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ADVANCES IN CHEMICAL PHYSICS

VOLUME II

ADVANCES IN CHEMICAL PHYSICS

Edited by I. PRIGOGINE
University of Brussels, Brussels, Belgium

VOLUME II

INTERSCIENCE PUBLISHERS, INC., NEW YORK
INTERSCIENCE PUBLISHERS LTD., LONDON 1959

First Published 1959 All Rights Reserved

Library of Congress Catalog Card Number 58-9935

Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y.
Interscience Publishers Ltd., 88/90 Chancery Lane, London W. C. 2

PRINTED IN THE NETHERLANDS
BY DIJKSTRA'S DRUKKERIJ N.V., VOORHEEN BOEKDRUKKERIJ GEBR. HOITSEMA, GRONINGEN

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INTRODUCTION TO THE SERIES

In the last decades, Chemical Physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of Chemical Physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern Chemical Physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into

something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained — a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

I. PRIGOGINE

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CLATHRATE SOLUTIONS

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I. INTRODUCTION

A. General Nature of Clathrates

Some ten years ago Palin and Powell[23, 24, 31, 32] studied the peculiar "compounds" which are formed by hydroquinone with a large number of gases and volatile liquids. They showed that in these compounds the hydroquinone molecules, as a result of hydrogen bonding, form two interpenetrating three-dimensional networks which enclose roughly spherical cavities, in a ratio of 1 cavity to every 3 hydroquinone molecules. If the cavities are all empty the crystal lattice is that of the metastable β modification of hydroquinone. However, if a certain fraction of the cavities is occupied by molecules of a second component, the crystals may be thermodynamically stable in a certain region of temperature and pressure. The type of molecules which may be bound in the cavities is very diverse, as it includes O_2, N_2, CH_4, C_2H_2, CH_3OH, HCl, SO_2 and even the noble gases A, Kr, Xe. Apparently almost any substance may be bound, provided its molecules are neither too large (CCl_4) nor too small (He).

Once such a molecular complex with hydroquinone has been formed it may persist under conditions where it is no longer thermodynamically stable. Because the molecules of the second component are enclosed in the cavities they cannot escape without breaking a number of hydrogen bonds in the β-hydroquinone lattice. This corresponds to a considerable energy of activation which may prevent the attainment of thermodynamic equilibrium.

An example is the complex with argon which can be kept indefinitely in an ordinary bottle, although the equilibrium pressure of argon over the crystal amounts to several atmospheres at room temperature. Powell[31] named these complexes "clathrate compounds," which according to him are those compounds "in which two or more components are associated without ordinary chemical union but through complete enclosure of one set of molecules in a suitable structure formed by another."

Not only hydroquinone, but also phenol and a number of related substances have been reported[20, 21, 33, 44] to form clathrate compounds of a similar type. But this class of substances proves to be

even larger. Before any structural information was available Nikitin[20] already expressed the opinion that the binding mechanism operating in the so-called gas hydrates, and which remained a mystery despite a century of extensive research, should be of the same type as that in the phenol compounds just mentioned. Recently Nikitin's contention was indeed confirmed by the results of the x-ray work on gas hydrates of von Stackelberg and Müller,[42,48] and Pauling and Marsh.[26] Before we come to a discussion of the work of these authors it seems appropriate to relate a few relevant facts from the earlier investigations on the nature of the gas hydrates.*

In 1810 Davy discovered chlorine hydrate when cooling a saturated solution of chlorine in water below 9°C. Research by Villard, de Forcrand and many others subsequently showed that this type of hydrate can be formed by water with a large number of gases or volatile liquids such as Cl_2, Br_2, H_2S, CO_2, CH_4, $CHCl_3$ and again the inert gases A, Kr, Xe. It was further established that the process

$$\text{water} + \text{gas} \leftrightarrows \text{hydrate}$$

is a univariant equilibrium, so that at a given temperature the pressure of the gas has a unique value. (According to de Forcrand krypton hydrate, for instance, has an equilibrium pressure of 14.5 atm at 0°C, which rises to 47.5 atm at 12.5°C.) In fact, the study of gas hydrates constituted an essential step in the development of the theory of heterogeneous equilibria by Bakhuis Roozeboom.[1]

The accurate composition of the gas hydrates for a long time remained a controversial subject, since direct analysis leads to ambiguous results owing to decomposition of the hydrate and/or inclusion of mother liquor in the crystals. Thus it was firmly believed that the nonstoichiometric compositions of gas hydrates found experimentally were all due to errors in the analysis. But more recent determinations of the composition by the indirect

* For a detailed account of the work on gas hydrates and references prior to 1925 the reader is referred to Schröder's historical account of this subject,[40] while later references are given in von Stackelberg's papers.[42-48]

method of Scheffer and Meyer (cf. Section III.C.(1)) in some cases also led to clearly nonstoichiometric results.

