naturwiss* **26**, 168 (1938).

[128] To avoid this uncertainty, Jeffery assumed that the particles preferred positions corresponding to a minimum of dissipated energy (viscosity). A film taken by F. Eirich and J. Sverak afforded confirmation only for compact rods while more extended ones were found in maximum positions. This behavior was explained by R. Simha in unpublished researches by the "method of small oscillations."

effect of the hydrodynamic forces will constantly be destroyed by the thermal impacts of the solvent molecules and the effect of Brownian motion is to change the mathematical results.

Jeffery's calculations were supplemented and extended by Boeder,[129] Eisenschitz,[130] Kuhn[131] and by Guth and Gold.[132] The result was a great number of relations between specific viscosity, concentration and axial ratio according to the special assumptions and approximations made about the suspended particles and their behavior in the field of flow.

For the case of comparatively high concentrations and no Brownian movement, Gold and Guth calculated the following approximate formula for Couette flow and rigid rod-like particles (comp. Table 83).[133]

$$\eta_c = \eta_o \left[1 + \left(\frac{f}{2(\ln 2f - \frac{3}{2})} + 2 \right) c + k \frac{f^3}{(2 \ln 2f - 3)^2} c^2 \right] \qquad (102)$$

f = axial ratio ($l \gg d$)

k = a constant independent of the axial ratio but depending upon the type of flow. It has the order of magnitude 1.

For partial Brownian motion of small rods, there is, as yet, no satisfactory solution. In any case, the viscosity will decrease with the flow gradient and increase with increasing Brownian motion (i.e. with kT). Because of the variable gradient in a capillary viscosimeter, different results are to be expected for Couette and Poiseuille flow.

Using certain assumptions, Kuhn has obtained the following expression for the specific viscosity of elongated particles ($l \gg d$) at low concentrations and Brownian motion occurring:

$$\eta_{sp} = [\tfrac{5}{2} + \tfrac{1}{16} f^2]\, c$$

$$f = l/d \text{ (axial ratio)}$$

Simha[134] has recently given a new treatment of the case of complete Brownian motion. The indeterminateness mentioned above disappears in

[129] P. Boeder, *Z. Physik*, **75**, 258 (1932).

[130] R. Eisenschitz, *Z. physik. Chem.*, **103**, 133 (1933).

[131] W. Kuhn, *Kolloid Z.*, **62**, 269 (1933); *Z. physik. Chem.*, (A) **161**, 1, 27 (1932).

[132] O. Gold, *Dissertation*, Vienna 1937; cf. F. Eirich and R. Simha, *Monatsh.*, **71**, 67 (1937) and *Progress in Physics*, 1940 (in press).

[133] For reasons of simplicity, only formulas for large (> 50) values of the axis ratio f are given in the following, although expressions are known over the whole range of f-values.

[134] R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

this case and a unique value for the viscosity may be obtained. One gets

$$\eta_{sp} = \left[\frac{f^2}{15(\ln 2f - \frac{3}{2})} + \frac{f^2}{5(\ln 2f - \frac{1}{2})} + \frac{14}{15}\right] c \qquad (103)$$

for f larger than 50.

The discussion of these equations and the experimental conditions in which they are valid can be read in the numerous summary abstracts and original papers.[135]

They all indicate that in rigid rods there is, in fact, a characteristic relation between the axial ratio and the rise in viscosity, in the sense that the specific viscosity rises steeply, according to the extent of Brownian motion, with the axial ratio. This hydrodynamic consequence, which is exceedingly important owing to its analogy with the phenomenon in the field of high polymers, has been re-tested experimentally in recent researches by F. Eirich and co-workers.[136] They used first model suspensions (cut silk) of which the particles were so large that Brownian motion could have no appreciable effect on the arrangement of them. These results must, therefore, be compared with those relations in which thermal motion can be ignored (Comp. Table 83).

Such a comparison showed, for moderate axial ratios (l/d = 5 to 30), both the linear rise with axial ratio required by the theory and also a satisfactory quantitative agreement with the relations of Table 83 over a fair range of concentration. With elongated rods, excessive viscosities were always found, even at the highest measurable dilutions. This means that in spite of the dilution (0.1% and below), there still exists an interaction of concentration which goes beyond the range of validity of formulas containing only terms with the first power of c. This reminds us not to draw too far-reaching conclusions from values which are derived from solutions of high polymers, even at apparently adequate dilution.

Owing to the great theoretical and experimental difficulties, it is possible only to make a qualitative comparison between the results in models displaying Brownian motion and the formulas. According to these, the viscosity rises as required, both with the axial ratio and the concentration, and does so more rapidly even if moderate Brownian motion occurs. An effect of flow gradient is also appreciable. If, in addition, the above statement on the restriction of the region of dilution is true, *a fortiori*, the special result of these experiments with rigid models may be summed up

[135] See especially M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939); *J. Applied Physics*, **10**, 700 (1939). Cf. also H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[136] F. Eirich with M. Bunzl, H. Margaretha and J. Sverak, *Kolloid Z.*, **75**, 20 (1936).

by saying that they exhibit in large measure many characteristics of high polymer solutions.

A direct application of these results to the behavior of high polymeric substances is not, however, feasible, because we seldom meet with rigid rods in the latter, but usually have to assume the existence of more or less mobile thread or worm-like structures. For this reason, Eirich and Sverak have extended their experiments to flexible model materials, which could be realized in the form of swollen fine filaments of artificial silk, or as thin flexible filament crystals (cholesterol, azo dyes etc.). Such preparations prove to be very uniform in regard to length and axial ratio of the separate particles, but they offer an irregular aspect under the microscope because of their flexibility.

Their viscosities in dilute solution appear to be essentially low compared with those caused by rigid rods and the concentration interaction is reduced. This behavior may be attributed to the curling, the deformability and to the changed orientation of such particles in the flow gradient.[137]

The results reported on the viscosity of suspensions may be summarized somewhat as follows: Attempts have been made, both theoretically and experimentally, to establish criteria based on hydrodynamics for judging behavior in solutions of high polymers. Theoretically, a series of equations has been obtained for spheres and for rod-shaped particles, which lay claim to validity according to the conditions obtaining. Experimentally, these equations have been examined by using model substances, the size and shape of which could be accurately ascertained under the microscope. As far as can be seen, the theoretical relations can be essentially confirmed. Moreover, independently of theory, the models have widened our outlook on important matters such as particle orientation, behavior of flexible fibers, effect of concentration, etc.

This line of research, founded on hydrodynamic principles of viscosity, which was recognized from the first as inadequate to describe the actual conditions in high polymers and merely aimed at the completion of our fundamental knowledge regarding the hydrodynamics of colloidal solutions, has been supplemented by the direct investigation of the systems concerned.

In particular, there are the viscosity determinations on well defined hydrocarbons and other long chain substances carried out first by Staudinger and Nodzu[138] and later, with considerably increased accuracy, by

[137] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939), has considered flexibility, using Kuhn's hydrodynamic approximations.

[138] See H. Staudinger, *Book*, p. 60 et seq.; *Z. Elektrochem.*, **40**, 436 (1934); *Naturwiss.*, **25**, 673 (1937); *Angew. Chem.*, **49**, 801 (1936); *Ber.*, **69**, 205, 1180 (1936); *Helv. chim. Acta*, **19**, 204 (1936); *Kolloid Z.*, **82**, 129 (1938).

K. H. Meyer and v. d. Wyk;[139] Tables 85 and 86 give some important results. From them it is evident that Staudinger's equation

$$\eta_{sp} = K_m \cdot M \cdot c \tag{105}$$

is valid only with limited accuracy over the range of these materials and, according to K. H. Meyer and v. d. Wijk, could better be replaced by the equation

$$\eta_{sp} = 145.5\, Mc - 15.981c \tag{106}$$

TABLE 85

INFLUENCE OF ABSOLUTE PRECISION OF MEASUREMENT OF η_{rel} ON THE ACCURACY OF η_{sp}

$\eta_{sp} \times 10^4$	Percentage error of η_{sp}, if the error in the measurement of η_{rel} is 0.04%; the sensitivity of η_{sp} is evident
150	2.6
200	2.0
300	1.3
400	1.0
500	0.8

TABLE 86

K_m VALUES FOR THE PARAFFINS FROM C_{17} TO C_{34} ACCORDING TO THE PRECISION MEASUREMENTS OF MEYER AND VAN DER WYK

Substance	Molecular weight	$K_m \cdot 10^6$	
		measured	calculated
$C_{17}H_{36}$	240.3	79 ± 2	(79.0)
$C_{18}H_{38}$	254.3	82 ± 2	82.4
$C_{19}H_{40}$	268.3	85 ± 2	86.0
$C_{20}H_{42}$	282.3	92 ± 2	88.9
$C_{22}H_{46}$	310.3	94 ± 2	(94.0)
$C_{26}H_{54}$	366.4	102 ± 2	101.9
$C_{30}H_{62}$	422.5	106 ± 1	107.6
$C_{34}H_{70}$	478.5	109	112.9

the constants relate to 20.0°C. and a solution of 0.886 per cent by weight in CCl_4. Fig. 85 shows the result more clearly. The continuous line corresponds to the empirical relation (106) and the broken line to the Staudinger equation; the circles indicate the experimental data.

A very important contribution to this problem has been made recently

[139] K. H. Meyer and A. J. A. v. d. Wyk, *Helv. chim. Acta.*, **18**, 1067 (1935); *J. chim. phys.*, **32**, 549 (1935); *Kolloid Z.*, **76**, 278 (1936); *Ber.*, **69**, 545 (1936); *Helv. chim. Acta*, **19**, 218 (1936). Comp. also E. L. Hirst and G. T. Young, *Proc. Chem. Soc.*, **7**, 1471 (1939).

by Fordyce and Hibbert.[140] They prepared[141] members of the polyoxyethylene glycol series, having uniform molecular weights, up to values around 8000 and determined with great care the specific viscosities of these substances in two solvents at three different temperatures.

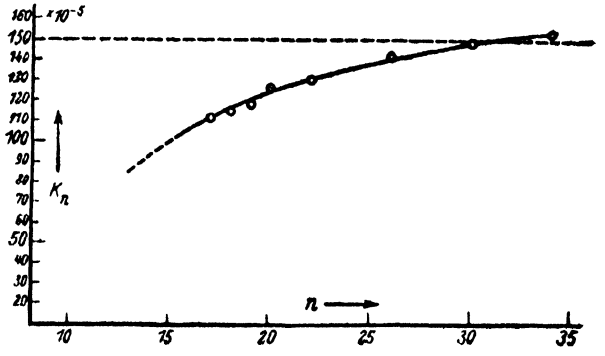


Fig. 85. The ratio $\frac{\eta_{sp}}{c}$ as function of chain length n.

If one plots the specific viscosity divided by c (intrinsic viscosity) against the molecular weight, one obtains a straight line within the molecular weight range 810–8200. Below this there is a sharp departure from linearity. Fordyce and Hibbert conclude from their experiments that the Staudinger equation is valid for high molecular weights but that it has to be replaced by

$$\eta_i = \frac{\eta_{sp}}{c} = K'_m M + \beta$$

as soon as lower members of a given polymeric homologous series are involved.

The experimental material which has been drawn on for proving this relation in the field of hemi- and eu-colloidal substances is very extensive; the particle weights measured osmotically by various authors have been compared with those calculated from equation (105) and it has been found in this field also that Staudinger's equation is certainly of considerable importance in the approximate estimation of molecular weights, although it cannot be considered being an exact law.

It is a problem to understand how the simple equation (105) which was formulated by Staudinger at a date when there was much less experimental material than today, is able to represent such complex conditions to such close approximation and wherein lie the physical reasons for this ability. Staudinger himself has expressed the opinion that the fiber

[140] R. Fordyce and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 1910, 1912 (1939).
[141] R. Fordyce, E. L. Lovell and H. Hibbert, *J. Am. Chem. Soc.*, **61**, 1905 (1939).

molecules in the solution are long, rigid rods which, by mutual hindrance in the course of their movements, produce the high viscosity of the solutions. Considerable difficulties arise, however, in applying this idea. One is that, in this case, the viscosity must increase proportionally to the square of the molecular weight, which is actually not so; another is that, in view of the numerous data regarding internal mobility of molecules, it is extremely difficult to assume the existence of very long, rigid, thread-like particles.

For a simple understanding of equation (105) it seems much more feasible to assume a certain internal mobility of long chain particles. H. Mark[142] first suggested this possibility; W. Kuhn,[143] simultaneously with E. Guth,[144] formulated it quantitatively, I. Sakurada,[145] Hess and Philippoff[146] and, especially, Huggins[147] have recently carried out an exhaustive examination on a large amount of experimental material.

In principle, this solution means an application of internal molecular statistics to the problem; in the presence of considerable internal mobility, the effective length of the thread-like molecules need not be identified with their maximum length; rather the effective length is actually proportional to the square root of the total length.

In addition to this simple consideration, which appears to present only a rough idea of the conditions, there is an exhaustive discussion in progress on the Staudinger equation.

Staudinger deduced several conclusions from the validity of his equation, which may perhaps best be described as follows:

1. All molecules in the solutions concerned are dispersed individually (macromolecularly) at sufficient dilution.
2. These molecules behave like extended, rigid rods.
3. The high viscosity is produced by the mutual hindrance of the rods

[142] H. Mark, *Congr. Int. Quim. pura y appl.*, Madrid 1934, Vol. 4, p. 197.

[143] W. Kuhn, *Kolloid Z.*, **68**, 2 (1934); *Angew. Ch.*, **49**, 858 (1936); also *Z. physik. Chem.*, (A) **161**, 1 (1932).

[144] E. Guth and H. Mark, *Ergeb. exakt. Naturwiss.*, **12**, 146 (1933); also E. Guth and H. Mark, *Monatsh.*, **65**, 93 (1934); E. Guth, *Kolloid Z.*, **74**, 147 (1936); **75**, 15 (1936).

[145] I. Sakurada, *Kolloid Z.*, **82**, 345 (1938); *Z. physik. Chem.*, (A) **179**, 227 (1937); also *Kolloid Z.*, **63**, 311 (1933); **64**, 195 (1935); **67**, 1045 (1934); *Cellulosechem.*, **17**, 130 (1936).

[146] W. Philippoff and K. Hess, *Z. physik. Chem.*, (B) **31**, 237 (1936); see also W. Philippoff, *Kolloid Z.*, **71**, 5 (1935); K. Hess, C. Trogus, L. Akine and I. Sakurada, *Ber.*, **64**, 408 (1931); K. Hess and B. Rabinowitsch, *Ber.*, **65**, 1409 (1932) and K. Hess, *Naturwiss.*, **22**, 469 (1934).

[147] M. L. Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939); *J. Applied Phys.* **10**, 700 (1939).

in Brownian motion, which thereby act as if they occupied a flat, cylindrical volume whose diameter equals the length of a particle.

4. On the basis of items 1 to 3 the linear relationship between viscosity and molecular weight in dilute solutions has proved accurate.
5. This relationship enables molecular weight to be determined over a range not possible by other methods.

It may be useful to discuss briefly these different statements.

The macromolecular isolated state will presumably be met with only in a fraction of the cases considered, for example, in the paraffins, polystyrenes, polyoxymethylenes and possibly also in rubber. But for cellulose and its esters, particularly, a different state of solution is indicated. For and against these views we may mention the effect of temperature on relative viscosity which is found to be small by Staudinger[148] and his collaborators, but considerable by others, for example, Danes,[149] Eckenstamm,[150] McBain,[151] K. H. Meyer,[152] Philippoff[153] and others. Lieser[154] has recently adduced important reasons for the existence of micellar thread-like molecular aggregates in solutions of cellulose xanthate.

The concept of the rigidity of dissolved, thread-like molecules is difficult to combine with the existing knowledge of structure, and behavior of long chain molecules described by Guth and Mark,[155] Meyer,[156] W. Kuhn,[157] Wo. Ostwald,[158] Sakurada[159] and others. In particular, W. Kuhn has calculated in a very interesting manner the form of long chain molecules on the basis of a certain amount of rotatory power; he arrived at the idea of loose coils with length and cross-section proportional to the root of the number of links in the chain. Kuhn considers that this result explains not only the observation of viscosimetry, but also those of double refraction accompanying flow, dielectric constant and other properties.[160]

According to the hydrodynamic theories discussed in the previous

[148] H. Staudinger and co-workers, in numerous treatises, e.g. *Ber.*, **61**, 29, 33 (1929).
[149] V. Z. Danes, *Kolloid Z.*, **68**, 110 (1934).
[150] A. von Ekenstamm, *Über Cellulose-Lösungen in Mineralsäuren.* Lund 1936.
[151] J. W. McBain, *J. Phys. Chem.*, **30**, 239 (1926); also *J. Phys. Chem.*, **38**, 1219 (1934) and *Ind. Eng. Chem.*, **28**, 470 (1936).
[152] K. H. Meyer and A. J. A. van der Wijk, *Kolloid Z.*, **76**, 278 (1936).
[153] W. Philippoff, *Angew. Chem.*, **49**, 855 (1936).
[154] T. Lieser, *Ann. Chem.*, **582**, 48, 56 (1936).
[155] E. Guth and H. Mark, *Erg. exakt. Naturw.*, **12**, 146 (1933).
[156] K. H. Meyer, e.g. *Kolloid Z.*, **76**, 278 (1936); or *Angew. Chem.*, **1934**, 359.
[157] W. Kuhn, e.g. *Kolloid Z.*, **68**, 2 (1934).
[158] Wo. Ostwald, *Kolloid Z.*, **70**, 73 (1935); **81**, 195 (1937).
[159] I. Sakurada, *Kolloid Z.*, **82**, 345 (1938); *Z. physik. Chem.*, (B) **38**, 407 (1938).
[160] W. Kuhn, *Angew. Chem.*, **57**, 648 (1938).

chapter, the third item is based on an accurate supposition in so far as viscosity can assume very high values with increasing axial ratio, even at low concentrations. The mechanism assumed by Staudinger is, however, certainly too simple and it will need a much more detailed discussion of all influences before a thorough understanding is reached.[161]

According to the discussion of items 1–3, a linear relation is actually possible but cannot be derived. In addition to this, the results of other workers and the interpretation of the Staudinger material have not indicated a strict proportionality in the sense of (105). According to Wo. Ostwald,[162] Staudinger's formula can express only a tangent to any curves, e.g. S-shaped, which may represent the actual function viscosity-molecular weight. K. H. Meyer and van der Wijk[163] consider the departures too great, even in paraffins, for a rule to be involved. According to these workers, constitutional influences are of greater importance, whereas Staudinger considers the degree of polymerization to be determinative.