The mechanism responsible for the formation of gas hydrates became clear when von Stackelberg and his school [42,43] in Bonn succeeded in determining the x-ray diffraction patterns of a number of gas hydrates and Claussen[6] helped to formulate structural arrays fitting these patterns. Almost simultaneously Pauling and Marsh[26] determined the crystal structure of chlorine hydrate.

According to these authors all gas hydrates crystallize in either of two cubic structures (I and II) in which the hydrated molecules are situated in cavities formed by a framework of water molecules linked together by hydrogen bonds. The numbers and sizes of the cavities differ for the two structures, but in both the water molecules are tetrahedrally coordinated as in ordinary ice. Apparently gas hydrates are clathrate compounds.

A common feature of all clathrates discussed so far is a host lattice, by itself thermodynamically unstable, which is stabilized by inclusion of the second component. The forces binding this component must be similar in nature to the intermolecular forces in liquids. It seems natural, therefore, to regard a clathrate "compound" as a *solid solution of the second component in the (metastable) host lattice.*

In the present review a description is given of the phase behavior of clathrates on the basis of a solution theory. The treatment is restricted to those cases where the empty host lattice ("solvent") is indeed unstable, although many of the present considerations also apply to the few cases known where the host lattice is stable. An example of the latter is the chroman complex first discovered by Dianin[9] and recently examined by Baker and McOmie and Powell and Wetters.[34]

Although it is difficult to predict exactly which solute molecules will form clathrate solutions in any given host lattice, the general principle is quite clear. All molecules which fit into the cavities will be able to stabilize the host lattice, unless they show a specific chemical interaction with the solvent molecules. HCl (or the other hydrogen halides), for instance, does not form a clathrate with water, but rather the stoichiometric compounds $HCl \cdot H_2O$,

$HCl \cdot 2H_2O$ and $HCl \cdot 3H_2O$; it readily forms a hydroquinone clathrate. Ammonia, on the other hand, does not form clathrates with either water or hydroquinone. Molecules with a very low polarizability (He, Ne, H_2) are not known to form clathrate solutions by themselves, but they do help to stabilize the clathrate of a more polarizable solute simultaneously present.[47] It is almost needless to say that in the following we shall only consider those hydrates which are in fact clathrates and which are frequently referred to as "gas hydrates," although the molecules of certain volatile liquids may also be included.

In the next section we shall give a brief account of the crystal structure of the hydroquinone clathrates and of the gas hydrates, as far as is needed for a proper understanding of the subsequent parts. The reader who is interested in the phenomenology of other clathrate compounds should consult one of the many review articles[7,8,39] on inclusion compounds.

Part II is devoted to a rigorous analysis of the thermodynamic behavior of clathrates on the basis of statistical mechanics, using a model analogous to that commonly employed for describing ideal localized adsorption. The formulas are derived for the general case of a clathrate containing n types of cavities and M different encaged solutes. Stability conditions are formulated for clathrates relative to the gaseous solutes and the stable modification of the solvent, and the method of Lennard-Jones and Devonshire is used in a quantitative analysis of the thermodynamic properties of some hydroquinone clathrates ($n = 1$) and gas hydrates ($n = 2$).

In Part III heterogeneous equilibria involving clathrates are discussed from the experimental point of view. In particular a method is presented for the reversible investigation of the equilibrium between clathrate and gas, circumventing the hysteresis effects. The phase diagrams of a number of binary and ternary systems are considered in some detail, since controversial statements have appeared in the literature on this subject.

B. Structural Information

(1) *Hydroquinone Clathrates*

Figure 1 illustrates the structure of β-hydroquinone as determined by Palin and Powell.[23,24] Some of the cavities are represented by transparent spheres containing a ball corresponding in size with an encaged argon atom. At the top and bottom of each cavity

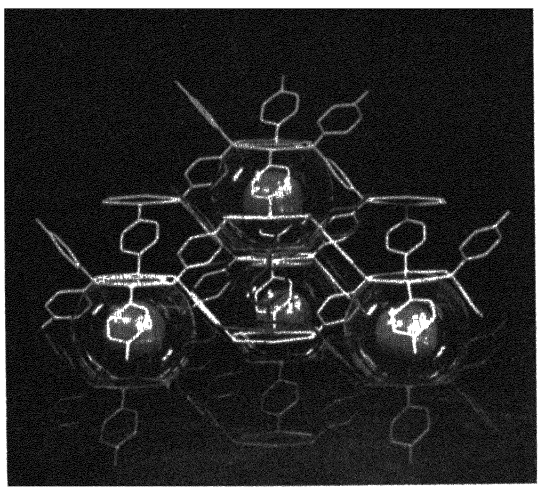

Fig. 1. The crystal structure of a hydroquinone clathrate according to Palin and Powell.[23] The balls inside the transparent spheres represent argon atoms encaged in the cavities formed by the two interpenetrating lattices. (photograph kindly supplied by Dr. Powell).

there is a hexagon of oxygen atoms formed by six hydroquinone molecules linked to each other by hydrogen bonds, three of them pointing upwards and three downwards (this is particularly clear at the top of the upper sphere in Fig. 1).

The cavity is further bounded by two carbon atoms and an adjacent hydrogen atom of each of six of the hydroquinone molecules in the manner shown in the figure. Hence, the wall of the cavity is formed by 12 oxygen atoms, 12 carbon atoms, and 18

hydrogen atoms, about evenly distributed over a sphere with radius 3.95 A. The field within the cavity, however, may not be expected to have complete spherical symmetry: a quadrupole placed at the center will show a preferred orientation because the oxygen atoms are all nearer the poles of the cavity and the carbon atoms nearer the equator.

The foregoing lattice is that which is found in the clathrates of hydroquinone with small molecules (C_2H_2, HCl, etc.). Powell[24] further showed that if larger molecules are included, the hydroquinone lattice is distorted to form oblong cavities; this distortion increases in the series CH_3OH, SO_2, CO_2 and has become extreme for CH_3CN.

(2) *Hydrates*

The unit cell of Structure I is illustrated in Fig. 2, taken from the paper by von Stackelberg and Müller.[48] It contains 46 water molecules which enclose two types of cavities. The smaller cavities are

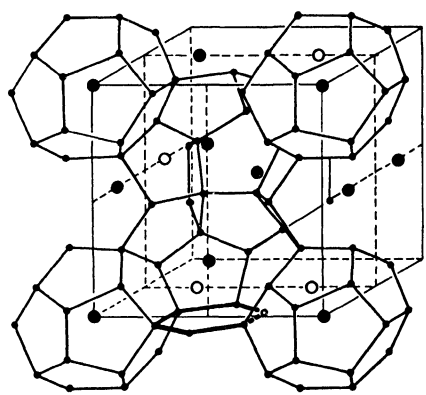

Fig. 2. Unit cell of a gas hydrate of Structure I according to von Stackelberg and Müller.[48] For the sake of clarity only the elements lying in the nearer half of the unit cell have been drawn. The smaller dots indicate the tetrahedrally surrounded water molecules, the larger dots represent the centers of the two types of cavities.

located at the vertices and the center of the unit cell; they are each formed by a pentagonal dodecahedral array of 20 water molecules. The remaining six water molecules in the unit cell form bridges

TABLE I. Thermodynamic Data and Lattice Constants of Some Hydrates

(The data in the table have been copied from the papers by von Stackelberg and Müller[a] and von Stackelberg and Jahns,[b] except when otherwise indicated.)

Solute (in order of increasing bp)	Dissoc. pressure at 0° C	Max. temp. at which hydrates exist, °C	Heat of formation from pure water and gas at 0° C kcal/mole solute	Lattice constant, A
A	95.5 atm [c]	no maximum exists		
CH_4	26.0 atm	no maximum exists	14.5	
Kr	14.5 atm	no maximum exists	13.9±0.5	
Xe	1.15 atm [d]	no maximum exists	16.7±0.5	12.0
C_2H_4	5.44 atm [e]	no maximum exists	15.0 [e]	
C_2H_6	5.2 atm	14.5	16.3 [f]	
N_2O	10 atm	12	14.7	12.03
C_2H_2	5.7 atm	16	15	
CO_2	12.47 atm [g]	10.20 [g]	14.4	12.07
H_2S	698 mm [h]	29.5 [h]	14.8 [i]	12.02
Cl_2	252 mm	28.7	16.0	12.03
CH_3Cl	311 mm	21	18.1	12.00
SO_2	297 mm	12.1	16.6	11.97
CH_3Br	187 mm	14.5	19.5	12.09
CH_3SH	239 mm	12	16.6	12.12
Br_2	43.90 mm [j]	5.81 [j]	20.83 [j]	12.1
C_3H_8	1.74 atm [k]	5.69 [l]	32 [k]	17.40
$CHCl_2F$	115 mm [m]	8.61 [m]	32.7 [m]	
C_2H_5Cl	201 mm	4.8	31.9	17.30
CH_2Cl_2	116 mm	1.7	29	17.33
CH_3I	74 mm	4.3	31.4	17.14
$CHCl_3$	(50 mm)	1.6	31	17.33

[a] Stackelberg, M. von, and Müller, H. R., *Z. Elektrochem.* **58**, 25 (1954), Table I.