The extrapolation of equation 105 to very large molecular weights has aroused particular controversy. Staudinger has attempted to confirm his results in the eu-colloidal field by introducing other methods. The molecular weights determined osmotically by G. V. Schulz,[164] to a few hundred thousand, which agree satisfactorily with viscosimetric data, are, of course, subject to a series of objections: On the one hand, they were obtained from comparatively concentrated solutions with the aid of constants taken from the dilute range; on the other, the corrections for the heterodispersion, which is always present, even in well fractionated products, and which affects osmotic pressure and viscosity differently, are certainly not reliable. Checking by rates of sedimentation and diffusion in the ultracentrifuge by Signer and Gross[165] gave good agreement in some cases but also variations of over 100% in others.

If we summarize the results of the above brief review of a field still in an active state of development, it is clear that the conditions obtaining

[161] See the detailed investigations of E. Guth and co-workers; e.g. *Kolloid Z.*, **74,** 147, 276 (1936); **75,** 15, 20 (1936); **76,** 16 (1936); **81,** 7 (1937). Further F. Eirich and R. Simha, *Monatsh.*, **71,** 67 (1937).

[162] Wo. Ostwald, *Kolloid Z.*, loc. cit. on page 235.

[163] K. H. Meyer and van der Wijk, *Helv. chim. Acta,* **18,** 1067 (1935); *Kolloid Z.*, **76,** 278 (1936).

[164] G. V. Schulz, *Ber.*, **68,** 2320 (1935); *Z. physik. Chem.*, (A) **176,** 317 (1936); (B) **32,** 27 (1936).

[165] R. Signer and H. Gross, *Helv. chim. Acta,* **17,** 59, 335 (1934); *Kolloid Z.*, **70,** 24 (1935); *Trans. Faraday Soc.*, **32,** 296 (1936).

are very much more complex than one would assume from the initial investigations. It is presumably impossible to explain all phenomena by one single model without its becoming too intricate and uncertain. Nor does the common division into molecular and micellar colloids hold in the original sense.

As American research workers[166] have long maintained, we must leave open the possibility in principle of different forms of solution for any substance; the type of dispersion or equilibrium established will depend on solvent, concentration, temperature and frequently even on pre-treatment, as well as other factors.

The effect of any one of these factors is, however, in no way simple. For the temperature effect, for example, the following mechanisms at least may be postulated: Fusion of micellae, desorption of solvent, dissociation or formation of aggregates resulting in change of particle size and shape, increase in external and internal Brownian motion and consequent contraction of the fiber molecule, and change in adjustment to the flow gradient. All these processes may occur individually or in combination and can be entirely or partially compensated by each other.

By and large, the Staudinger equation represents a generally applicable, simple and, therefore, very useful means of estimating approximate molecular weights. Nevertheless, it hardly allows of any reliable conclusions regarding molecular peculiarities in the system being investigated.

In attempting to summarize to what extent viscosity measurements contribute to our present knowledge of high molecular weight solutions, we may say: Viscosimetry confirms in principle the ideas which have been worked out on the basis of other methods (vapor pressure, osmotic pressure, ultracentrifuging). In highly dilute solutions the macromolecules represent mainly isolated, flexible chains, which are in a curled up or tangled condition and which perform an external, as well as an internal, Brownian movement (macro- and micro- Brownian movement, according to Kuhn). These soft, worm-like particles have no definite shape but carry out irregular motions under the influence of thermal impacts by the molecules of the surrounding liquid. They can, to a certain extent, attach solvent molecules to their surfaces by means of forces and they may carry with them still more solvent molecules, which are immobilized by geometrical means. In a field of flow they move according to the laws of hydrodynamics.

Such a conception seems to be in agreement with the absolute values

[166] e.g. E. O. Kraemer and R. V. Williamson, *J. Rheol.*, **1**, 76 (1929); S. E. Sheppard, *J. Rheol.*, **1**, 471 (1930); J. W. McBain, *J. Phys. Chem.*, **30**, 239 (1926); further H. Fikentscher and H. Mark, *Kolloid Z.*, **49**, 135 (1930); H. Mark, *Kolloid Z.*, **53**, 1 (1930); Further F. Eirich and H. Mark, *Erg. exakt. Naturw.*, **15**, 1 (1936).

of viscosity in highly dilute solutions; also, with the dependence of viscosity upon temperature and molecular weight; it is, furthermore supported by the osmotic behavior of such solutions and, finally, by their rates of diffusion and sedimentation.

Even at concentrations which are still very low, interactions between these particles take place and result in a rapid rise of osmotic pressure and viscosity with concentration. It will be appropriate, therefore, to pass to the description of conditions at higher concentrations.

f) Expressions Relating to the Effect of Concentration upon Viscosity

The somewhat detailed discussion of the Staudinger rule permits a briefer account of a series of empirical formulas dealing with the effect of concentration upon viscosity. More extensive discussion of all relevant problems will be found in Hatschek,[167] Guth and Mark,[168] Hess,[169] Bredée and de Booys,[170] Houwink,[171] Philippoff[172] and Sakurada.[173] Generally speaking, it is possible to establish very useful equations over a fairly wide range. The many attempts, however, to attribute a physical significance to the constants involved, which, from the nature of things, they can possess at best only in a few cases and over a limited range of concentration, must be regarded with a certain amount of caution.

We shall now enumerate a few of the principal equations which have proved valid in a series of cases:

Arrhenius;[174]

$$\log \eta_r = k \cdot c \tag{I}$$

In connection with this equation see also Berl and Büttler,[175] Duclaux and Wollmann,[176] Bredée and de Booys.[177]

Arrhenius;[178]

$$\log \eta_r = k \frac{100c}{100 - nc} \tag{II}$$

---

[167] E. Hatschek, *Die Viskosität der Flüssigkeiten.* Dresden 1929.

[168] E. Guth and H. Mark, *Erg. exakt. Naturw.*, **12**, 146 (1933).

[169] K. Hess, *Z. physik. Chem.*, (B) **31**, 237 (1936).

[170] H. L. Bredée and J. de Booys, *Kolloid Z.*, **79**, 31, 43 (1937).

[171] R. Houwink, *Kolloid Z.*, **79**, 138 (1937).

[172] W. Philippoff, *Z. physik. Chem.*, (B) **70**, 639 (1937).

[173] I. Sakurada, particularly *Kolloid Z.*, **82**, 345 (1938); also *Z. physik. Chem.*, (B) **38**, 407 (1938).

[174] S. Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

[175] E. Berl and R. Bütler, *Z. ges. Schiess- und Sprengstoffwesen*, **5**, 92 (1910).

[176] J. Duclaux and R. Wollmann, *Compt. rend.*, **152**, 1580 (1911).

[177] H. L. Bredée and J. de Booys, *Kolloid Z.*, **79**, 31, 43 (1937).

[178] S. Arrhenius, *Medd. Vetenskapakad., Nobel-inst.*, **4**, 13 (1916).

Fikentscher;[179]

$$\log \eta_r = k + \frac{75k^2}{1 + 1{,}5 \cdot kc} \tag{III}$$

Papkov;[180]

$$\log \eta_r = k \cdot c^{\alpha} \tag{IV}$$

Houwink,[181] Bungenberg de Jong, Kruyt and Lens;[182]

$$\log \eta_r = ac + bc^2 \tag{V}$$

Fikentscher and Mark;[183]

$$\eta_{sp} = k \frac{bc}{1 - bc} \tag{VI}$$

Sakurada,[184] Baker and Mardles;[185]

$$\eta_r = (1 + ac)^n \tag{VII}$$

Bredée and de Booys;[177]

$$\eta_r = \left[1 + \frac{2.5\, b}{6} \cdot c\right]^6 \tag{VIII}$$

These equations were tested over the whole known concentration range on numerous sols of synthetic and natural high polymers, particularly on synthetic resin suspensions, such as polystyrenes, polyethylene oxides on proteins, gum arabic, cellulose, cellulose esters, rubber and others. In general, it was found that equations with one and two constants prove capable of expressing the viscosity—concentration function, by suitable choice of constants (see further below). In many cases it is astonishing how great a concentration range can be covered by using a single constant; with two or more constants, particularly if they are in the exponent, the fit is so close that it is possible to express approximately the most diverse functions of concentration.

The best way to reach a basis for comparing all these equations seems to be the one adopted by Bredée and de Booys. This consists of expanding η_{sp} in a power series of the volume concentration c and obtaining

$$\eta_{sp} = Ac + Bc^2 + Cc^3 + \cdots \tag{107}$$

---

[179] H. Fikentscher, *Cellulosechem.*, **13**, 58 (1932).

[180] S. Papkov, *Kunststoffe*, **25**, 253 (1935).

[181] R. Houwink, *Kolloid Z.*, **79**, 138 (1937).

[182] H. G. Bungenberg de Jong, H. R. Kruyt and W. Lens, *Kolloid Beihefte*, **36**, 429 (1932).

[183] H. Fikentscher and H. Mark, *Kolloid Z.*, **49**, 135 (1930).

[184] I. Sakurada, *Z. physik. Chem.*, (B) **38**, 407 (1938).

[185] F. Baker and E. W. J. Mardles, *Trans. Chem. Soc.*, **103**, 1655 (1913); *Trans. Faraday Soc.*, **18**, 3 (1923).

As in the case of osmotic pressure (compare page 230), all terms in higher powers than one can be neglected at very low concentrations and the first coefficient of this expansion, A, allows an approximate estimation of the size and shape of the particles under certain favorable conditions (compare the relations in Table 83 on page 279). Yet, with the interpretation of B, we immediately meet very considerable difficulties and its meaning, to date, is understandable only in the case of spherical suspensions. There it assumes according to equation (101) on page 282 a value of about 14. In all other cases the analysis has not yet been carried far enough to warrant an interpretation of B from the standpoint of molecular theory.

In order to show to what extent the various equations cited above differ, some of them are here expanded into series and compared:

(I) $$\eta_{sp} = 2.30kc + \frac{2.30^2}{2} k^2 c^2 + \cdots$$

The second coefficient B corresponds to $\frac{2.30^2}{2} k^2$.

(III) $$\eta_{sp} = \frac{2.30}{4} (3k^2 + 4k)c + \text{higher terms}$$

B corresponds to a complicated function of k.

(VI) $$\eta_{sp} = kbc + \frac{kb^2}{2} c^2 + \cdots$$

B corresponds to kb^2 where b is the co-volume.

(VIII) $$\eta_{sp} = 2.5bc + \frac{15 \times 2.5}{6^2} b^2 c^2 + \cdots$$

A corresponds to a term similar to the Einstein term; B corresponds to the square of b, which denotes the co-volume.

No thorough comparison of all these empirical formulas with the relations contained in Table 83 has yet been made, nor with the other experimental data available today. However, the importance of this problem suggests that an attempt be made in that direction and it is planned to bring out in this series on High Polymeric Chemistry a volume devoted solely to viscosity.

It suffices to say that, in whatever direction this field develops, a series of empirical constants, e.g. the characteristic viscosity of Fikentscher or the intrinsic viscosity of Kraemer[186] are already serving a useful purpose in industry as a means of testing solutions used in manufacturing processes.

[186] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

G. KINETIC PHENOMENA IN HIGH POLYMER CHEMISTRY

1. The Phenomena of Diffusion

In the chemistry of high molecular weight substances, questions of velocity, in addition to those of equilibrium, often play a very important rôle in the preparation and in the technical handling of these substances, for instance, the rates of chemical reaction, of diffusion and of sedimentation are of preeminent importance. In many cases a combination of diffusion and chemical reaction is involved, because the chemically active substance in such systems cannot be brought to the place of reaction by mechanical convection, as is possible in homogenous gaseous or liquid phases, but only by way of a diffusion process. It will be convenient therefore to give a short account if the phenomenon of diffusion, its measurement, the interpretation of such measurements and the principal results are obtained heretofore. It may be mentioned here that high polymeric chemical reactions will be treated more exhaustively in another volume of this series.

a) The Free Diffusion of Dissolved Particles; General Principles

If particles of dimensions having the order of magnitude 1 μ or less are placed in a liquid, an irregular swarming, the so-called Brownian movement, occurs. Quantitative examination of this phenomenon and its theoretical interpretation have led to the conviction that the momentum acquired by the suspended particle is transmitted through collisions with the molecules of the solvent in very rapid motion, so that the Brownian movement reveals the irregular molecular motion of the liquid.

As calculated by Einstein and Smoluchowski and proved experimentally by Perrin and Svedberg, the mean square distances traversed by the moving particles are proportional to the duration of their movement, and a particle occupies, in the course of sufficient time, every volume element of the vessel provided for it remaining, on an average, for the same length of time in volume elements of identical size.

Given a large number of particles, each one of them moves independently under the influence of the thermal impacts of the molecules of the liquid,

travels around the containing vessel, occupies all volume elements and remains, on an average, equally long in each. If the observed particles are at first confined in a given space, they disperse in course of time and finally spread uniformly throughout the whole volume at their disposal.

This phenomenon is termed *free diffusion.* Statistical considerations indicate the possibility of calculating the concentration of the diffusing particles with a given initial situation as a function of space and time. Assume that no force effects exist between the suspended particles and the molecules of the solvent, but only that occasional transmissions of collision momentum occur, and further, that the particles do not interfere with each other's movements and are very small in comparison with the dimensions of the vessel; in a unidimensional diffusion process, we obtain, for the probability dW that at a time t a particle will be encountered in the plane between x and $x + dx$, the relation

$$dW = \frac{1}{\sqrt{\pi D t}} \cdot e^{-\frac{x^2}{4Dt}} \cdot dx. \tag{108}$$

D = coefficient of diffusion.

(This presumes that the observed process has begun in the plane $x = 0$ at the time $t = 0$.)

Obviously this probability dW is proportional to the concentration of the diffusing particles in the plane between x and $x + dx$ at the time t. If it is possible, therefore, to measure, by any experimental method, the magnitudes dW, x and t, the coefficient of diffusion D may be calculated from equation (108). A few recent methods of performing this task will be described below; it need only be added that, with certain assumptions, it is possible to estimate, from the coefficient of diffusion, the size of the suspended particles. If we assume that the diffusing particles are spherical, or, at least, approximately spherical, and are large in comparison with the molecules of the liquid, D, according to Stokes, Nernst and Einstein,[1] bears the following relation to the radius r of the particle

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r}. \tag{109}$$

In this equation, R is the gas constant, T the absolute temperature, N the Loschmidt number and η the viscosity of the solvent.

It is, of course, essential that Fick's law, according to which the coefficient of diffusion should be independent of concentration, hold in all

[1] W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888); A. Einstein, *Ann. Physik*, **77**, 549 (1905); see also *Ostwald's Klassiker d. exakten. Naturwiss.*, Vol. 199.

cases; accordingly, the measurement of D must be performed in such a way that the accuracy of this proviso can be examined simultaneously.

By inserting the absolute values of R and N in equation (109) and by assuming a temperature of 300° absolute and an absolute viscosity of solvent of 0.01 (H_2O at 20°) we obtain the very simple relation

$$D \cdot r \sim 2 \times 10^{-13},$$

by which the coefficient of diffusion is given in absolute measure, cm^2 per sec. To bring out more clearly the meaning of the value D, it may be observed that it indicates the mean path travelled by a particle of given size in one second if its diffusion proceeds at unit concentration gradient.

b) Measurement of Rate of Diffusion

It would lead too far afield to recount all the arrangements that have been proposed during the years for determining coefficients of diffusion experimentally; a summary will be found e.g. in the articles of Ulmann,[2] Lehner and Smith[3] or in the book of Valkó.[4] In view of the great importance of diffusion measurements, which has been reaffirmed recently, especially through newer work in estimating the dispersivity of dyestuff solutions, it may be fitting to describe briefly at least a few of the most important and recently employed methods.

A precision method for determining D was devised by E. Cohen and Bruins;[5] it allows of measurements with a limit of error of a few thousandths and constitutes, at present, the most accurate and reliable method for systematic experiments in this field.

If, as may often be the case in the examination of high polymeric substances, precision measurements are not required, but merely an estimation of particle size, it is possible to use considerably simpler arrangements, for example, those of Oeholm[6] or of Northrop and Anson;[7] they have been used in the field of the cellulose derivatives, particularly by Herzog and his co-workers[8] and by McBain and his school.[9] The micro-method of Fürth[10] has however, attained great importance recently; it eliminates

[2] M. Ulmann, *Molekülgrössenbestimmung hochpolymerer Naturstoffe.* Dresden and Leipzig 1936, p. 80 et seq.

[3] S. Lehner and J. E. Smith, *Colloid Symposium Monograph*, **13**, 65 (1936).

[4] E. Valkó, *Die kolloidchemischen Grundlagen der Textilchemie.* Berlin **1937.**

[5] E. Cohen and H.R. Bruins, *Z. physik. Chem.*, **103**, 349, 404 (1923).

[6] L. W. Oeholm, *Z. physik. Chem.*, **50**, 309 (1905).

[7] J. H. Northrop and M. L. Anson, *J. gen. Physiol.*, **12**, 543 (1929).

[8] R. O. Herzog and A. Deripasko, e.g. *Kolloid Z.*, **39**, 250, 252 (1926).