[b] Stackelberg, M. von, and Jahns, W., *Z. Elektrochem.* **58**, 162 (1954), Table II.

[c] Diepen, G. A. M., private communication.

[d] Schroeder, W., *Die Geschichte der Gashydrate*, F. Enke, Stuttgart, 1925, p. 87.

[e] Diepen, G. A. M., and Scheffer, F. E. C., *Rec. trav. chim.* **69**, 593 (1950).

[f] Roberts, O. L., Brownscombe, E. R., and Howe, L. S., *Oil Gas J.* **39**, No. 30, 37 (1940).

between these dodecahedra in such a way that a second type of cavity is formed: a tetrakaidecahedron having two opposite hexagonal faces and twelve pentagonal faces. (One of these hexagons has been marked by heavier lines in the lower center of Fig. 2.)

Although the agreement between the observed x-ray intensities and those calculated from the aforementioned model is not perfect, the latter is thought to be essentially correct. The "composition" of a gas hydrate of Structure I is then characterized by

46 water molecules,

2 smaller cavities: $z_1 = 20$, $a_1 = 3.95$ A

6 larger cavities: $z_2 = 24$, $a_2 = 4.30$ A

The number of oxygen atoms surrounding the two types of cavities are denoted by z_1, z_2, and a_1, a_2 are the average distances of these atoms to the centers of the cages. The smaller cavities are very nearly spherical and have a free diameter of approximately 5.1 A when assuming Pauling's value[25] of 1.4 A for the van der Waals radius of oxygen. The larger cavities are slightly oblate, since the distances from the center to the surrounding oxygen atoms vary between 4.04 A and 4.65 A. Their free diameter is approximately 5.8 A. (Cf. ref. 30; figures are based on a unit cell edge = 12.0 A.)

According to von Stackelberg and Müller,[48] the hydrates tabulated in the top section of Table I all crystallize in Structure I.

The molecules of the gases bound in these hydrates are relatively small and in general occupy both types of cavities. If all cavities were filled, the composition would be 1 gas $5\frac{3}{4}$ H_2O, but as we shall see, a certain fraction of the cavities must remain empty when the

---

[g] Herreilers, H. W., Thesis, Amsterdam, 1936.

[h] Selleck, F. T., Carmichael, L. T., and Sage, B. H., *Ind. Eng. Chem.* **44**, 2219 (1952).

[i] Scheffer, F. E. C., and Meyer, G., *Proc. Acad. Sci. Amsterdam* **21**, 1338 (1919).

[j] Mulders, E. M. J., Thesis, Delft, 1937.

[k] Frost, E. M., and Deaton, W. M., *Proc. Nat. Gas Dept.*, AGA, 1946.

[l] Miller, B., and Strong, E. R., Jr., AGA Monthly, **28**, No. 2, 63 (1946).

[m] Banks, W. P., Heston, B. O., and Blankenship, F. F., *J. Phys. Chem.* **58**, 962 (1954).

hydrate is formed in equilibrium with an aqueous phase. The molecules of CH_3Br, CH_3SH, and Br_2 have such dimensions that while they are still crystallizing in Structure I, they cannot occupy the smaller cavities. This is supported by the high water content of the bromine hydrate (1 $Br_2 \cdot 8.47\ H_2O$) found by Miss Mulders[19] and further proved by the intensity of its x-ray diffraction pattern.[48]

The unit cell of the hydrates crystallizing in Structure II is rather complicated, and for a detailed description the reader is referred to the original publications.[6,48] Its "composition" is characterized by:

136 water molecules,

16 smaller cavities: $z_1 = 20$, $a_1 = 3.91$ A

8 larger cavities: $z_2 = 28$, $a_2 = 4.73$ A

The smaller cavities are distorted pentagon dodecahedra (distance of oxygen atoms to center varies between 3.77 and 3.95 A); their average free diameter is only about 5.0 A. The larger cavities are almost spherical; the oxygen atoms lie at the vertices of hexadecahedra and their free diameter is 6.7 A. The distances have been calculated on the basis of a unit cell edge of 17.40 A as found for propane hydrate.