[9] See J. W. McBain and T. H. Liu, *J. Am. Chem. Soc.*, **53**, 59 (1931).

[10] R. Fürth, *Z. Physik*, **79**, 275, 277 (1932).

several of the sources of error met with in the ordinary arrangements and permits a relatively accurate measurement of the coefficient of diffusion in a very short time (20–30 minutes). Fürth and his collaborators[11] and Lehner and Smith[12] have carried out a series of measurements on dyestuff solutions and have ascertained the influence of different conditions on the dyeing process. The diffusion process is carried out in a small cell cemented to a microscope slide and the change of concentration followed under the microscope by comparison with a standard solution. The observations are then extrapolated graphically to infinite dilution if the validity of Fick's law is not evident from the experiments themselves. An accurate micro-method has also been described by Lamm.[13]

c) *A Few Important Results*

Experiments with two azo dyes gave, in this way, values for D of 4.3 and 3.5×10^{-6}, which correspond to particle diameters of 4.6 and 5.8 Å calculated from equation (109); these values are in excellent agreement with expectation from the structure of the two dyes. With increasing concentration, the coefficients of diffusion decrease, a circumstance which is attributable to an increase in particle radius by association. Table 87 gives coefficients of diffusion for several dyestuffs of different origin with a reference to the literature; it is evident that relatively high D values occur; these are attributed by Valkó to electro-kinetic effects, since, in the cases considered, fairly strong mono- or di-basic acids are involved.

Table 88 by Lehner and Smith[14] shows the influence of the addition of electrolyte on the coefficient of diffusion; in this case there is evidently association to larger secondary particles.

Table 89 shows the effect of temperature[15] in presence of electrolytes; between 25° and 95° the particle size decreases materially. It is clear from the last column that in Dyestuff I, for example, the degree of association is reduced from 28 to 5.

We see from this short account that measurements of free diffusion, with the present state of experimental technique, are able to afford a very good picture of the behavior of large molecules in solution; the investigations on high polymeric substances will be described with all details in

[11] R. Fürth and co-workers, *Kolloid Z.*, **41**, 300, 304 (1927).

[12] S. Lehner and J. E. Smith, *J. Am. Chem. Soc.*, **56**, 999 (1934); **57**, 497, 504 (1935).

[13] O. Lamm and J. Polsen, *Biochem. J.*, **30**, 528 (1936). Compare also recent measurements of L. Friedman and P. G. Carpenter, *J. Am. Chem. Soc.*, **61**, 1745 (1939).

[14, 15] S. Lehner and J. E. Smith, *Colloid Symposium Monograph*, **13**, 65 (1936).

another volume of this series. It may merely be pointed out here that the molecular weights which have been obtained by different authors with

TABLE 87

Dyestuff	Concentration g per l	$D \cdot 10^6$	Literature
Azogrenadine S	0.5—5.0	8.38—7.86	[1]
Congored	0.1—5.0	6.63—7.73	[1]
Benzopurpurin 4 B	0.2—5.0	6.12—7.48	[1]
Bordeaux Extra	0.8—2.5	5.42—5.66	[2]
Congorubin	5.0	5.51—5.59	[2]
Dyestuff II	0.5	7.73	[3]

[1] E. Valkó, *Trans. Faraday Soc.*, **31**, 230 (1935).

[2] C. Robinson, *Trans. Faraday Soc.*, **31**, 245 (1935).

[3] S. Lehner and J. E. Smith, *Colloid Symposium Monograph*, **13**, 65 (1935); Dyestuff II is p-sulfobenzazobenzazo-6-benzoyl-p-aminobenzoyl-amino-naphthol-3-sodium sulphonate.

TABLE 88

Dyestuff in gms. per liter	Addition	$D \cdot 10^6$	r in Å	Degree of association
Dyestuff II	0.027-n. NaCl	2.08	11.7	11
0.5	0.107-n. NaCl	1.25	16.0	28
Dyestuff II	0.027-n. NaCl	0.71	33.7	205
0.5	0.107-n. NaCl	0.72	34.2	214
Benzopurpurin 4 B	0.01- n. NaCl	2.69	9.0	4
	0.025-n. NaCl	0.92	26.4	105
1.0	0.05- n. NaCl	0.39	62.2	370
	0.1- n. NaCl	1.64	14.8	19

TABLE 89

Dyestuff in 0.5 gm. per liter	Temperature	$D \cdot 10^6$	r in Å	Degree of association
	25.0°	1.52	16.0	28
	50.1°	3.10	13.7	18
Dyestuff I	80.0°	7.10	9.3	5.5
	95.5°	10.05	9.0	5.0
	25.1°	0.96	25.3	87
	50.1°	1.75	24.6	80
Dyestuff II	80.6°	3.86	18.8	36
	95.4°	7.80	11.3	7.7

the diffusion method agree fairly well with the results of osmotic and viscosimetric measurements. Table 90 shows some examples.

TABLE 90

APPLICATION OF THE ULTRACENTRIFUGE FOR THE DETERMINATION OF THE MOLECULAR WEIGHT

Substance	Method Applied	Molecular Weight (Particle Weight)	Remark	Reference
Cotton cellulose	Sedimentation equilibrium	200,000-300,000	In Cuoxam sol. calculated for $(C_6H_{10}O_5)x$	1
"	"	40,000	Presumably not diluted enough; calculated for $(C_6H_{10}O_5)x$	2
Regenerated cellulose	"	90,000-110,000	In Cuoxam sol. calculated for $(C_6H_{10}O_5)x$	1
Cellulose acetate	"	50,000-250,000	In acetone, different fractions	3
Cellulose nitrate	"	100,000-160,000	In acetone	3
Ethyl cellulose	"	125,000	In dioxane	3
Methyl cellulose	"	14,000-38,000		4
Poly-ω-hydroxy decanoic acid	"	27,000		5
Polystyrene	Sedimentation equilibrium and velocity	30,000-270,000		6
Polychloroprene	Sedimentation equilibrium	153,000-225,000		4
Rubber	"	64,000	In toluene	4
Ovalbumin	Sedimentation equilibrium	34,500	—	7
Cellulose acetate	Free diffusion	10,000-50,000	In acetone calculated	8
Cellulose nitrate	"	75,000	for $(C_6H_{10}O_5)x$	9
Ovalbumin	"	29,000	In water	10
Haemoglobin	"	65,000-68,000	"	11

[1] E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 753 (1935).

[2] A. J. Stamm, *J. Am. Chem. Soc.*, **52**, 304 (1930).

[3] E. O. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

[4] The Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Oxford 1940; article of E. O. Kraemer.

[5] E. O. Kraemer and W. D. Lansing, *J. Am. Chem. Soc.*, **55**, 4319 (1933).

[6] R. Signer and H. Gross, *Helv. chim. Acta*, **17**, 59, 335, 726 (1934); ibidem, **18**, 701 (1935).

[7] The Svedberg, *Kolloid Z.*, **67**, 2 (1934).

[8] D. Krüger and H. Grunsky, *Z. physik. Chem.*, (A) **150**, 115 (1930); D. Krüger, *Celluloseacetate*, Dresden & Leipzig, 1933.

[9] R. O. Herzog and H. Kudar, *Z. physik. Chem.*, (A) **167**, 841 (1933); see also R. O. Herzog and A. Deripasko, *Cellulosechem.*, **13**, 25 (1932); R. O. Herzog and W. Herz, *Trans. Faraday Soc.*, **25**, 57 (1933).

[10] R. O. Herzog, *Z. Elektrochem.*, **13**, 533 (1907); J. Gróh, *Biochem. Z.*, **173**, 249 (1926).

[11] K. G. Stern, *Z. physiol. Chem.*, **217**, 237 (1933).

d) The Application of High Centrifugal Fields; General Principles of Centrifugal Analysis

The Svedberg[16] was the first to use high speed centrifuges for the analysis of colloidal systems; he has brought the method to a high state of perfection in the course of twenty years and one can predict a very successful development in the future. The possibilities of the ultracentrifuge are very numerous. They range from the separation of isotopes to the field of medical chemistry. It is a fact of great importance that Svedberg's original apparatus, which was rather costly to make, has been simplified in past years by Bechhold and Schlesinger,[17] Elford,[18] Henriot and Guguenard,[19] McBain,[20] Beams,[21] Biscoe, Pickels and Wyckoff,[22] and while the highest efficiency is not reached in these modifications, very useful results are obtainable in special problems. In particular, the application of air drive and the separation of the actual centrifuge from the drive have brought great advantages with them. Recently a comprehensive book on the ultracentrifuge was published by Svedberg and his co-workers containing all details of construction and use. It will, therefore, be sufficient to give a rather brief outline of the principles and just mention some of the most important results.

The ultracentrifuge makes possible the estimation of several important constants of a suspension by measuring

a) the sedimentation rate
b) the sedimentation equilibrium
c) the coefficient of diffusion.

a) The rate of sedimentation is determined by observing the rate of fall of a meniscus which separates the solution from the pure solvent; in the majority of cases the color of the solution, its absorption in the ultraviolet or its refractive index serves for this. The observations are evaluated by the following procedure:

If particles of mass m and specific volume V fall to the ground in a centrifugal field of angular velocity w, the particles acquire a constant

[16] Th. Svedberg, see e.g. *Chem. Rev.*, **20**, 81 (1937); detailed Literature there. See also Th. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Oxford 1940.

[17] H. Bechhold and M. Schlesinger, *Kolloid Z.*, **67**, 135 (1934).

[18] W. J. Elford, *Brit. J. exper. Path.*, **17**, 399, 422 (1936).

[19] Henriot and Guguenard, *J. phys. radium*, **8**, 433 (1927).

[19] J. W. McBain, *J. Am. Chem. Soc.*, **57**, 780, 2631 (1935); **59**, 2489 (1937).

[21] J. W. Beams, *Rev. Sci. Instrum.*, **6**, 299 (1935).

[22] J. Biscoe, E. G. Pickels and R. W. G. Wyckoff, e.g. *Rev. Sci. Instruments.*, **7**, 246 (1936).

velocity u under the mutual influence of buoyancy, friction and acceleration of field.

$$u = \frac{dr}{dt} = mrw^2 \frac{(1 - V\sigma)}{f} \tag{110}$$

r = distance of particles from the axis of rotation.
σ = density of solvent or medium of suspension.
f = coefficient of friction of the particles.

If the values u, r and w, to be measured by the experiment, are placed on one side, the other side of the equation contains only material constants

$$\frac{u}{w^2 r} = m\frac{(1 - V\sigma)}{f} = s \tag{111}$$

and, according to Svedberg, defines the so-called *sedimentation constant*. If it is applied, by suitable reduction of f and σ, to water at 20° it represents a true sedimentary constant of the substance settling.

To calculate s, we integrate (110) between two values of r which correspond to the beginning ($r_1 t_1$) and the end ($r_2 t_2$) of the observation period and obtain

$$s = \frac{\ln \frac{r_2}{r_1}}{w^2(t_2 - t_1)}.$$

For a solution instead of a single particle (having now concentration c instead of distance r), we obtain

$$s = \frac{1}{2} \frac{\ln \frac{c_1}{c_2}}{w^2(t_2 - t_1)} \text{ or}$$

$$c_2 = c_1 e^{-2sw^2 \Delta t}. \tag{112}$$

If now, we introduce special conditions regarding the shape of the particles, we may employ (112) for determining particle size. If, for example, spherical or nearly spherical form is assumed, we obtain:

$$f = 6\pi\eta\rho \tag{113}$$

$$\rho = \sqrt{\frac{9\eta s}{2(\sigma_t - \sigma_e)}}$$

ρ = particle radius (average).
η = viscosity of solvent.
σ_t = density of particles in the solution.
σ_e = density of pure solvent.

The estimation of σ_t affords the greatest difficulty, because we never know how much solvent is carried by the particles either adsorbed on their surface or enclosed within them. If, however, this determination is successful, and if we are measuring spherical particles in sufficiently dilute solutions, it is possible by (113) to determine average particle radius with great reliability.

If we are interested, not in particle radius, but only in the average weight of particle, the following values may be introduced:

$M = m \cdot N$ = molecular weight (N = Loschmidt number)
$F = f \cdot N$ = molar coefficient of friction.

Without reference to particle shape, the relation holds generally

$$FD = RT$$

D = coefficient of diffusion.

Thus one obtains from (111)

$$M = \frac{s \cdot RT}{(1 - V\sigma)D}, \tag{114}$$

from which molecular weight can be determined, regardless of the shape of the particle. It is, of course, a necessary proviso in this derivation that the coefficient of friction for a moving particle in a given liquid be the same whether the movement of the particle is one of diffusion or of sedimentation. Since sedimentation results when a homogeneous field of force acts continuously on the particle, whereas diffusion proceeds discontinuously under the influence of irregular impacts by the solvent, it is perhaps not necessary for this assumption to be invariably true; wherever it is valid, however, it is possible to determine particle weight entirely satisfactorily in this way.

For calculating V, Svedberg generally employs the equation

$$V = \frac{gl_0 - (gl - gs)}{\sigma gs}.$$

In this

gl_0 = weight of a given volume of pure solvent.
gl = weight of the same volume of solution.
gs = amount of dispersed substance weighed out.
σ = density of the pure solvent.

From this definition of V, it is evident that the water of solvation which may be entrapped by the dissolved particles, is not measured with them in a calculation of this kind.[23]

[23] Unless it possesses a different density from that of the ordinary water of the solvent.

If the suspension is entirely homogeneous and contains only particles of one definite size, the boundary between the solution and the pure solvent is sharp (apart from diffusion in the case of very small particles, which will be referred to later) and we may conclude that a monodisperse system exists. It should, of course, be emphasized that this holds only for spherical or at least for nearly spherical particles, for with elliptical particles, there may be a different adjustment of the particle axes to the direction of the field, resulting in a different rate of sedimentation of particles of the same size but of different orientation.[24]

In polydisperse systems the boundary between solution and pure solvent is vague and, from its shape at different times, one can draw deductions concerning the distribution curve of the particles in the solution.

In this case the following expression of Svedberg holds for spherical particles, diffusion being neglected:

$$\frac{dc}{dr} = \frac{dc}{dx} \cdot \frac{dx}{dr}\left(\frac{x_2}{x_1}\right)^2.$$

In polydisperse systems, which exhibit only a few and relatively widely differing particle sizes, the individual components may be separated deliberately under certain conditions by centrifuging; two more or less sharp boundaries are then visible and one can determine separately the particle weight or particle radius by direct measurement.[25] Svedberg found this to be true for many proteins.

b) A colloidal system may be centrifuged until the boundary between solution and pure solvent is no longer displaced; sedimentation equilibrium has then set in, with a balance between the centrifugal force acting downward and diffusion acting upward. For particles of a definite size, the particle weight can be calculated by the equation

$$M = \frac{2RT \ln \frac{c_2}{c_1}}{(1 - V\sigma)w^2(r_2^2 - r_1^2)}. \tag{115}$$

The designations are the same as in the previous formulas; the above equation is independent of the shape of the particles.

Here, again, the boundary is sharp for homogenous systems and indis-

[24] See R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 726 (1934); also E. O. Kraemer and W. H. Lansing, *J. Am. Chem. Soc.*, **55**, 4319 (1933) and especially the two articles of E. O. Kraemer and R. Signer in the book of Th. Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Oxford 1940.

[25] See Th. Svedberg, *Kolloid Z.*, **51**, 10 (1930).

tinct for polydisperse suspensions (and in the case of very small particles). From the lack of sharpness one may calculate the distribution curves of the particles, taking into account the effect of diffusion.

c) Finally, observations with the ultracentrifuge permit the calculation of the true coefficient of diffusion. If the particles are sufficiently small, the sedimentation meniscus will spread because of their diffusion—whether the velocity or the equilibrium method is being used. If we determine this spread in a suitable manner, we may calculate from it the diffusion constant D; in this case, for uniform particle size, the following expression of Svedberg holds

$$\frac{dn}{dz} = \frac{n_1 - n_0}{2\sqrt{\pi D t}} \cdot e^{-\frac{z^2}{4Dt}}.$$

In this

n_1 = refractive index of the solution.
n_0 = refractive index of the pure solvent.
dn/dz = change of refractive index in the region of the meniscus.
z = distance of the point of measurement from the position of maximum concentration.

The above information shows that the ultracentrifuge affords a means of a very intimate study of colloidal systems.

A few figures will serve for clearer illustration of the equations and research methods outlined above.

e) *A Few Important Results*

Figure 86, due to Svedberg, shows the photometric registration of the meniscus during four exposures of sedimenting haemocyanine from Helix pomatia at *pH* 5.5 in a centrifugal field of 45,000 g. The separate exposures were made at 5 minute intervals; the lower part of the cell was filled with solution, the upper with the pure solvent (water). It is immediately evident from the curves that the sedimentation process was very rapid and complete; after about 20 minutes all the protein had been forced to the bottom and the supernatant liquid was quite clear. Further, the meniscus was very sharp, indicating large particles and a uniform degree of dispersion. This case is ideally suited to the application of the velocity and equilibrium method and indicates a monodisperse system with $M = 6{,}740{,}000$.

In this connection, the centrifuging of the proteins of tobacco mosaic virus, as well as of α-lactalbumin, may be cited as examples of a heterodisperse system involving large particles and a homodisperse system involv-

ing very much smaller ones. For the latter, especially, very intense fields are required for centrifuging and the apparently vague boundary is to be attributed to the influence of diffusion. Fig. 87 represents the curves obtained directly by a sedimentation measurement on α-lactalbumin at an acceleration of 310,000 that of gravity. Here there was a period of 40 minutes between successive determinations; the value of M was 17,000. The full lines are those obtained experimentally; the points are calculated on the assumption that a homodisperse suspension of the molecular weight indicated above broadens the meniscus by diffusion. It is evident that there is very marked agreement between the points calculated and the curves obtained experimentally. Fig. 88 relates to tobacco mosaic virus and indicates a high molecular dispersion of heterogeneous character.