Hydrates of Structure II are formed only by molecules which are too large to be accommodated in Structure I. This implies that they occupy only the larger cavities. Also very common are the so-called mixed hydrates discussed by von Stackelberg and Meinhold[47] in which large molecules (e.g. $CHCl_3$) occupy the larger cavities of Structure II and small molecules (e.g. CO_2, N_2, H_2S) occupy the smaller cavities as well as some of the larger ones. In Section III. C. (2) (b) a quantitative discussion is given of the phase behavior of the system methane-propane-water in which such a mixed hydrate occurs.

II. STATISTICAL THEORY

A. Basic Assumptions

The thermodynamic properties of clathrates can be derived from a simple model which corresponds to the three-dimensional generalization of ideal localized adsorption. In ref. 52 the deriva-

tion was explicitly given for a hydroquinone clathrate, in which only one component was enclosed in a single type of cavity, using ordinary partition functions. Although the extension of this theory to the most general case of a clathrate with cavities of different sizes and several occluded components (e.g., a mixed hydrate) is straightforward, it is more appropriate to use a grand partition function.

Let us consider a clathrate crystal consisting of a cage-forming substance Q and a number of encaged compounds ("solutes") $A, B, \ldots, M$. The substance Q has two forms: a stable modification, which under given conditions may be either crystalline (α) or liquid (L), and a metastable modification (β) enclosing cavities of different types $1, \ldots, n$ which acts as host lattice ("solvent") in the clathrate. The number of cavities of type i per molecule of Q is denoted by ν_i. For hydroquinone $\nu = \frac{1}{3}$; for gas hydrates of Structure I $\nu_1 = 1/23$ and $\nu_2 = 3/23$, for those of Structure II $\nu_1 = 2/17$ and $\nu_2 = 1/17$.

Our analysis is, furthermore, based on the following assumptions:

(a) The contribution of the Q molecules to the free energy is independent of the mode of occupation of the cavities. This excludes clathrates in which the encaged molecules have such dimensions that they seriously distort the host lattice; e.g., CO_2 or CH_3CN in hydroquinone.

(b) The encaged molecules are localized in the cavities and a cavity can never hold more than one solute molecule.

(c) The mutual interaction of the solute molecules is neglected; i.e., the partition function for the motion of a solute molecule in its cage is independent of the number and types of solute molecules present.

(d) Classical statistics are valid.

The assumptions (a)–(d) are believed to give an adequate description of the physical situation in the great majority of clathrates. Assumption (a) implies that the spectrum of the host lattice is not affected by the presence of the solute molecules. Little is known about this, but since the host lattice in general is a com-

paratively rigid structure, held together by hydrogen bonds, one would expect little influence of the weakly bound solute molecules on the vibrational and electronic modes of the solvent molecules. For the clathrates reported so far, assumption (b) seems to be correct, but it might conceivably fail in a compound with large cavities and comparatively small solute molecules. Clathrates containing Ne, He, or H_2 as major occluded components have not been reported, but if they exist they might constitute interesting violations of assumptions (b) and (d). Although assumption (c) can never be strictly true, numerical calculations and experimental evidence show that the contribution of solute-solute interaction to the configurational energy is at most a few per cent of the energy of binding of the solute molecules in their cages (cf. ref. 11).

B. Construction of Partition Function

As our system we choose a clathrate crystal containing N_Q molecules of Q and occupying a volume V at the temperature T. We further suppose that it has been crystallized while in equilibrium with the solutes $A, \ldots, J, \ldots, M$, having absolute activities $\lambda_A, \ldots, \lambda_M$, i.e., chemical potentials

$$\mu_J = kT \ln \lambda_J \tag{1}$$

This system is most conveniently described by the independent variables

$$T, V, N_Q, \lambda_A, \ldots, \lambda_M \tag{2}$$

and a generalized partition function Ξ which corresponds to these variables.*

If the cavities of type i were known to contain N_{Ji} molecules of each species J, the ordinary partition function (PF) would be:[52]

* The reader who is less familiar with the theory of grand partition functions may directly proceed to Eqs. 12a and 13. The physical basis of these formulas and the significance of the quantities C_{Ki} will then become apparent in the subsequent paragraph; p_K is the vapor pressure (or fugacity) of solute K and y_{Ki} is the probability of finding a K molecule in a cavity of type i.

$$(\mathrm{PF}) = \exp\left(-\frac{F^\beta}{kT}\right) \prod_i \left[\frac{(\nu_i N_Q)!}{(\nu_i N_Q - \sum_J N_{Ji})! \prod_J N_{Ji}!} \prod_J h_{Ji}^{N_{Ji}} \right] \qquad (3)$$

where F^β is the free energy of the "empty" β lattice for the given values of T, V, N_Q. The combinatorial factor expresses the number of distinct ways in which the $N_{Ai}, \ldots, N_{Mi}$ solute molecules can be distributed over the $\nu_i N_Q$ cavities of type i, and $h_{Ji}(T, V)$ is the partition function of a J molecule when encaged in a type i cavity. (Capital subscripts throughout refer to chemical compounds, lower case subscripts to cavities of different types. If the clathrate has only one type of cavity, the second subscript will be omitted.)

In order to obtain the function Ξ we have to multiply Eq. 3 by the product

$$\lambda_A^{N_{A1}} \lambda_A^{N_{A2}} \ldots \lambda_B^{N_{B1}} \ldots \lambda_M^{N_{Mn}} = \prod_i \prod_J \lambda_J^{N_{Ji}}$$

and to sum the resulting expression over all possible values of the N_{Ji}. One obtains

$$\Xi = \exp\left(-\frac{F^\beta}{kT}\right) \sum_{N_{Ji}} \prod_i \left\{ \frac{(\nu_i N_Q)!}{(\nu_i N_Q - \sum_J N_{Ji})! \prod_J N_{Ji}!} \prod_J h_{Ji}^{N_{Ji}} \lambda_J^{N_{Ji}} \right\}$$

i.e., after summing with the aid of the multinomial theorem

$$\Xi = \exp\left(-F^\beta/kT\right) \prod_i \left(1 + \sum_J h_{Ji} \lambda_J\right)^{\nu_i N_Q} \qquad (4)$$

The function Ξ is a grand partition function with respect to the solutes, but an ordinary partition function with respect to the solvent; it is linked to thermodynamics by the relation

$$d(kT \ln \Xi) = SdT + PdV + \sum_K N_K d\mu_K - \mu_Q dN_Q$$

or in terms of the absolute activities

$$kTd \ln \Xi = (U/T)dT + PdV + \sum_K kTN_K d\lambda_K/\lambda_K - \mu_Q dN_Q \qquad (5)$$

The relation is the same as that for grand partition functions (cf., e.g., Rushbrooke[37]), evidently with the exception of the term $\mu_Q dN_Q$.

The composition of the clathrate under the given conditions follows immediately from Eqs. 4 and 5,

$$N_K = \sum_i N_{Ki} = \lambda_K(\partial \ln \Xi/\partial\lambda_K)_{T,\,V,\,N_Q,\,\lambda_J\,(J\neq K)}$$
$$= \sum_i \nu_i N_Q h_{Ki}\lambda_K/(1+\sum_J h_{Ji}\lambda_J)$$

Since N_K must be a linear and homogeneous function of the numbers of cavities of different types, it follows directly from the previous equation that

$$N_{Ki} = \nu_i N_Q h_{Ki}\lambda_K/(1+\sum_J h_{Ji}\lambda_J)$$

which can also be written

$$y_{Ki} = h_{Ki}\lambda_K/(1+\sum_J h_{Ji}\lambda_J) \tag{6}$$

where $y_{Ki} = N_{Ki}/(\nu_i N_Q)$ is the probability of finding a molecule of K in a cavity of type i.

The chemical potential of the solvent similarly follows from the pair of Eqs. 4, 5,

$$\mu_Q/kT = -(\partial \ln \Xi/\partial N_Q)_{T,\,V,\,\lambda_J}$$
$$= \mu_Q{}^\beta/kT - \sum_i \nu_i \ln (1+\sum_J h_{Ji}\lambda_J) \tag{7}$$

where $\mu_Q{}^\beta = \partial F^\beta/\partial N_Q$ is the chemical potential of the β modification.