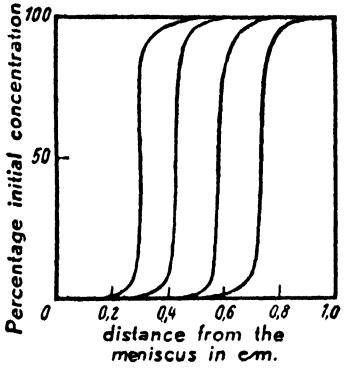


Fig. 86. The meniscus between the solution of sedimenting haemocyanine and the pure solvent, recorded photometrically at four different positions.

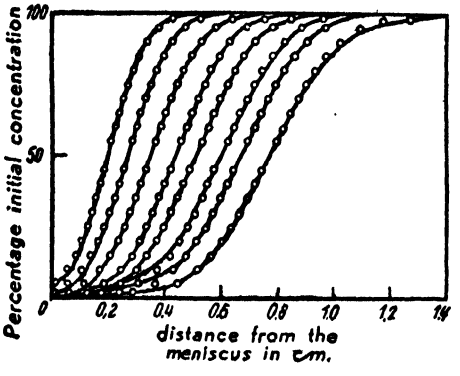


Fig. 87. Photometric curves of sedimentating lactalbumin.

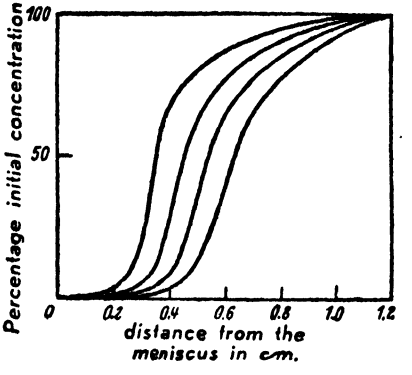


Fig. 88. Photometric curves of sedimentating tobacco mosaic virus.

It may be appropriate to close this short report on the ultracentrifugal research with two tables.

Table 90 shows a series of average molecular weights of different high polymers obtained in the ultracentrifuge and by free diffusion.

Table 90a contains the result of a recent research of Mehl, Oncley, and

Simha[25a] concerning the dissymetry of protein molecules. The axis ratio f of an ellipsoid of revolution, which represents the particle, is calculated from diffusion measurements in the ultracentrifuge (column 2) and compared with values obtained from viscosity measurements using equation (103) on page 285. The agreement between the two methods is rather satisfactory.

Any further information concerning the technical application of the equipment, the carrying out of the experiments and the final interpretation of the results can be found in the recent book of Svedberg and K. O. Pedersen, *The Ultracentrifuge*, Oxford, 1940.

TABLE 90a

COMPARISON OF AXIS RATIOS f AS DETERMINED BY DIFFUSION AND VISCOSITY

Protein	f Calculated from Diffusion Experiments	f Calculated from Viscosity Measurements
Egg albumin	3.8	5.0
Serum albumin	5.0	5.6
Hemoglobin	3.7	4.6
Amandin	5.4	6.0
Octopus hemocyanin	7.2	7.3
Gliadin	10.9	10.5
Homarus hemocyanin	5.2	5.5
Helix pom. hemocyanin	4.8	5.5
Serum globulin	7.6	7.3
Thyroglobulin	7.8	7.9
Lactglobulin	5.2	5.1
Pepsin	2.5	4.5

2. The Mechanism of Formation and Degradation of Long Chain Molecules

The development of high polymer chemistry was, naturally, first directed mainly to the properties of substances of high molecular weight,[26] to their methods of investigation and their reaction capacity. It was only after a certain amount of knowledge had been amassed in this field that the need was recognized for quantitative investigation into the mechanism of the formation and dissociation of long chain molecules.[27] This has led in recent years to a series of researches on the mechanism

[25a] J. W. Mehl, J. L. Oncley and R. Simha, *Science*, **92**, 132 (1940).

[26] Compare W. H. Carothers, *Collected Papers*, New York 1940.

[27] Compare R. E. Burk, *Polymerization*, New York 1937.

of polymerization and condensation reactions,[28] which, although they may not yet furnish a final picture of the conditions, have established the general principles with sufficient certainty for it to appear reasonable to present the results briefly here. The same holds for experiments on the degradation of long chains, which has been studied especially in natural high polymers and has yielded interesting information regarding the type of linkage of the glucose residues in cellulose and starch.

a) Short Outline of the Mechanism of Polymerization Reactions

It may be sufficient for the following discussion to visualize the formation of a long chain molecule from an ethylene derivative as representative of a polymerization reaction. The whole chemical process in such a reaction may be expressed by the empirical equation

$$n \text{ times } (CH_2{=}CHX) \rightarrow (CH_2 \cdot CHX)_n \qquad (116)$$

The left hand side of this equation represents n small molecules which move in a gas, in solution or in the pure liquid system independently or nearly independently of one another; let n be a number between 100 and 1000; x denotes any substituent (C_6H_5, OH, OCH_3, Cl etc.); on the right hand side stands the macro-molecule produced during the course of the reaction; our only certain knowledge about it is that it comprises all the atoms of the n separate molecules, linked together by primary valences; for the sake of simplicity, it will be assumed that the macromolecules have a purely chain-like structure. Acting on this, we may then write equation (116) in somewhat greater detail

$$n \cdot (CH_2{=}CHX) \rightarrow CH_2{=}CX{-}CH_2{-}CHX{-}\ldots.CH_2{-}CH_2X$$

Whether the substituents are in such regular sequence as is represented here or distributed at random over the chain following the laws of probability, is as yet an undecided question and is counted among the problems of high polymer chemistry awaiting solution.[29]

All our knowledge of simple chemical reactions appears practically to exclude the idea that the n single molecules on the left hand side of equation (116) associate instantaneously and that the primary valence chain is formed suddenly by a single complicated collision of many particles.

[28] Such polymerization processes have been called A-and C-polymerization by W. H. Carothers. See Volume I of this series.

[29] Compare a series of very interesting recent papers by A. C. Marvel, e.g. J. Am. Chem. Soc., **61**, 3156, 3241 3244 (1939).

We must rather look for a growth-like process, during which the individual constituents slowly aggregate to build a long chain, i.e. a gradual process of propagation similar to that by which the chain polymers occurring in nature, e.g. rubber, cellulose, proteins, chitin, etc. are produced.

Through the experiments of Bonhoeffer, Hinshelwood, Nernst, Polany, Semenoff, Taylor[30] and others, we have for some years recognized in the kinetics of rapid gas reactions a series of typical processes which have been designated *chain reactions* because they consist of a long series of separate interactions occurring in quick succession. They do not, indeed, give rise to large molecules, because in the individual steps energy is merely exchanged between the isolated particles. But these chain reactions in gaseous systems lead to large outputs within short periods, and the experience gained by an exhaustive study of them has, up to the present, proved most useful in application to polymerization reactions.

If such a reaction is considered to be a chain reaction—as was shown for the first time quantitatively by W. Chalmers[31]—the whole process may be divided up into the following separate stages.

a) The start of a chain: A peculiarly reactive nucleus is first formed by a thermal collision of particularly high energy value, by absorption of a light quantum or by some other process (surface-catalysis, homogenous catalysis, etc.). The formation of such a nucleus or germ may be represented for example by one of the following chemical equations

$$\begin{aligned}
&CH_2{=}CHX + CH_2{=}CHX \rightarrow {-}CH_2{-}CHX{-}CH_2{-}CHX{-}\\
&CH_2{=}CHX + h\nu \rightarrow {-}CH_2{-}CHX{-} \text{ or } (CH_2{=}CHX)^*\\
&CH_2{=}CHX + M \rightarrow {-}CH_2{-}CHX{-} \text{ or } (CH_2{=}CHX)^*\\
&\qquad\qquad\qquad\qquad\qquad\quad \text{or } (CH_2{=}CHX)\,M
\end{aligned}$$

M is inserted for any substance with catalytic action; the star (*) indicates that the molecule to which it is attached is in a reactive state.

It is an open question whether the nucleus represents only a high energy molecule (denoted by a star) or a radical with one or more free valences; the only important essential is that it possess great reactivity. Owing to the high energy required for the activation necessary to nucleus formation, the latter is a relatively rare process and consequently the start of the chain is generally a slow reaction.

b) The growth of the chain: If a nucleus is present in the reaction mixture, it is able, by reason of its high reactivity (intense internal vibra-

[30] See e.g. M. Polany, *Atomic Reactions*, London 1932; N. Semenoff, *Chain Reactions*, Oxford 1935; L. Farkas and H. W. Melville, *Chemical Kinetics*, Cambridge 1939; H. J. Schumacher, *Chemische Gasreaktionen*, Dresden 1938.

[31] W. Chalmers, *Can. J. Research*, **7**, 113, 472 (1932).

tions or rotations or free chemical valence), to accumulate other monomeric molecules of the same substance very rapidly (i.e. almost at each collision with it). In this process much energy is liberated and the reactivity of the nucleus or the free valence at the end of the resulting product of growth is always regenerated after the acquisition of a new group; a normal individual act of growth does not destroy the reaction capacity of the growing chain but preserves it (not always completely but usually to a large extent). The low energy requirement of the growth reaction causes it to proceed much more rapidly than the start of the chain and can, therefore, lead to the development of long chains.

c) The chain rupture. If the free valence at the end of a growing chain could only react with the monomer in the way described, it would be possible for the chain to elongate further and further until all the original monomeric material was exhausted. Actually, it never or practically never proceeds so far, but a third elementary process sets in which interrupts the growth of the chains. Owing to the high reactivity, the free ends of the growing chains may react differently from the normal manner shown under (b) leading to the lengthening of the chain by a link.

The migration of a hydrogen atom along the chain or during a collision, may result in saturation of the free valence at the end of the chain; multi-membered rings may be formed or a chain may react with impurities present (possibly oxygen) and thus restrict its capacity for further growth. It is evident that there are many possibilities for interrupting the chain and that it will not be easy to decide in a given case which of them played the decisive rôle.

We must now consider these three separate processes jointly; from their velocities, the experimentally observed process has somehow to be constructed. The principal cases concerned will be illustrated by a few simple examples.

We shall imagine N individual particles as gas or dilute solution placed in a wide vessel and produce in them a single nucleus by any method. This will collide in course of time with all $(N - 1)$ other molecules and aggregate them gradually to a single chain. The speed of the process will gradually fall off, because the decreasing number of free molecules makes the probability of collision with the lengthening chain always smaller and smaller. In such cases, the equation for a monomolecular reaction describes the process. If we plot the quantity of polymer formed (in our case simply the length of the resulting chain) against the period t of the reaction, we obtain a curve similar to that in Fig. 89; the rate is initially relatively great and decreases with increasing time of reaction. Since we

have formed only a single nucleus in the solution, the whole course of the reaction is very slow; the angle α is small.

If we produce initially, not one, but several (e.g. n) nuclei, and assume that they do not disturb one another during growth, we obtain the same kinetic result, namely a monomolecular reaction. But the entire process is now n times as rapid; the length of the resulting chain is no longer that of N single molecules but averages N/n; several short chains are formed simultaneously. For graphic representation we have simply to combine n separate reactions of the type of Fig. 89 beginning at $t = 0$. The result for $n = 3$ is shown in Fig. 90. The curve now rises from the origin at an inclination three times as great.

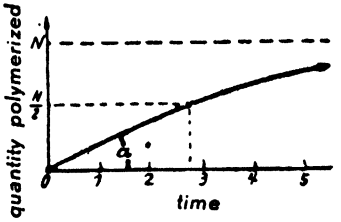


Fig. 89. Monomolecular course of a polymerization reaction.

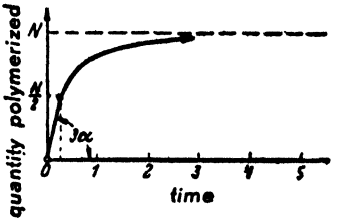


Fig. 90. More rapid monomolecular course of the reaction.

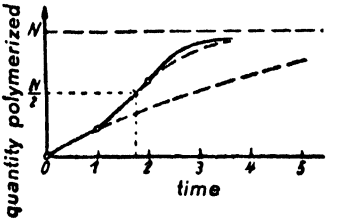


Fig. 91. Course of reaction with induction period.

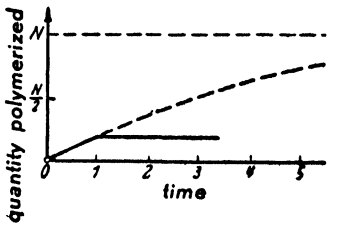


Fig. 92. Course of reaction with chain rupture.

To obtain a closer approximation to the actual conditions obtaining, we must assume that the different nuclei do not all enter into reaction simultaneously at the beginning of the process, but that they are formed in succession by high energy collisions, by the absorption of light quanta etc. In representing the results for the case $n = 3$ we have, obviously, to combine the individual elementary chain growth reactions in such a way that there is overlapping between the immediate and the preceding one at the instant when a new nucleus is formed. This must be done always on the assumption that there is little or no interference between the grow-

ing chains. The three separate monomolecular processes of Fig. 89 do not then all begin at the same time $t = 0$, but start one after another at intervals which are the reciprocal of the rate of the nucleus formation. The result is shown in Fig. 91. While the two previous processes show the typical curve of a monomolecular reaction, that is no longer the case; a new type of behavior ensues. The complete reaction exhibits an induction period. It proceeds relatively slowly in the initial stage, owing to scarcity of nuclei (flat rise from the origin), then quickens with the supply of new nuclei (steeper rise) and slows down again only when the collisions requisite for growth become more infrequent owing to lack of monomers (saturation).

In this case, chains of entirely different length are present in the reaction product; that formed from the oldest nucleus has had the whole reaction period for its growth and is consequently relatively long, that derived from nucleus 2, begins to grow a little later (say, at $t = 1$) and is accordingly shorter. If the nuclei are formed in rapid succession, the chains are similar in length; if the development of nuclei is slow, the chains formed later suffer in consequence.

Useful data are obtainable directly on the average period of growth or life of the individual chains in all three cases. In cases 1 and 2 all chains grow equally long, i.e. during the whole period of observation to complete synthesis of the basal substance; in case 3, however, the length of life of the three chains differs because 2 and 3 are formed later than 1 and have, therefore, less time for growth. Both the distribution of chain lengths and the growth period of the separate chains are, therefore, related very closely to the development of the nuclei; i.e. to the ratio of nucleus formation and growth rate. It will be shown later how this ratio may be expressed mathematically.

We have now to deal with the rupture reaction for a still closer approach to reality. We will consider first the case of Figure 89 and assume that a substance interrupting chain growth is present in low concentration. The chain, after starting, will grow freely in monomolecular fashion and then —with the entry of the inhibiting substance—will suddenly become incapable of further extension. The result is shown in Fig. 92. With the interruption, the reaction is brought to a sudden end—not, as earlier, to an asymptotic end. If the interruption of reaction is rapid, the horizontal line of Fig. 92 appears after a short time and a short chain results; if it is comparable in speed with the growth reaction, no chains are formed at all but only small molecules (dimers, trimers, etc.) will result. It is evident in this simple case that the reciprocal rate of the interruption reaction is proportional to the life of the individual chain and therefore proportional to the resulting chain length.

Similar conditions hold for the case of Fig. 90 with three chains starting simultaneously. If the interruption reaction is rapid, the chains are soon terminated; their growth is brief and they can only build up a few links.

In the latter case of chains starting at a succession of time intervals, and ended by a rupture reaction, the conditions are also relatively easy to follow; if the first chain is interrupted before the second begins, the second ended before the third starts and so on, we must simply draw Fig. 92 three times in succession to obtain the complete result. If, for example, there is a time period of unity between the completion of the first chain and the beginning of the second, we obtain the conditions shown in Fig. 94. This indicates a more gradual rise of the whole reaction distributed over many nuclei than is shown in Fig. 90; there is here a certain time interval during which there is no reaction at all, namely, the time between the death of the first chain and the birth of the second.

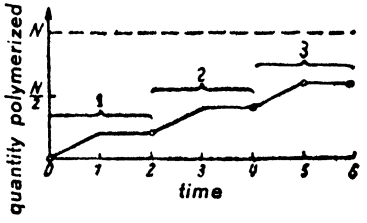


Fig. 93. Interruption reaction with three chains (rapid interruption).

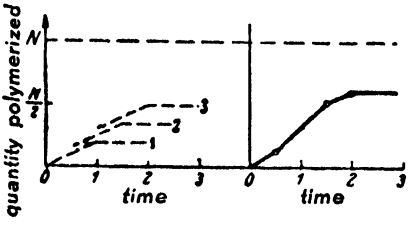


Fig. 94. Interruption reaction with three chains (slower interruption).

If, on the contrary, the first chain is destroyed only after the start of the second and so on (Fig. 94), we obtain, on considering many nuclei, a curve which begins by a linear rise from zero, for which, as the figure shows, nuclear formation and rupture are decisive. The growth reaction itself is practically eliminated from the picture; it is sufficiently rapid for each nucleus to be built up into a chain as far as the inhibiting effect of the destructive reaction allows. The whole process in this case is decided by the interaction of chain birth and chain rupture. The number of chains growing in the mixture at any particular time is given directly by the ratio: rate of beginning reaction to rate of destructive reaction. The average life period is again calculated directly from these two values, as also, are the average chain length, distribution curve, etc.

After these general remarks on the interrelation of the separate reactions, an attempt will be made to represent the conditions mathematically.

With this object in view, it is necessary to inquire whether the starting, growing and rupture reactions are monomolecular or bimolecular, whether

they are subject to catalytic influence or in what way they depend on the experimental conditions. The result of this examination will, of course, depend very greatly on the particular system studied and it is not possible to generalize for a large number of polymerization reactions.