Finally we have for the energy U from Eqs. 4 and 5

$$\frac{U}{kT^2} = \left(\frac{\partial \ln \Xi}{\partial T}\right)_{V,N_Q,\lambda_J} = \frac{U^\beta}{kT^2} + \sum_i \nu_i N_Q \frac{\sum_J \lambda_J\,\partial h_{J_i}/\partial T}{1+\sum_J h_{Ji}\lambda_J}$$

On substituting from Eq. 6 this gives

$$\frac{U-U^\beta}{kT^2} = N_Q \sum_{J,i} \nu_i y_{Ji} \frac{\partial \ln h_{Ji}}{\partial T} \tag{8}$$

Equations 6 and 7 determine the composition and chemical potential of the solvent in a clathrate as a function of the variables, Eq. 2. Their physical significance can best be appreciated if we

introduce the assumption that the vapors of the solutes behave as ideal gases so that

$$\lambda_K = p_K/(kT\Phi_K(T)) \tag{9}$$

The function $\Phi_K(T)$ is the molecular partition function of gaseous K with the volume factor removed,

$$\Phi_K(T) = (2\pi m_K kT/h^2)^{\frac{3}{2}} j_K(T) \tag{10}$$

where m_K is the mass of a K molecule and $j_K(T)$ its internal partition function including rotations. Even if the vapors are not ideal, the formulas remain valid, but p_K then denotes the fugacity of K and not simply its partial pressure.

On substituting Eq. 9 into Eq. 6 and using the abbreviation

$$C_{Ki} = \frac{1}{kT}\frac{h_{Ki}(T, V)}{\Phi_K(T)} = \frac{h_{Ki}(T, V)\lambda_K}{p_K} \tag{11}$$

one obtains

$$y_{Ki} = C_{Ki}p_K/(1 + \sum_J C_{Ji}p_J) \tag{12}$$

Since according to Eqs. 6 and 12

$$1 - \sum_K y_{Ki} = (1 + \sum_J h_{Ji}\lambda_J)^{-1} = (1 + \sum_J C_{Ji}p_J)^{-1}$$

this can also be written as

$$p_K = \frac{1}{C_{K1}}\frac{y_{K1}}{1 - \sum_J y_{J1}} = \frac{1}{C_{K2}}\frac{y_{K2}}{1 - \sum_J y_{J2}} = \ldots \tag{12a}$$

By a similar substitution we have from Eq. 7

$$\mu_Q = \mu_Q^\beta + kT\sum_i \nu_i \ln (1 - \sum_K y_{Ki}) \tag{13}$$

The pair of Eqs. 12, 13 epitomizes the relation between the equilibrium vapor pressure, composition, and chemical potential of the solvent in a clathrate obeying the present model. These expressions were used in the calculation of the thermodynamic properties of gas hydrates[30] and have also been formulated by Barrer and Stuart;[4] for a clathrate with a single type of cavity and one occluded component they reduce to the equations of ref. 52.

C. Nature of the Approximation

Equation 12 is Langmuir's isotherm, while Eq. 13 clearly is a generalization of Raoult's law. Considering the nature of our model this is not surprising: Langmuir's isotherm is characteristic for localized adsorption without interaction of the adsorbed molecules and Raoult's law for the properties of the solvent in a solution where solute-solute interaction can be neglected. The situation may perhaps be illustrated by the following qualitative argument.

Consider the simplest type of clathrate having only one kind of cavity so that we can drop the i subscripts. If a gaseous molecule K is encaged in one of the cavities this corresponds to the process

$$\text{empty cavity} + K \rightarrow \text{occupied cavity}$$

In other words: the empty cavity *binds* the molecule K to form an occupied cavity. If we denote an empty cavity by X and an occupied one by Y this can be described as a reversible chemical reaction

$$X + K \leftrightarrows Y$$

If we may neglect interaction between neighboring K molecules the reaction will have an equilibrium constant

$$C_K \sim [Y]/[X][K]$$

where the square brackets denote concentrations.

Assuming that K is the only solute present one further has

$$[Y] \sim y_K, \qquad [X] \sim 1-y_K, \qquad \text{and } [K] \sim p_K$$

On substituting these values into the previous relation one obtains (when expressing C_K in the proper units)

$$C_K = y_K/(1-y_K)p_K, \quad \text{or} \quad p_K = C_K^{-1}\, y_K/(1-y_K) \tag{14}$$

which is precisely Eq. 12a for a clathrate with one type of cavity and a single solute.

But Langmuir's isotherm for the solute entails the generalized form of Raoult's law (Eq. 13) as a necessary thermodynamic consequence. This can best be seen from the Gibbs-Duhem equation,

$$N_Q d\mu_Q + N_K d\mu_K = 0 \tag{15}$$

According to Eq. 14

$$d\mu_K = kTd \ln p_K = kT\{y_K(1-y_K)\}^{-1} dy_K \tag{16}$$

and further from the definition of y_K,

$$N_K = \nu N_Q y_K \tag{17}$$

By substituting Eqs. 16 and 17 into Eq. 15

$$N_Q \int d\mu_Q = -kT\nu N_Q \int \frac{dy_K}{1-y_K},$$

$$\mu_Q - \mu_Q{}^\beta = kT\nu \ln (1-y_K) \tag{18}$$

which is identical with Eq. 13 for the present simple case.