Since the polymerization of ethylene derivatives, particularly styrene, has been studied most exhaustively from the kinetic standpoint, it may suffice for the purpose of the present work to confine ourselves to this case and to cite it as exemplifying the treatment of a polymerization reaction. We shall keep mainly to a recently published treatise of Breitenbach,[32] who has discussed current researches on this substance in detail.

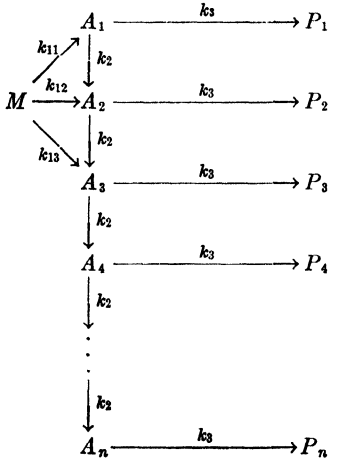


Fig. 95. Scheme of a polymerization reaction. M = monomeric initial material; A = activated intermediate product; P = polymeric end product.

For nucleus formation, monomolecular and bimolecular mechanism are involved. For example, by the accumulation of energy within the monomeric molecule, in consequence of inherent interference of the natural vibrations, the activation of the double bond can be effected in a monomolecular way, just as large organic molecules (azomethane, propionic aldehyde, etc.) are known to dissociate preferably according to the monomolecular equation.

Such activation can, however, be produced on bimolecular lines by a particularly high-energy collision of two styrene molecules.

Finally, it should be remembered that catalytically active substances or the action of light may confer a yet more complicated character of the starting reaction.

The growth reaction is generally to be regarded as bimolecular, because, owing to the low heat of activation characteristic for it, the majority of the collisions of monomeric molecules with the activated or radical-like nuclei may be effective.

For the rupture reactions, on the contrary, entirely different mechanisms are again possible and the kinetic principle responsible for a given rupture reaction has hardly been determined with certainty in any single case.

Finally, it may be observed that in most of the polymerization reactions

[32] W. Breitenbach, *Monatsh.*, **71**, 721 (1938).

there is also a branching reaction to be taken into account; this is always important if the resulting product has not pure chain structure. We shall leave them out of the discussion, since, in the case of styrene, the formation of purely chain molecules is very likely to be preponderant.

We shall consider the following scheme in the light of this information. M would characterize the monostyrene; the starting reaction with the velocity k_1 leads to the activated molecules or nuclei A. The indices to A would indicate the number of primary molecules in the nucleus. In case A_1 it consists of a single styrene molecule, A_2 consists of two and so on. The growth reaction k_2 leads from one nucleus to the next above and is indicated in the scheme by the velocity constant k_2, while the rupture reaction, which leads from the activated particles A to the corresponding stable polymerization products P, is measured by k_3.

If now, we assume for the sake of simplification, that k_2 and k_3 are independent of chain length, which is certainly not true exactly but might be a suitable approximation in many cases, it is evident that, for a given concentration of A_n, a definite fraction of them, namely αA_n, increases to $A_n + 1$, whereas the remainder $(1 - \alpha)A_n$ is stabilized to P_n by the rupture reaction. The concentration of A_n is, therefore, given by

$$[A_n] = [A_1]\alpha^{n-1}. \tag{117}$$

From this we obtain, according to G. V. Schulz,[33] to whom we are indebted for very informative work in this field, the distribution curve of the degree of polymerization in polymers for the case of a differential reaction.

We shall now introduce definite assumptions for the individual steps of the above scheme. The starting reaction shall be of the first, second or third order.

$$+\frac{dc^*}{dt} = k_{11}c \ldots\ldots\ldots\ldots\ldots \text{ first order}$$

$$+\frac{dc^*}{dt} = k_{12}c^2 \ldots\ldots\ldots\ldots\ldots \text{second order}$$

$$+\frac{dc^*}{dt} = k_{13}c^3 \ldots\ldots\ldots\ldots\ldots \text{third order}$$

c^* measures the concentration of the A, c that of the M molecules; k_{11}, k_{12} and k_{13} are designated as starting reaction constants by the first index, while the second indicates the order of the process.

[33] G. V. Schulz, *Z. physik. Chem.*, (B) **30**, 379 (1935).

For the growth reaction we may use with fair accuracy the simple expression

$$-\frac{dc}{dt} = k_{22}cc^*;$$

it states that a step of growth may ensue by the collision of an activated molecule with a monomer and that the concentration of the monomer decreases proportionally to the number of these collisions. In the first stage, monomer c is used up and nuclei c^* are formed, in the second stage further monomers are used but the concentration of the nuclei remains unaltered because they are regenerated during the reaction.

Finally, in the rupture reaction, during which nuclei are used up, we shall assume first and second order for the nuclei and add that a nucleus may also be deactivated by a collision with a monomeric molecule. We arrive at the following possibilities

$$-\frac{dc^*}{dt} = k_{31}c^*$$

$$-\frac{dc^*}{dt} = k_{32}c^{*2}$$

$$-\frac{dc^*}{dt} = k_{311}c^*c$$

If the possibility exists for first and second order rupture, the former may predominate at low concentrations and the latter at higher.

Frequently, the rate of the growth reaction is high compared with the two other component reactions; this is essential for obtaining true high polymeric products. Then this reaction alone is determinative for the consumption of the monomer and the rate of the empirical reaction which can be followed experimentally is

$$-\frac{dc}{dt} = k_{22}cc^*. \tag{118}$$

If this equation is to be compared with the experimental data, we must try to express c^* as a function of c. It should be observed that, in accordance with our assumptions, activated molecules A are produced only by the starting reaction and destroyed by the rupture reaction. Under the influence of this supply and of this exhaustion of A, a stationary concentration c^* will set in after a short induction period. For the different possibilities discussed earlier, the result of this calculation is given in Table 91. It is clear that many expressions are possible for the stationary concentration of the activated molecules A and that it is not at all easy to decide on one of these expressions by experiment.

If this has been done, however, the empirical rate of reaction is obtained directly by inserting c^* in (118). With the different c^* values from Table 91, we obtain the $-dc/dt$ values tabulated in Table 92. It is evident from this table that three different possible explanations are

TABLE 91

STATIONARY CONCENTRATION OF ACTIVATED MOLECULES

	$k_{31}c^*$	$k_{32}c^{*2}$	$k_{311}c^*c$	Rupture
$k_{11}c$	1 $\frac{k_{11}}{k_{31}}c$	4 $\left(\frac{k_{11}}{k_{32}}\right)^{\frac{1}{2}}c^{\frac{1}{2}}$	7 $\frac{k_{11}}{k_{311}}$	
$k_{12}c^2$	2 $\frac{k_{12}}{k_{31}}c^2$	5 $\left(\frac{k_{12}}{k_{32}}\right)^{\frac{1}{2}}c$	8 $\frac{k_{12}}{k_{311}}c$	
$k_{13}c^3$	3 $\frac{k_{13}}{k_{31}}c^3$	6 $\left(\frac{k_{13}}{k_{32}}\right)^{\frac{1}{2}}c^3$	9 $\frac{k_{13}}{k_{311}}c^2$	
Start				

TABLE 92

EMPIRICAL RATE OF REACTION $-\frac{dc}{dt}$

1 $\frac{k_{11}k_2}{k_{31}}c^2$	4 $\left(\frac{k_{11}}{k_{32}}\right)^{\frac{1}{2}}k_2c^{\frac{1}{2}}$	7 $\frac{k_{11}k_2}{k_{311}}c$
2 $\frac{k_{12}k_2}{k_{31}}c^3$	5 $\left(\frac{k_{12}}{k_{32}}\right)^{\frac{1}{2}}k_2c^2$	8 $\frac{k_{12}k_2}{k_{311}}c^2$
3 $\frac{k_{13}k_2}{k_{31}}c^4$	6 $\left(\frac{k_{13}}{k_{32}}\right)^{\frac{1}{2}}k_2c^{\frac{3}{2}}$	9 $\frac{k_{13}k_2}{k_{311}}c^3$

available, for example, for an empirical reaction recognized experimentally as bimolecular; namely 1, 5 and 8.

In the quantitative treatment of polymerization reactions, we must, therefore, seek further quantities accessible experimentally which may give us additional information concerning the process; the average degree of polymerization of the resulting product is one of these. Its kinetic evalu-

ation is due mainly to Süss, Pilch and Rudorfer,[34] H. W. Melville[35] and G. V. Schulz.[36]

It was found that this value is dependent upon solvent, temperature and initial concentration of the monomer. For sufficiently small conversions, when the change of concentration of the monomer may be neglected, the average degree of polymerization remains constant under otherwise equal conditions. There corresponds to each activated molecule, on an average, an equal number of aggregated monomeric basal molecules.

The rate of the entire reaction is obviously obtained by multiplying the rate of activation by the average number of the monomers bound per chain, i.e. by the average degree of polymerization $\bar{P}$

$$\frac{dc}{dt} = \frac{dc^*}{dt} \cdot \bar{P}. \tag{119}$$

$\bar{P}$ may be calculated herefrom. By doing this for the different cases discussed above, we obtain the expressions contained in Table 93.

TABLE 93

AVERAGE DEGREE OF POLYMERIZATION $\bar{P}$

Start	$\bar{P}$		
$k_{11}c$	1 $\frac{k_2}{k_{31}}c$	4 $(k_{11}k_{32})^{-\frac{1}{2}}k_2c^{\frac{1}{2}}$	7 $\frac{k_2}{k_{311}}$
$k_{12}c^2$	2 $\frac{k_2}{k_{31}}c$	5 $(k_{12}k_{32})^{-\frac{1}{2}}k_2$	8 $\frac{k_2}{k_{32}}$
$k_{13}c^3$	3 $\frac{k_2}{k_{31}}c$	6 $(k_{13}k_{32})^{-\frac{1}{2}}k_2c^{-\frac{1}{2}}$	9 $\frac{k_2}{k_{31}}$

The three tables embody a certain classification of polymerization reactions similar to that of the much simpler division of ordinary gas reactions into mono-, bi- and tri-molecular. However, through the inevitable overlapping of the three component reactions described, the conditions prove more complex and the systematization of polymerization reactions is less simple.

[34] H. Süss, K. Pilch and H. Rudorfer, *Z. physik. Chem.*, (A) **179**, 361 (1937).
[35] H. W. Melville, *Trans. Faraday Soc.*, **32**, 315 (1935).
[36] G. V. Schulz and E. Husemann, *Z. physik. Chem.*, (B) **35**, 184 (1937).

It would lead too far to give more detailed results here as to how to evaluate quantitatively the experimental data of a polymerization reaction, but it may be emphasized that further complications are introduced when branching reactions occur, so that in applying the above equations, care must be taken to ascertain that any branching reaction is excluded.

It is planned to describe more completely our present knowledge of the mechanism of polyreactions in another volume of this series. At present the best comprehensive information on polymerization reactions can be found in the book on *Polymerization*, by Burk, Thompson, Weith and Williams.[37]

A very important question is about the nature of the reactive nucleus or complex (denoted with A in the above scheme), which propagates the reaction. It seems that it can vary very widely and that sometimes the intermediate products are best formulated as free radicals; e.g.

$$CH_2{=}CHX + CH_2{=}CHX \rightarrow CH_2{-}CHX{-}CH_2{-}CHX{-}$$

Much points in the direction that polymerization of styrene in the gaseous phase, the photopolymerization of acetylene[38] and the photosensitized polymerization of methylmethacrylate[39] follows such a course. Highly reactive radicals, having a very short average lifetime, are produced by the starting reaction, grow rapidly into comparatively long chains and are then stabilized by a cessation reaction of a type not yet quite understood. The time which the chains require for their propagation is short. Melville and Schulz found 10^{-2} seconds as an upper limit.

On the other hand, the normal polymerization of methylmethacrylate and methylacrylate follow another mechanism. H. W. Melville[40] found that the lifetime of the intermediate products is very long and they are certainly very much more stable than a free organic radical of this size could possibly be. It is therefore probable that in these (and possibly in some other) cases the double bond of the original molecule is always reproduced at the end of the chain, thus leading to the following scheme:

$$CH_2{=}CHX + CH_2{=}CHX \rightarrow CH_3{-}CHX{-}CH{=}\overset{*}{C}HX$$

$$CH_3{-}CHX{-}CH{=}\overset{*}{C}HX + CH_2{=}CHX \rightarrow CH_3{-}CHX{-}CH_2{-}CHX{-}CH{=}\overset{*}{C}HX$$

and so on.

---

[37] R. E. Burk, H. E. Thompson, A. J. Weith and I. Williams, *Polymerization*. New York 1937.

[38] H. W. Melville, *Trans. Faraday Soc.*, **32**, 258 (1936); also S. C. Lind and Livingstone, *J. Am. Chem. Soc.*, **54**, 94 (1932).

[39] H. W. Melville, *Proc. Roy. Soc. London*, **163 A**, 511 (1937).

[40] H. W. Melville, *Proc. Roy. Soc.*, **A175**, 392 (1940).

The reactive double bond at the end of the chain may or may not be in excited state; it has, in any case, a certain inclination to add a new link to the chain, but does not react as quickly as a free radical would.

This type of slow polymerization leads us to polycondensation processes in which the bifunctional molecules react with each other to effect the formation of long chains or large multi-dimensional networks.

b) The Kinetics of Condensation Reactions

High polymeric, particularly long chain, products, can be produced, as is known, by condensation reactions in course of which the macromolecule is gradually formed during the reaction of two molecules with the elimination of a third. Carothers[41] in his systematic treatment of polyreactions has called such processes C-polymerization. An example is the formation of glyptals from glycol and succinic acid according to the equation:

$$HOOC\cdot CH_2\cdot CH_2\cdot COOH + HOCH_2\cdot CH_2OH \rightarrow HOOC\cdot CH_2\cdot CH_2\cdot COO\cdot CH_2\cdot CH_2\cdot OH + H_2O$$

$$HOOC\cdot CH_2\cdot CH_2\cdot COOCH_2\cdot CH_2\cdot OH + HOOC\cdot CH_2\cdot CH_2\cdot COOH \rightarrow HOOC\cdot CH_2\cdot CH_2\cdot COOCH_2CH_2OOC\cdot CH_2\cdot CH_2\cdot COOH + H_2O$$

etc.

Similar poly-condensation reactions can be carried out also with oxy-acids, amines and acids, urea or phenol and formaldehyde, etc.; they yield in part chain and in part reticulate products, which have been discussed, particularly by W. H. Carothers and his collaborators.[41] A more detailed description of such products will be given in another volume of this series (comp. also vol. I). The mechanism of such processes will likewise be discussed more extensively in another volume.

The task now presents itself to describe briefly previous endeavors in kinetic research into the course of such condensation reactions investigated in recent years, particularly by P. J. Flory,[42] by R. H. Kienle,[43] and by H. Mark and his co-workers.[44] In contrast to the polymerization reactions discussed earlier, here the separate condensation stages are more or less equivalent to one another and do not lead to the formation of particularly highly activated unstable and reactive products. It is not a question of differentiating between a nucleus-formation reaction of slow velocity

[41] W. H. Carothers, *Collected Papers*, New York 1940.

[42] P. J. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

[43] R. H. Kienle, *J. Soc. Chem. Ind.*, **55**, 229T (1936); *Trans. Faraday Soc.*, **32**, 54 (1936); *J. Am. Chem. Soc.*, **52**, 3643 (1930).

[44] H. Mark and H. Dostal, e.g. *Z. physik. Chem.*, (B) **29**, 299 (1935); E. Marecek, *Z. physik. Chem.*, (B) **32**, 117 (1936).

and a related growth reaction of greater velocity; growth is completed in similar successive stages, induced by the fact that reactive groups are always regenerated at the end of the chain molecules. We have before us a step, not a chain, reaction. If we assume that the rate of the esterification or other condensation process building up the chain is independent of the length of chain attained at any moment, which certainly does not hold exactly, we arrive at the following results.

The probability W_n that any basal molecule will constitute a member of a chain of n links is given by[45]

$$W_n = np^{n-1}(1 - p)^2 \tag{120}$$

In this p denotes the extent of the reaction. If N_0 is the number of the reactive alcohol or acid groups[46] originally present and N the number still remaining free at time t, p is defined by the equation

$$p = \frac{N_0 - N}{N_0}.$$

p therefore indicates the relative number of reactive groups already used up in the condensation. Now, it is clear that the number of chains of length n must be proportional to the probability that a primary molecule will be met with in such a chain.

$$N_n = \frac{N_0 \cdot W_n}{n} = N_0 p^{n-1}(1 - p)^2.$$

Provided that no small molecules (H_2O etc.) are split off during the condensation, the molecular weight of the resulting chain is then exactly proportional to the number of chain links and W_n indicates the relative weight of the n-mer fraction. If water is eliminated, this relation is vitiated in the very low members ($n = 2$, 3 and 4) but to a less extent in the higher, so that it is a sufficiently close approximation to put W_n proportional to the weight of the n-mer fraction in all cases of longer chains.

W_n is then nothing but the total number of primary molecules present in n-mer chains divided by the total number N_0 of the monomeric components initially present.

These weight fractions for different degrees of reaction p are represented in the curves of Figs. 96 and 97; the first represents a reaction which has not yet proceeded very far, $p = 0.5$–0.9, Fig. 97 the case in which the

[45] See particularly P. J. Flory, loc. cit.; compare also P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1064 (1940).

[46] We assume for the sake of simplicity that the two reacting substances are initially present in equivalent quantities.

primary substance is practically exhausted. The abscissa scale is naturally different in the two figures. The curves demonstrate that a certain polymer, judged by the weight fraction, occurs very frequently (maximum of the function W_n) and that this maximum is displaced with progressive reaction towards greater chain length and always tends to flatten out.

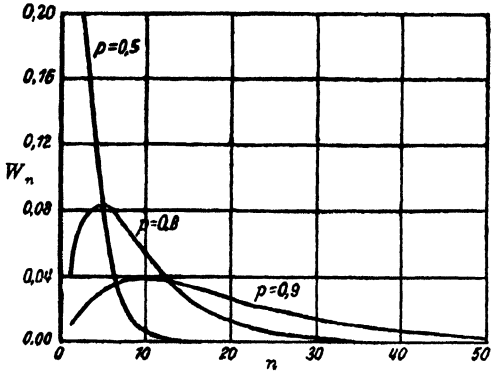


Fig. 96. Weight fractions W_n for different degrees of polycondensation n at reaction range p of 0.5 to 0.9.

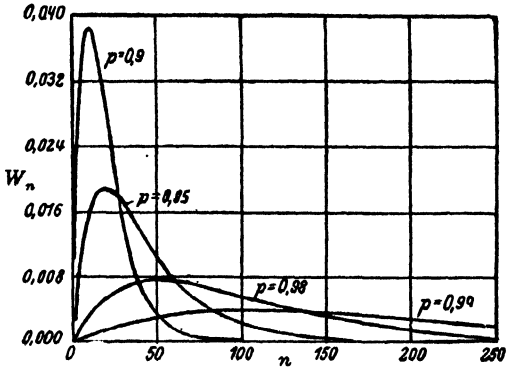


Fig. 97. Weight fractions W_n for different degrees of polymerization n at reaction range p of 0.9 to 0.99 (different abscissa scale).

Mathematically, the most probable weight fraction is obtained by differentiating and equating the differential quotient to zero; it is

$$n_{max} = \frac{1}{\ln p},$$

simultaneously

$$W_{n\,max} = \frac{1-p}{e}.$$

Thus, as long as $p < 0.5$, the monomer always predominates on a weight basis (definition of p), while later, the primary substance aggregated in the higher polymers must inevitably far exceed the monomer by weight.

Numerically, however, the monomer is always preferred on account of its small molecular weight. At any time during the reaction, there are never more of any given species of chains than there are monomeric molecules. This is readily seen by calculating the mol fraction. If P_n is the mol fraction of the n-mers, it is obviously obtained according to the equation

$$P_n = \frac{N_n}{N_o} = p^{n-1}(1 - p).$$

This function is represented in Figures 97 and 98 for different p values. It has no maximum but assumes its greatest value at $n = 1$.

It may be justifiable to point out in this connection that, in a mixture of polymeric homologs, different definitions of the molecular weight are possible which must be sharply differentiated if we are not to arrive at false conclusions in evaluating experimental results. Kraemer and Lansing,[47] Dostal and Mark[48] and J. P. Flory[49] have called attention to this fact and drawn different conclusions from it. One has to distinguish between the following average values of the molecular weight M:

$$M_n = \frac{\Sigma M_i N_i}{\Sigma N_i}$$

$$M_w = \frac{\Sigma M_i^2 N_i}{\Sigma M_i N_i}$$

$$M_s = \frac{\Sigma M_i^3 N_i}{\Sigma M_i^2 N_i}.$$

M_n is the molecular weight averaged over the *number of particles*; it is obtained, for example, by osmotic determinations or by the use of any chemical terminal group method.

M_w is the molecular weight averaged over the *particle weights*; it is obtained by the Staudinger viscosity method and also by evaluating measurements with the ultracentrifuge.

M_s is a third average value which results by evaluating sedimentation equilibrium data with the ultracentrifuge.

It is clear that, in comparing molecular weights which have been ascertained by different methods, these differences must be distinguished if

[47] E. O. Kraemer and W. Lansing, *J. Am. Chem. Soc.*, **57**, 1364 (1935).
[48] H. Dostal and H. Mark, *Trans. Faraday Soc.*, **32**, 54 (1935).
[49] J. P. Flory, *J. Am. Chem. Soc.*, **58**, 1877 (1936).

erroneous results are to be avoided. For the case of the polycondensation reactions considered here, the different molecular weights have been calculated by Flory as a function of p.

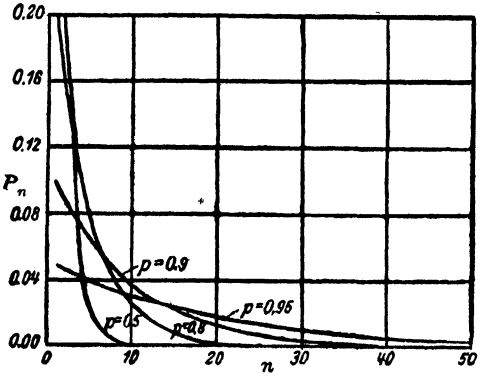


Fig. 98. Mol fraction P_n for different degrees of polymerization n in the reaction range 0.5 to 0.95.

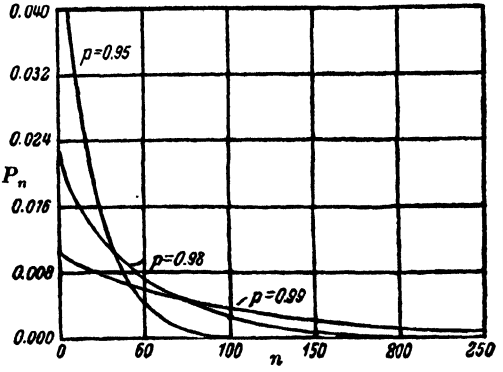


Fig. 99. Mol fraction P_n for different degrees of polymerization n in the reaction range 0.95 to 0.99.

If $p = 0.9$ (which means that 90% of the reactive groups are already consumed) one gets

$$M_n = M_0 \frac{1}{1-p}$$

$$M_w = M_0 \frac{1+p}{1-p}$$

$$M_z = M_0 \frac{1+4p+p^2}{1-p^2}$$

M_0 being the molecular weight of the elementary unit; in the case of cellulose, it would be that of the glucose residue.

If p is very near unity, the following simple and important relation is valid

$$M_n : M_w : M_z = 1 : 2 : 3. \tag{121}$$

It may be emphasized that, in employing the Staudinger viscosity method and, particularly, in comparing it with osmotic methods, the above line of thought must be borne in mind although this is not always sufficiently done.

If the two interacting monomeric primary molecules are not present in equivalent amounts, the conditions are more complicated but remain in principle within the scope of the present discussion. It would lead too far to examine these more complex conditions further and it will suffice to cite the literature,[50] especially Flory's work mentioned previously.[51]

c) *The Degradation of Long Chain Molecules*

During the technical handling of natural high polymers such as cellulose, rubber, etc. a chemical or mechanical degradation of long chains is often effected partly by design and partly as an unavoidable evil; synthetic high polymers, e.g. polystyrene and polyacrylic esters, may be split up by heat fairly readily into low molecular components and, ultimately, into monomers. Accordingly, it appears convenient to indicate the principal considerations that have been advanced regarding the mechanism of the breakdown of long chains. We may point first to a research by R. O. Herzog and O. Kratky[52] and to a work of N. Meer[53] in which the present problem was formulated and attacked theoretically and experimentally. The degradation of cellulose, however, was first treated quantitatively by K. Freudenberg[54] and W. Kuhn;[55] the latter in particular derived formulas which are important in any degradation reaction of high polymer chain

[50] W. D. Lansing and E. O. Kraemer, *J. Am. chem. Soc.*, **57**, 1369 (1935); *J. Phys. Chem.*, **39**, 153 (1935); R. Signer and H. Gross, *Helv.*, **17**, 335 (1934), see also *Kolloid Z.*, **70**, 24 (1935).

[51] Compare also P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940); H. Hibbert and S. Z. Perry, *Can. J. Research*, **8**, 102 (1933).

[52] O. Kratky, *Naturwiss.*, **18**, 732 (1930).

[53] N. Meer, see *Handb. d. Biochemie. Erg.-Bd.* 1930, p. 53.

[54] K. Freudenberg, e.g. *Ann.*, **460**, 288 (1928); *Ber.*, **63**, 1510 (1930).

[55] W. Kuhn, *Ber.*, **63**, 1503 (1930); compare also H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611 (1940); W. H. Durfee and Z. T. Kertesz, *J. Am. Chem. Soc.*, **62**, 1196 (1940).

molecules. We shall, therefore, describe his reasoning in close relation to the paper cited above.[56]

If a chain of $n + 1$ links is the basis of the initial material, the number of the linkages originally present is n, which is assumed in the following discussion to be infinitely great. If s of these n linkages are split by any cause, the modified product may be denoted by the degree of cleavage.

$$\alpha = s/n$$

If all the bonds are identical, the probability that any one of them, for example, the k^{th}, will be split up is given by

$$W_k = s/n = \alpha$$

and accordingly the probability that it has not been split up by

$$W_{k'} = \frac{n - s}{n} = 1 - \alpha.$$

We shall now calculate the probability that the portion between the $(r + 1)^{\text{th}}$ and the $(r + i)^{\text{th}}$ term has been split off the original chain as a coherent i-membered fragment. For this, it is obviously essential that the r^{th} bond be dissolved, the successive i bond exempted and the $(r + i)^{\text{th}}$ again dissolved. This probability is indicated, as suggested above, by the product of the previously calculated probabilities W_k and $W_{k'}$ and is equal, therefore, to

$$W_i = \alpha^2 (1 - \alpha)^{i-1}$$

If r varies according to the series

$$0, 1, 2 \ldots\ldots, n - i$$

then we obtain all the possibilities for the formation of fragments with i chain members. The number of i-fragments is, accordingly, equal to the sum of these probabilities; i.e., since n has been assumed to be very great, it is equal to

$$n \cdot W_i = n \cdot \alpha^2 (1-\alpha)^{i-1} = Z_i.$$

Consequently, the number of elementary units which are found associated in i-numbered fragments is given by

$$i \cdot Z_i = n \cdot i \cdot \alpha^2 (1-\alpha)^{i-1}$$

---

[56] See also H. Mark, *Physik and Chemie der Zellulose.* Berlin 1932, pp. 293 et seq.

or the maximum possible yield of i-numbered fragments, (i.e. if the whole chain had been cut up carefully into exactly equal parts), is

$$\varphi_i = \frac{i \cdot Z_i}{n} = i \cdot \alpha^2 (1 - \alpha)^{i-1}.$$

Now there is the further condition that the sum of all 1, 2, 3 etc. numbered fragments times their numerical index must be equal to the number of units present in the beginning, a requirement which may be confirmed easily by a short calculation.

In the course of the degradation, the large fragments are first preponderant, to be followed gradually by the appearance of smaller ones. The number of the fragments which contain e.g. 5 or 6 single molecules will increase initially but later, with progressive degradation, will decline and finally become zero towards the end of the reaction. The number of the i-membered chains present in the mixture must, therefore, pass through a maximum; the degree of degradation at which this maximum is reached is given from the above formulas by

$$\alpha_{max} = \frac{2}{i + 1}.$$

The optimum yield of i-membered fragments which can be obtained is calculated from

$$\varphi_{max} = \left(\frac{i - 2}{i + 1}\right)^2 \left(\frac{i - 1}{i + 1}\right)^{i-1}.$$

Table 94 records data calculated by the aid of the above equations for the optimum degree of cleavage for a few i values and the anticipated yields. If, for example, in the hydrolytic degradation of cellulose, cellotriose fragments are to be obtained in maximum yield, the degradation must be continued to a 50% conversion, when a yield of about 18.7% may be expected; the total quantity of cellotriose molecules resulting during the entire degradation amounts to 50%.

An essential condition is the complete identity of all bonds capable of decomposition and the infinite length of the original chains.

As long as interest is concentrated on the relative amount of degradation products with short chains, the assumption of an infinite length of the initial chain does not appreciably falsify the results. In fact, it is easy to conceive that at such an advanced stage of a degradation process as was stated in the investigations described above, the influence of the original chain length has already disappeared. Whether e.g. one produces cello-

biose and glucose from original chains with 500 or 1000 links will not make any great difference.

It is a very different situation when information is wanted concerning the distribution curve of high molecular weight compounds. If we interrupt the degradation process in an early stage so that really high molecular weight substances are still present in the reaction mixture, then, of course, the length of the original chain would be very influential on the distribution of the resulting products. Experiments in this direction have been carried out during the last few years by E. Broda, F. Breuer and H. Mark.[57] Recently R. Simha has worked out a preliminary formula which permits evaluation of these measurements and includes the influence of the original chain length.[57]

As mentioned above, the calculation of Kuhn was carried out on the assumption that the probability of breaking any link in the original chain

TABLE 94

OPTIMUM DEGREE OF DEGRADATION (α), MAXIMUM YIELDS (φ) AND TOTAL QUANTITY (M) FORMED FOR A FEW FRAGMENTS OF LENGTH (i)

i	α	φ	M
2	$\frac{2}{3}$	0.248	0.667
3	$\frac{1}{2}$	0.187	0.500
4	$\frac{2}{5}$	0.138	0.400
5	$\frac{1}{3}$	0.110	0.333
6	$\frac{2}{7}$	0.091	0.286
7	$\frac{1}{4}$	0.078	0.250
10	$\frac{2}{11}$	0.064	0.182

of infinite length is the same throughout the whole reaction. All individual elementary processes by which the probabilities of different events are calculated are taken as independent of one another. If products of probability have to be figured out, absolute probabilities are always applied instead of relative ones.

To improve this procedure at least to a first approximation Simha reasons as follows:

One has to calculate the probability that in a chain having originally n links one single link is broken, the next s remaining intact, and then again one single link is opened. In such a way one cuts out, of course, a chain of s links from the original molecule having n links.

[57] H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611, (1940). cf. also E. W. Montroll and R. Simha; *J. Chem. Phys.* **8**, 721 (1940).

If we denote the total number of links which have been opened by r, we can again define the degree of splitting by

$$\alpha = \frac{r}{n}$$

While the Kuhn and Flory calculation holds for high degrees of decomposition, where r is of the same order of magnitude as n, the Simha formula aims at describing the conditions if α is a very small number.

The probability of cutting one individual link of the original n-membered chain if r is the total number of opened links is, apparently, equal to

$$\alpha = \frac{r}{n}$$

The probability of the second step, namely that the next link should be left unattacked, apparently, is

$$\frac{n-r}{n-1}$$

This results in the fact that, now, only $(n-1)$ links are available for the splitting, whereas at the beginning n were present. Naturally, if n is infinitely large, we can replace $(n-1)$ by n. In the present case, however, we shall not do this.

Continuing in this way we get the probability that the next and the following links shall remain intact, as

$$\frac{n-r-1}{n-2}, \quad \frac{n-r-2}{n-3} \quad \text{and so on.}$$

Finally, the last step of the excision of a short chain from a long one, namely, that at the end of a chain with s links one bond is opened again, will be represented by

$$\frac{r-1}{n-s-1}.$$

In this way we get, for the probability which we wish to find, the expression

$$w_s = \frac{r}{n}\left\{\frac{n-r}{r-1}\,\frac{n-r-1}{r-2}\cdots\cdots\frac{n-r-s+1}{n-s}\right\}\frac{r-1}{n-s-1}. \tag{122}$$

In this equation n denotes the total number of links in the original chains, r the number of links which have been opened, on the average, and s the length of the chains which have been produced by the degradation process.

To find all possible chains with s links we have, apparently, to multiply the expression (122) by the factor $(n-s)$. This means only that, in cutting out s-membered chains, we have to start at any bond of the original molecule which gives us the possibility of having an s-membered chain left.

This leads, for the total probability of chains with s links, to the relation

$$W_s = (n-s)w_s$$

For comparison with experimental fractionation results, we have to find the total number of monomeric molecules which are contained in chains of a definite length. This number, as a function of the chain length, would give us the distribution curve of the molecular weight fractions, as defined on page 323. As a chain of s links contains $(s+1)$ monomeric molecules, the total number of fundamental molecules embodied in chains with s links would be

$$Z_s = (n-s)\frac{(n-r)!}{(n-1)!}\frac{(n-s-2)!}{(n-r-s)!}(n-s)(s+1). \tag{123}$$

This equation evidently allows us to calculate the distribution curve of the molecular weight fractions at any given degree of decomposition r if the length n of the original chains is known. Putting

$$\begin{aligned} n &\gg s \\ n-r &\gg s \\ r &\gg 1 \\ s &= i-1 \end{aligned}$$

we again neglect the influence of the original chain length and return to the formula of Kuhn.

Equation (123) was compared with the results of the above mentioned fractionation experiments which have been carried out by a mild acetolysis of cellulose acetate. The first proviso is, apparently, to start with a material which consists, at least to a certain extent, of molecules of the same length. For this purpose, a technical preparation of cellulose acetate corresponding to an acetylation degree of about 2.5 was fractionated according to the process worked out by W. Kumichel,[58] H. J. Rocha,[59] F. Ohl,[60] R. O. Herzog,[61] W. Herz,[62] R. Obogi,[63] S. D. Douglas,[64] S. Ro-

[58] W. Kumichel, *Kolloid Beihefte*, **26**, 161 (1929).
[59] H. J. Rocha, *Kolloid Beihefte*, **30**, 230 (1930).
[60] F. Ohl, *Kunstseide*, **12**, 468 (1930).
[61] R. O. Herzog and A. Deripasco, *Cellulosechem.*, **13**, 25 (1932).
[62] W. Herz, *Cellulosechem.*, **15**, 95 (1934).
[63] R. Obogi and E. Broda, *Kolloid Z.*, **69**, 172 (1934).
[64] S. D. Douglas and W. N. Stoops, *Ind. Eng. Chem.*, **28**, 1152 (1936).

gowin,[65] H. Lachs,[66] E. W. Mardless[67] and recently applied practically by W. Schieber.[68]

The average chain length of the original material was estimated by viscosity measurements in dilute solution (0.01%). To get an idea of the homogeneity of this starting material, a fractionation curve was worked out for it. A fairly homogeneous product was obtained, 82% of which showed an average polymerization degree of 340 only 7% was below and 12% above. If one calculates from the distribution curve the average degree of polymerization, he gets 345, which corresponds sufficiently with the directly measured values of 350.

This material was depolymerized under mild conditions with the aid of acetic acid. After certain times, fractions were removed from the reaction vessel, stabilized, washed, and analyzed.

Four degradation products at different stages of the decomposition process were secured. The corresponding average degrees of polymerization were 158, 100, 54, and 31, all estimated by the aid of the Staudinger equation from directly measured viscosities.

These four samples were then fractionated, the viscosity of the resulting fractions determined, and the results compared with the equation (123). The agreement[69] may be considered satisfactory if one takes into account that the experiments had only a very limited degree of accuracy and that the formula still contains certain approximations.

The equations of Kuhn and Simha give the distribution functions of the degradation products for a certain degree of cleavage but they do not permit calculation of the degree of degradation as a function of time.

To follow the temporal course of a degradation reaction of the above type, Kuhn has developed several expressions, which may be considered as first approximations to solution of this problem.[70]

a) All linkages are split up independently of one another and have the same reaction constant k.

Then at unit time,

$$dn' = k^2 \cdot n'$$

linkages are dissolved if

$$n' = (1 - \alpha)n$$

---

[65] R. Neumann, R. Obogi and S. Rogowin, *Cellulosechem.*, **17**, 87 (1936).

[66] H. Lachs, I. Kronman and I. Wajs, *Kolloid Z.*, **79**, 91 (1937); **84**, 199 (1938); **87**, 195 (1939).

[67] E. W. J. Mardles, *Kolloid Z.*, **49**, 4 (1939).

[68] W. Schieber, *Papierfabr.*, **37**, 245 (1937).

[69] H. Mark and R. Simha, *Trans. Faraday Soc.*, **36**, 611 (1940).

[70] W. Kuhn, *Ber.*, **63**, 1503 (1930).

For the kinetics of the degradation, it follows that

$$\alpha = 1 - e^{-k}$$

therefore

$$1 - \alpha = e^{-k}$$

and

$$d\alpha = k_1 \cdot e^{-k}\, dt.$$

b) All linkages react independently and similarly with k_1; only the binary groups (bioses or, better, disaccharides) split according to a different (greater) constant k_2. Here, integration of the reaction equation for the number of binary groups n'' as function of the time is given by:

$$n'' = n \cdot k_1 \left[\frac{1}{3k_1 - k_2} e^{-3k_1} - \frac{1}{2k_1 - k_2} e^{-2k_1} + \frac{k_1}{(2k_1 - k_2)(3k_1 - k_2)} e^{-k_2 t} \right].$$

For the degree of degradation α there is also obtained a somewhat complex expression composed of factors k_1 and k_2 together with powers of e having k_1 and k_2 in the exponent.

Kuhn has worked out a few more cases in which, for example, the binary group splits with a definite speed but an explicit account of the mathematical procedure would be out of place here.

It is planned to describe more extensively the mechanism of degradation reactions in another volume of this series and it is hoped that it will be possible to give then more details on the current work of Flory and Simha.

Finally it may be pointed out that the degradation and disaggregation of synthetic high polymers has permitted interesting conclusions on biological systems. F. F. Nord[1] has used organic high polymers as model substances during his investigations of freezing colloids and has succeeded in establishing general rules of the behavior of homopolar colloids in nonpolar and polar liquids. The numerous links which combine high polymeric systems with biological substances will be discussed more intensively in one of the next volumes of this series.

[1] F. F. Nord and collaborators: *Erg. Enzymforschg.*, **2**, 23 (1933); *Nature*, **135**, 1001 (1935); *Biochem. Z.*, **295**, 226 (1938); *Ber.*, **71**, 1217 (1938); *Biodynamica*, **3**, No. 57 (1940) etc., etc. Compare also H. B. Bull: *Z. physik. Chem.*, (A) **161**, 192 (1932).

AUTHOR INDEX

Adair, G. S., 233, 234, 236
Adam, N. K., 111, 130, 144, 172
Akine, L., 289
Andrade, E. N. da C., 265, 274
Anson, M. L., 299
Arrhenius, S., 293
Astbury, W. T., 158, 168
Avery, J. W., 57

Baker, F., 294
Baker, W. O., 204, 251
Bancelin, J., 280
Barlow, W., 141
Barr, G., 258
Bartholomé, 56
Batschinski, A. J., 266
Beach, T. Y., 10, 15, 59, 62
Beams, J. W., 303
Bechhold, H., 303
Berl, E., 258, 259, 293
Bernal, J. D., 127, 134, 135, 150, 168, 175, 176, 188, 189, 190
Bertram, A., 43
Bethe, H., 90
Betz, 254
Biltz, W., 258, 259
Bingham, E. C., 258, 265, 267, 268
Biscoe, J., 303
Bjerrum, N., 46
Boeder, P., 284
Boer, J. H. de, 104, 105, 161
Böhm, J., 8, 61
Boissonnas, C. G., 224, 225, 232, 239, 240, 242
Boltzmann, L., 72
Bonhoeffer, K. F., 311
Booys, J. de, 293, 294
Born, M., 34, 35, 83, 124, 125, 132
Börnstein, 11, 26
Bragg, W. H., 2, 3, 4, 5, 9, 117
Bragg, W. L., 2, 3, 4, 5, 9, 84, 117, 119, 124, 151, 169, 173, 174
Bredée, H. L., 293, 294
Breitenbach, W., 316
Breuer, F., 330
Bridgman, W. B., 65, 66
Briegleb, G., 30, 86, 98, 99, 100, 103, 106, 107, 108
Brill, R., 83, 88, 138, 139, 195, 197
Briner, E., 51
Brockway, L. O., 11, 15, 61, 110
Broda, E., 232, 330, 332
Broglie, M. de, 2, 203
Brönsted, J. N., 224, 225, 239
Bruins, H. R., 299
Bruni, G., 106, 147, 174, 175
Buchholz, K., 15
Büchner, E. H., 233, 234, 240
Bulkly, R., 270
Büll, R., 68
Bungenberg, H. G., 294
Bunzl, M., 259, 285
Burgers, R., 283
Burk, N. E., 236
Burk, R. E., 66, 70, 309, 321
Burnham, H. O., 10
Busse, W. F., 34, 66
Butler, R., 293

Campen, H. van, 232
Carothers, W. H., 309, 310, 322
Carpenter, D. C., 11
Carpenter, P. G., 300
Caspari, W. A., 234, 240
Chalmers, W., 311
Ciamician, G., 175
Clark, G. L., 9, 117, 168, 199
Cohen, E., 299
Colmant, P., 224, 225, 239
Coolidge, A. S., 110
Corey, R. B., 168
Corrigan, K. E., 168
Corruccini, R. J., 68
Couette, J., 263, 280, 281

Crawford, B. L., 57, 62
Crawford, D. M., 169, 175

Danes, V. Z., 290
Davidson, P. M., 87
Davisson, I., 2
Dawson, W. E., 4, 8
Debye, P., 2, 3, 4, 6, 9, 10, 30, 91, 114, 178, 179, 180, 182, 184, 185, 186, 196, 197
Debye, P., Jr., 10
Dennison, D. M., 45
Deripasko, A., 299, 302, 332
Devoto, G., 64
Dickinson, R. G., 138
Dippel, C. I., 161
Dobry, A., 232, 233, 234
Dostal, H., 75, 322
Douglas, S. D., 332
Duclaux, J., 234, 258, 293
Duden, P., 143
Duhem, C. R., 220
Dunkel, M., 86, 112, 113, 239
Durfee, W. H., 327

Ebert, F., 68
Ehrenfest, P., 9
Einstein, A., 277–283, 297, 298
Eirich, F., 259, 272, 275, 278, 281–286, 291, 292
Eisenschitz, R., 91, 93, 95, 178, 267, 279, 283, 284
Ekenstamm, A. von, 290
Elford, W. J., 303
Engler, C., 261
Erk, S., 261
Eucken, A., 43, 56, 66, 112, 114, 219
Ewald, P. P., 200
Ewell, R. H., 275
Eymers, J. G., 76
Eyring, H., 55, 62, 64, 66, 70, 178, 267, 275, 285

Fajans, K., 25, 85, 112, 119, 121
Farkas, L., 311
Farr, W. K., 199
Fent, R., 233, 234
Fenton, M., 110
Ferri, C., 76
Fikentscher, H., 283, 292, 294, 295
Finch, B. G. J., 2
Flory, P. J., 322, 323, 325, 326, 327, 331, 334
Foëx, G., 201
Fordyce, R., 288
Fowler, R. H., 134, 135, 188, 189, 190, 226
Fox, J. J., 87
Frei, 171
Frenzel, A., 160
Freudenberg, K., 327
Freundlich, H., 236, 268, 271, 280
Friedel, E., 145, 200, 203, 204
Friedel, G., 200, 203
Friedman, L., 300
Friedrich, W., 2
Fröhlich, K., 90
Fuchs, O., 62
Fuller, C. S., 140
Fuoss, R. M., 34
Fürth, R., 299, 300

Gans R., 35
Garner, W. E., 110, 249
Garelli, F., 175
Germer, L. H., 2
Gervaise-Le Bas, 141, 143
Giauque, W. F., 44
Gilbert, E. C., 68
Gilette, R. H., 102
Gilman, H., 14, 28, 88
Glamann, P. W., 201
Goeppert-Mayer, M., 83, 85
Gold, O., 279, 282, 284
Goldschmidt, O., 278
Goldschmidt, V. M., 117, 119, 120, 122, 123, 130, 147, 151
Gonell, H. W., 138
Gordy, W., 102
Gorin, E., 62
Grandjean, 200
Greenberg, D. M., 236
Grimm, H. G., 83, 88, 90, 117, 118, 119, 123, 127, 128, 138, 147, 148, 149, 171
Gróh, J., 302
Gross, H., 291, 302, 306, 327
Grüneisen, E., 261
Grunsky, H., 302
Guggenheim, E. A., 226, 238

Guguenard, E., 303
Guth, E., 70, 259, 279, 282, 290, 291, 293

Haber, F., 85, 128
Hagger, O., 241
Halban, H. v., 107
Halla, F., 3, 4, 5, 119, 196, 226, 232, 235, 244, 267
Harrocks, H., 21
Hartley, G. S., 254
Hassel, O., 160
Hatschek, B. E., 283, 293
Heisenberg, W., 125
Heitler, W., 55, 87, 238
Hellmann, H., 27, 28, 88
Hendricks, S. B., 171
Hengstenberg, J., 164, 166, 167, 196
Henriot, E., 303
Hermann, C., 83, 88, 138, 201, 202
Hermans, P. H., 199, 204, 205
Herschel, W. H., 270
Hertel, E., 106
Hertz, W., 29, 233, 234, 303, 332
Herzberg, G., 88
Herzfeld, K. F., 178
Herzog, R. O., 8, 299, 303, 332
Hess, K., 232, 289, 293
Hibben, J. H., 28, 46
Hibbert, H., 288, 327
Hildebrand, J. H., 222, 238, 247
Hinshelwood, C. N., 311
Hirst, E. L., 287
Hoffmann, H., 136
Hofman, U., 160
Höjendahl, K., 69
Houwink, R., 267, 293, 294
Howard, J. B., 43, 57
Hückel, E., 15, 27, 28, 55, 66, 88, 104
Huggins, M. L., 85, 102, 111, 124, 259, 279, 283, 285, 289
Hull, A. W., 2, 4, 6
Hund, F., 88, 125
Husemann, E., 320

Inoue, R., 49
Irany, E. P., 265
Jäger, G., 177
James R. W., 21, 191
Jancke, W., 8
Jeffery, G. B., 279, 283
Jellinek, K., 231
Jenkins, H. O., 21
Johnston, H. L., 44
Jona, M., 98
Jong, de, 294

Karweit, J., 56
Kast, W., 200, 201
Katz, J. R., 192
Katzoff, S., 191
Kautsky, H., 161
Keesom, W. H., 91
Kendall, J., 273
Kertesz, Z. T., 327
Kienle, R. H., 51, 322
King, A. M., 249
King, C., 21
King, H., 176
Kirkwood, J. C., 30, 66, 91, 93, 182, 215, 238
Kistiakowsky, G. B., 43, 57
Kistler, S. S., 178
Klemm, W., 103
Knaggs, J. E., 13
Knipping, P., 2, 3
Knorr, F., 25
Kohlrausch, K. W. F., 28, 46, 60
Kohlschütter, V., 161
Kopp, H., 141
Kornfeld, G., 132
Kossel, W., 82
Kraemer, E. O., 292, 295, 302, 306, 325, 327
Kratky, O., 178, 182, 232, 233, 236, 238, 327
Krishnamurti, P., 192
Krishnan, K. S., 42
Kronman, I., 333
Krüger, D., 302
Krummacher, A. H., 201, 202, 205
Kruyt, H. R., 294
Kudar, H., 267, 302
Kuhn, R., 27, 109
Kuhn, W., 62, 64, 66, 70, 75, 76, 77, 244, 259, 283, 284, 289, 290, 327, 331, 332, 333
Kumichel, W., 332

Laar, J. J., van, 112, 237, 238
Lacher, J. R., 57
Lachs, H., 333
Landolt, 11, 26
Lamm, O., 300
Langevin, P., 34, 35
Langmuir, I., 85, 104, 111, 130, 144, 168, 172
Lansing, W. D., 302, 306, 325, 327
Laskowsky, L., 66, 70
Lassetre, E. N., 102
Laue, M. von, 2, 3, 4, 6, 177, 195
Lauppe, J. H., 103
Lazlo, H., de, 61
Lehmann, O., 199
Lehner, S., 299, 300, 301
Lennard-Jones, J. E., 13, 106, 124
Lens, W., 294
Levy, E., 29
Lewis, G. N., 82, 85, 213, 219, 251
Lieser, T., 290
Lind, S. C., 321
Linnett, J. W., 57
Liu, T. H., 299
Livingstone, 321
Lomax, R., 168
London, F., 55, 87, 91, 93, 95, 132
Lonsdale, K., 13
Lorenz, R., 237
Lossen, F., 141
Lovell, E. L., 288
Luede, F., 43
Lühdemann, R., 224
Luttringhaus, A., 15

Machatschky, F., 169
Mack, E., 62
Magnus, A., 120
Manegold, E., 233
Mardles, E. W. J., 294, 333
Maracek, E., 322
Margaretha, H., 259, 285
Margenau, H., 132
Margules, H., 220
Martin, A. E., 87
Marvel, A. C., 310
Mauguin, C., 200
Mayer, J. E., 83, 85, 124
McBain, J. W., 254, 290, 292, 299, 303
McMeekin, T. L., 66
Mecke, R., 46
Meer, N., 327
Meerwein, H., 99, 101
Megaw, H. D., 176
Mehl, J. W., 309
Melville, H. W., 311, 320, 321
Menke, H., 180, 182, 184, 186, 187
Meulen, v. d., 51
Meyer, H. H., 188
Meyer, K. H., 70, 76, 139, 219, 223, 224, 226, 232, 239, 241, 242, 244, 245, 249, 252, 287, 290, 291
Mie, G., 164
Mizushima, S., 49
Monnier, D., 51
Moog, H., 130
Morino, Y., 49
Morrow, R. M., 144, 192
Morse, J. H., 231
Morse, P. M., 87
Moschel, W., 110
Motz, H., 110
Müller, A., 13, 62, 110, 139, 164, 166, 175, 191
Mulliken, R. S., 28, 55, 66, 88
Musil, A., 236, 238

Naudé, S. M., 44
Nazmi, F., 43, 57
Nernst, W., 219, 298, 311
Neumann, R., 333
Nieuwenburg, C. J. van, 261
Niggli, P., 123, 151, 153
Nodzu, 286
Nord, F. F., 334
Northrop, J. H., 299

Obogi, R., 232, 233, 234, 332, 333
Oden, S., 280
Oeholm, L. W., 299
Ohl, F., 332
Oldham, I. W. H., 166
Oncley, J. L., 309
Onsager, L., 62, 101
Ornstein, I. S., 76
Oseen, C. W., 145, 263
Ostwald, Wo., 226, 233, 235, 236, 257, 281, 290, 291, 298

Palmer, K. J., 10, 15
Papkov, S., 294
Parker, E. A., 168, 199
Partington, J. R., 43
Parts, A., 43, 56
Patterson, A. L., 196
Pauli, Wo., 233, 234
Pauling, L., 10, 11, 13, 14, 15, 27, 28, 55, 61, 88, 110, 111, 117, 119, 169, 171
Pedersen, K. O., 302, 303
Pelmore, D. R., 62
Pelzer, H., 75, 195, 197
Perrin, J. B., 297
Perry, S. Z., 327
Peterlin, A., 283
Peters, C., 83, 88, 138
Petke, F. E., 51
Pfeiffer, P., 106
Philippoff, W., 289, 290, 293
Pickels, E. G., 303
Pierce, W. C., 191
Pilch, K., 320
Piper, L., 166
Polanyi, M., 7, 8, 311
Polsen, J., 300
Pope, W. J., 141
Pöschl, G., 87
Prins, J. A., 178, 179, 182, 183, 185

Rabinowitsch, B., 267, 269, 270, 289
Raman, C. V., 42, 178
Randall, J. T., 3, 10, 177, 194
Randall, M., 213, 219
Rayleigh, Lord, 34, 35
Raymond, A. L., 138
Redwood, B., 261
Rebaag, H., 193
Reiner, M., 267, 268, 270
Reis, A., 146, 149, 151
Rice, W. W., 43, 57, 62
Rideal, E. K., 111, 130
Rinde, A., 198
Ritter, G. J., 199
Robertson, J. M., 11, 13, 22, 102, 136, 175
Robinson, C., 301
Rocha, H. J., 332
Rochemont, R. de, 70
Roger, 201
Rogowin, S., 333
Rosen, N., 87
Rosenheim, O., 176
Rudorfer, H., 320
Rushbrooke, G. S., 226
Rydberg, R., 87

Sackur, O., 236
Sakurada, I., 289, 290, 293, 294
Sauter, E., 8
Scatchard, G., 223
Schaad, J. A., 168
Schachowsky, Z., 107
Schäfer, K., 43, 56
Scharff, M., 143
Schenck, R., 200
Scherrer, P., 2, 3, 4, 6, 8, 195, 197
Schiebold, E., 4, 7, 8
Schieber, W., 333
Schleede, A., 160
Schlesinger, M., 303
Schmidt, G. C., 222, 223
Schomaker, V., 10
Schossberger, F., 11
Schulz, G. V., 232, 233, 236, 240, 257, 291, 317, 320
Schumacher, H. J., 311
Schumann, O., 200
Seifriz, F., 271
Seitz, F., 90
Semenoff, N. N., 311
Shearer, E., 166, 175
Sheppard, S. E., 274, 292
Sherman, A., 102
Sidgwick, N. V., 30, 102, 111
Signer, R., 49, 291, 302, 306, 327
Silber, P., 175
Simha, R., 259, 275, 282, 291, 309, 327, 333
Simons, L., 28
Sisson, W. A., 199
Slater, J. C., 15, 27, 55, 66, 88, 91, 93
Smedt, J. de, 192
Smekal, A., 42
Smith, J. E., 299, 300, 301
Smoluchowski, M. v., 282, 297
Smyth, C. P., 58, 64, 204, 251
Sogani, C. M., 191, 192
Sommerfeld, A., 90, 127

Sörensen, S. P. L., 233, 234
Speakman, T. B., 158
Sponer, H., 11
Springhall, H. D., 10, 15
Spurlin, H. M., 232
Stamberger, P., 236
Stamm, A. J., 302
Stanford, S. C., 102
Staudinger, H., 164, 167, 232, 239, 259, 277, 286, 290
Steutel, H. E., 240
Stern, K. G., 302
Stevenson, D. P., 10
Stewart, G. W., 144, 178, 188, 191, 192
Stitt, F., 43, 57
Stokes, G. G., 281, 298
Stookey, S. D., 265
Stoops, W. N., 332
Stuart, H. A., 11, 15, 18, 31, 35, 36, 37, 58, 61, 68, 99, 193
Sturdivant, J. H., 13
Sugden, S., 143
Susich, G. v., 70
Süss, H., 320
Susz, B., 51
Svedberg, T., 297, 302–307
Sverak, J., 259, 283, 285
Szegvari, A., 268

Taylor, G. I., 279
Taylor, H. S., 219, 311
Teller, E., 67, 87
Thiessen, P. A., 201
Thompson, H. E., 321
Thomson, G. P., 2, 10
Tiganik, R., 62
Trautz, M., 110
Trillat, J. J., 110, 139, 144, 178
Trogus, C., 289
Turkevitch, A., 59, 62

Ubbelohde, A. R., 166
Ulich, H., 100
Ulmann, M., 232

Valkó, E., 70, 299, 301
Villiger, V., 147
Vleck, J. H. van, 66
Vorländer, D., 145, 200, 205

Waals, Jr., J. D. van der, 265
Walls, W. S., 64
Walter, J., 62
Warren, B. E., 192
Warren, W. I., 168, 169
Wassermann, A., 227
Weigert, K., 43, 56, 67
Weiler, H., 49
Weinberg, A. v., 112
Weissenberg, K., 4, 7, 8, 131, 146, 151, 153, 155, 159, 162, 267, 269
Weith, A. J., 321
Wellman, W., 160
Wieland, H., 176
Wiemann, H., 2
Wierl, R., 3, 10, 61
Wigner, E., 90
Williams, I., 321
Williams, J. W., 63, 66
Williamson, R. V., 292
Willstätter, R., 156, 175
Wilson, D. A., 191
Wilson, E. B., 28, 59, 88
Windaus, A., 176
Winterstein, H., 109
Wöhlisch, E., 70
Wolff, E., 241
Wolff, K. L., 35, 58, 86, 99, 112
Wollmann, R., 293
Woodward, J., 136
Wouda, J., 76
Wrinch, D., 168
Wyckoff, R. W. G., 9, 13, 117, 303
Wyk, A. van der, 219, 223, 226, 241, 249, 252, 267, 273, 276, 287, 290

Young, G. T., 287

Zachariasen, W. H., 13
Zacher, J. R., 43
Zahn, C. T., 63
Zawidski, Z., 220
Zernicke, F., 179, 182, 185
Zimpelmann, Z., 107
Zocher, H., 145, 200

SUBJECT INDEX

Acids, carboxylic, molecular association of, 110–11
—, —, lattice plane distances of, 192–193
Analysis, centrifugal, 302–309
Anisotropy of polarizability and degree of depolarization, 36
Apolar substances, 246, 248
Arrhenius—Trautz equation, 69
Association constant of solutions, 252
Asterisms in Laue diagrams, 4
Athermal mixtures, 223
Atomic distances, 8, 78, 79
— — in organic molecules (Tables), 12, 13
Atomic form factor and intensity distribution in liquids, 179
Atomic refraction, 26

Bayer tension theory, 18
Binary mixtures, properties of, 210–241
— —, viscosity of, 276
Boiling points and molecular shape, 105
Boltzmann constant, 30
Boltzmann equation, 215, 274
Bond constant of Mecke, 46, 47
Bond types and crystal lattices (Table), 118
Bragg's law of reflection, 3, 5
Break oscillations, 39, 51–53
Brownian motion, 284, 285, 297

C—polymerization, 322
Cadmium iodide lattice, 161
Calcium silicide lattice, 160, 162
Carbon tetrachloride, intensity curves of, 180–181
Carboxylic acids, molecular association of, 110–111
Cathode rays for determination of structure in gases, 2, 10, 78, 79
Cell volume in crystals, 9
Centers of mass of atoms in crystals, 9
Centrifugal analysis, 302–309
Chain compounds, dimensions, volumes and densities of, 139–142
Chain lattices, primary valence in, 162–168
Chain length and number of atoms, 66
— —, statistical treatment of, 70–74
Chain molecules, degradation of, 327–334
— —, internal mobility of, 62–66, 78–79
— —, orientation of, 144–145
Chain reactions, 311–322
Clausius—Mosotti equation, 24, 30
Cis—trans isomerism, 68–69, 174–175
Cohesion, molecular, 112–115
Compressibility and lattice distances, 125
Concentration, dependence of viscosity on, 293–295
Condensation reactions, kinetics of, 322–327
Co-ordination number and ionic radius, 121
Couette streaming, 278–280
Coulomb's law, 67, 83, 123, 128
Crystal lattices, classification from the aspect of forces, 117–150
— —, classification from the aspect of symmetry, 151–157
Crystalline liquids, 199–206
Crystallites, size and form by x-rays, 194–199
Cybomas, 178

Debye, the, 30
Deformability of ions, 121–123
Deformation force, 51, 53, 78, 79
Degradation of chain molecules, 327–334
Density and secondary valence, 129–131
Depolarization, degree of, 35–37, 78–79

Deuterium in evaluation of heat capacities, 43
— in interpretation of rotatory power, 57
Deviation of x-rays, 5
Diamond-type lattice, 126-127
Dielectric constant of liquid phases, 200-202
Diffraction angle and intensity of scattered beam in gas exposures, 10
Diffraction cones by linear point lattice, 163
Diffusion, coefficient of, 298 301, 307
— of dissolved particles, 297-299
p-Dinitrobenzene, structure of, 30
Dipole attraction, equations of, 92
Dipole forces and aggregate formation, 98-103
Dipole moments and cis- trans-isomerism, 32, 33
— — for deducing valence angles, 32, 33
— — of groups, 31, 32
— — of molecules, 23, 24, 33, 64, 65
Dispersion forces and aggregate formation, 103-105
— — of secondary valence, 93, 94, 96, 97, 132, 133
Dissociation from molecular spectra, 43, 44, 45
Distribution of chain molecules in solution, 252-254
Double bond, rigidity of, 67
— — and cis- trans-isomerism, 66-69

Eigen functions, 69, 88
Eigen values, 69
Einstein's viscosity equation, 278, 281, 282
Elastic modulus of rubber, 76, 77
Electrical polarization of molecules, 23, 78, 79
Electric field, behavior of molecules in, 22, 23
Electric moments of molecules, 23, 24, 78, 79
Electron density in ionic lattices, 84
Entropy, curling, of chain compounds, 227, 244, 245
Entropy, gain and melting point lowering, 251
— of gas mixing, 212-215
— of liquid mixing, 216-218, 222-227, 242-244
— and osmotic pressure, 236-239
— of primary valence chains, 74
— of rubber, 75

Fibre diagrams of interference patterns, 8
Fibre (or chain) lattices, 162, 164
Free energy of gas mixing, 212
— — of liquid mixing, 216, 247
Fugacity of mixture components, 219, 225

Gibbs-Helmholtz equation, 249
Glancing angle in x-ray reflection, 5
Gold sols, particle size in, 198
Goniometers, x-ray, 8
Graphite and graphitic acid lattices, 159, 160, 162
Group frequencies in molecular spectra, 49-51, 78-79

Hagen-Poiseuille law of viscosity, 262-267, 269, 271, 272
Hardness and lattice structure, 122
Harmonic analysis of x-ray interferences, 9
Heat content of gas mixture, 212
— — of liquid mixture, 216, 222-224
Heat of dissociation, 45
— of fusion and solubility, 248-251
— of solution and solubility, 248
— of sublimation and dispersion forces, 132, 133
— of sublimation and lattice energy, 124-126
Heteropolar linkage between oppositely charged ions, 82-85
Hexagonal close packing in monatomic liquids, 182-188
Hexamethylenetetramine lattice, 136-139, 143
Homopolar linkage between neutral atoms, 85-89

Hooke's law, 46
Hydrocarbons, unsaturated, in molecular association with nitro compounds, 106–110
Hydrogen bond or bridge, 102–103

Ice modifications, 134–135
Identity period for axis of crystal rotation, 7, 166–168
Induced dipole moments in molecules, 23, 24
Induction effect of permanent dipoles, 92, 93, 96, 97
Intensity of scattered x-rays in gas exposures, 10
— of scattered x-rays in liquids, 179
Interaction between solute and solvent, 254–258
— term of energy equation for solutions, 238–239
Interatomic distance and primary valence, 11–13, 21
Interference intensities, harmonic analysis of, 9
—, inner and outer, of liquids, 179
—, x-ray diagrams, 3
Interferometric measurement of gas molecules, 9, 78, 79
Inter-planar distance in crystals, 7
Intra-molecular distance in gases, 9
Ionic lattices, 119–126, 157–158
Ionic radii, 124
— — and co-ordination number, 121
Island chains in crystals, 155, 162
Isomerism, cis- trans-, 68, 69
Isomers, rotation, 58
Isomorphism and constitution of molecules, 174, 175
Isotopes, proportion of from molecular spectra, 44, 79

Kekulé formula for benzene, 28
Kerr effect and molecular shape, 34, 37, 38, 78, 79
Kinetics of condensation reactions, 322–327
Kink vibrations from variation of valence angle, 51
Kraemer's intrinsic velocity, 280

Lactalbumin, sedimentation, 308
Laminar flow in liquids, 273–275
Lattice, atomic, 126–127
— classification by symmetry, 151–157
— — by type of forces, 117–150
— energy and heat of sublimation, 124–126
— distances and compressibilities, 125
— distortions from Lauegrams, 4
—, ionic, 119–126, 157–158
—, metallic, 127–129
—, network or layer, 159–162
—, primary valence chain, 162–168
—, secondary valence type of, 129–147
— structure and hardness, 122
Laue diagrams, 4
Layer-line relation of Polanyi, 7
Layer orientation of solvent, 257
Liquids, crystalline, 199–206
—, monatomic, hexagonal close packing in, 182 188
—, molecular arrangement in, 177–206
—, scattering of x-rays by, 179–194
Lorentz-Lorenz equation, 25
Loschmidt number, 35

Magnetic susceptibility of liquid phases, 201, 202
Maxwell-Boltzmann distribution curve, 73
Maxwell relation, 25
Melting points of chain compounds, 250, 251
Mesophases, 199–206
Metallic lattice, 127 129
— linkage, 89–90
Mixtures, binary, properties of, 210–241
Mobility, internal, of chain molecules, 62–66, 78–79
—, —, and lattice structure, 171
Modulus of elasticity of rubber, 76, 77
Molar refraction, 25, 27–29
Molecular arrangement in liquids, 177–206
— association of carboxylic acids, 110, 111
— — of unsaturated hydrocarbons with nitro compounds, 106–110

Molecular cohesion, 112–115
— form factor and intensity distribution in liquids, 180
— weight by centrifugal analysis, 302–307
— — of high polymers from osmotic pressure, 232–236
— — of rubber from elastic modulus, 76
— — from viscosity measurements, 287–291
Molecules, internal motions of, 39–43, 62–66, 78–79
Moments, dipole, of chain molecules, 64, 65, 78, 79
— of inertia of molecules, 43, 44
Mosaic structure of molecules, 4

Nematic state, 203–205
Network lattices, primary valence, 159–162
Newton's law of viscosity, 260
Nitro compounds, molecular association of with unsaturated hydrocarbons, 106–110
Nuclear distances from band spectra, 44, 45, 52, 53, 78, 79

Octet theory, 85
Order of a valence bond, 13
Orientation of chain molecules, 144, 145
— effect of rigid dipoles, 91, 92, 96
Oscillations, break, 39
—, valence, 39
Osmotic behavior of solutions, 228–241
Osmotic pressure, effect of temperature on, 241–245
— — of high polymers and molecular weight, 232–236
Oxalic acid lattice, 136, 137, 162

Paraffin chain dimensions, 139–141
— compounds, melting points of, 250, 251
Partial pressure of liquid mixtures, 220–222
Permanent moments of polar molecules, 29
Permutoid reaction, 161, 162
Poiseuille's law of viscosity, 262, 267, 269, 271, 272
Polarity of molecules, 29, 65
Polarizability, anisotropy of, 36
— of ions, 121–123
— of molecules, 24, 26, 78, 79, 92, 93
— and refractive index, 25, 29
Polarization of molecules by electric field, 23
Polymerization, degree of, 322–327
—, degree of from Raman spectrum, 50, 51
— reactions, mechanism of, 310–322
Polymorphism in long chain compounds, 139, 140
Potential curves for bonds and molecules, 47–49
— — of cis- trans-isomerism, 68
— — for homopolar linkages, 86
— — of molecular energy, 83
Potential function for ions, 83, 85
— — for molecules, 87
Potential, internal molecular, and free rotatory power, 55–57, 63
Powder method of debye-Scherrer and Hull, 6, 196–198
Probability of chain degradation, 328–331
— and entropy of gas and liquid mixing, 214–216

Raman effect and free rotatory power, 60
Raman spectrum, 2, 42, 54, 78, 79
— — of styrene, 49
Ramie fibres for interference diagrams, 8
Rates of chain reactions, 317–320
Refraction, atomic, 26
—, molecular, 25, 27–29
Resonance effect in association of molecules, 101, 110
Rotation isomers, 58
Rotations within molecules, 39
Rotatory power, free, 53–63, 72
Rubber, equation of state of, 75, 77
—, heating effect of stretching, 74, 75
—, modulus of elasticity of, 76, 77
—, molecular weight from elastic modulus, 76
Scattering of x-rays by crystallites, 194–199
— of x-rays by liquids, 179–194

Shape of molecules by Kerr effect, 37
Silicate crystal structure, 169–171
Smectic state, 203–205
Solubility and choice of solvent, 245–251
Solute and solvent interaction, 254–258
Solutions of high polymeric substances, 207–210
—, types of, 240
Solvation pressure, 236
Space group of a crystal, 9, 156
Spring force of Kohlrausch, 46, 47
Statistical treatment of chain lengths, 70–74
Staudinger's equation, 280, 287–294, 325, 327
Sterols, unit cells of, 176
Stokes' law, 263
Structure, determination of molecular, 2
Styrene, polymerization of, 49, 50
Symmetry elements of crystals, 151–157

Temperature change in rubber by stretching, 74–75
Temperature effect on osmotic pressure, 241–245
Tension Theory of Bayer, 18
Tobacco Mosaic Virus, Sedimentation of, 308
Topochemical reactions, 161
Translation group of a crystal, 9

Ultracentrifuge, analysis by, 302–307
Unsaturated hydrocarbons, molecular association with sodium compounds, 106–110

Valence Angle, constancy of, 14–16
— —, deformities of by substituents, 17, 18, 20
— —, deformities and heat of combustion, 19
— —, deformities from dipole moments, 32, 78, 79
— —, methods of determination, 1, 8, 16, 78, 79
Valence Angle, variations and production of break vibrations, 51
Valence, Bjerrum's theory of internal force fields, 46
—, chain lattices, primary, 162–169
Valence distance, constancy of, 11
— distance, variation in, 12, 13, 21
Valence force, 51, 52
Valence networks, primary, 159–162
Valence oscillations, 39
Valence, primary, 81–90, 157–159
Valence, secondary and density, 129–131
—, — or residual, 91–98
Van der Waals constants, 94–95
Van der Waals forces and constant, 91, 95, 96
Van't Hoff's law, 230–231
Vapor pressure lowering in binary mixtures, 219–228
Vibration spectrum, 50–54, 57
Viscosity, binary, 276
— of crystalline liquids, 201
—, determination of coefficient of, 260–265
— effect of concentration on, 293–295
—, intrinsic, 280
— and molecular weight, 287–291
— of pure liquids, 258–272
— of solutions, 272–277
—, specific, 277, 280
— of suspension, 277–293

Water, arrangement of molecules in liquids, 188–191

X-ray examination of crystallites, 194–199
X-ray goniometers for characterizing lattice planes, 8
X-rays, scattering of, by liquids, 179–194
—, use of interference point diagrams in the determination of molecular structure, 2, 78, 79

Zig-zag form of chain molecules, 71–73, 164–165, 174–175, 191, 205