Equation 13 has an important implication: a clathrate behaves as an ideally dilute solution insofar as the chemical potential of the solvent is independent of the nature of the solutes and is uniquely determined by the total solute concentrations $\sum_K y_{K1} \cdots \sum_K y_{Kn}$ in the different types of cavities. For a clathrate with one type of cavity the reverse is also true: for a given value of μ_Q (e.g. given concentration of Q in a liquid solution from which the clathrate is being crystallized) the fraction of cavities occupied $\sum_K y_K$ is uniquely determined by Eq. 13. When there are several types of cavities, however, this is no longer so since the individual occupation numbers $\sum_K y_{K1}, \ldots, \sum_K y_{Kn}$, and hence the total solute concentration

$$\sum_{K,i} \nu_i y_{Ki}$$

in moles solute/mole solvent will depend on the properties of the solutes. For clathrates with a very low solute content the logarithms in Eq. 13 may be expanded and this equation then reduces to van 't Hoff's law

$$\mu_Q = \mu_Q{}^\beta - kT \sum_{K,i} \nu_i y_{Ki}$$

as might have been expected.

D. Stability of Clathrate and the Equilibrium Q^α-clathrate-A (gas)

For a clathrate to be stable with respect to Q^α it must have

$$\mu_Q \leqq \mu_Q{}^\alpha \tag{19}$$

If we write

$$\Delta\mu(T, P) = \mu_Q{}^\beta - \mu_Q{}^\alpha \tag{20}$$

for the difference between the chemical potentials of the two modifications, which is a function of temperature and total pressure, substitution of Eq. 13 into Eq. 19 gives

$$\sum_i \nu_i \ln (1 - \sum_K y_{Ki}) \leqq -\Delta\mu/kT \tag{21}$$

With the aid of Eq. 12 the condition may alternatively be expressed as

$$\sum_i \nu_i \ln (1 + \sum_K C_{Ki} p_K) \geqq \Delta\mu/kT \tag{21a}$$

A clathrate which under given conditions can exist in equilibrium with Q^α will be named "equilibrium clathrate" and for this the $=$ sign holds.

From the condition 21a it immediately follows that if the clathrate is formed in the presence of a number of compounds which are potential solutes, i.e., sufficiently small to have $C_{Ki} \neq 0$ for some i, all these compounds contribute to its stability. As has already been pointed out by Barrer and Stuart[4] this at once explains the stabilizing influence of "Hilfsgase" such as air, CO_2, or H_2S on the formation of gas hydrates discussed by Villard[49] and von Stackelberg and Meinhold.[47] If there is only one solute, Eq. 21a with the $=$ sign determines the minimum vapor pressure p_A necessary to make the clathrate stable relative to Q^α. Since all cavities contribute to the stabilization, one cannot say that this minimum pressure is controlled by a specific type of cavity.

The consequences of the stability condition are clearly demonstrated by considering the univariant equilibrium

$$Q^\alpha\text{-clathrate-}A\,(\text{gas}) \tag{22}$$

between two solids and a single gaseous solute. Of the various three-phase equilibria involving clathrates this is the one most amenable

to theoretical treatment since the clathrate then coexists with a phase consisting of pure Q only.

There is one other three-phase equilibrium involving clathrates which is of considerable practical importance, namely that between a solution of Q, the clathrate, and gaseous A. For this equilibrium the previous formulas and many of the following conclusions also hold when replacing $\mu_Q{}^\alpha$ by $\mu_Q{}^L$, the chemical potential of Q in the liquid phase. But a complication then arises since $\mu_Q{}^L$ and the difference $\mu_Q{}^\beta - \mu_Q{}^L$ are not only determined by P, T, but also depend on the solubilities of the solute in the liquid phase and thus vary with the nature of the solute. Since $\mu_Q{}^L$ is in general not known we shall not consider this equilibrium explicitly.

The equilibrium 22 requires the equality of the chemical potentials

$$\begin{aligned} \mu_A &= \mu_A{}^G \\ \mu_Q &= \mu_Q{}^\alpha \end{aligned} \tag{23}$$

As before μ's without superscript refer to the clathrate; for convenience we neglect the vapor pressure of Q, but this is not essential. Equilibrium between clathrate and gas was implicitly assumed in our derivation; it led to Eq. 12. Equilibrium between clathrate and Q^α is governed by Eq. 21 with the $=$ sign. Repeating these equations for a single solute A we have

$$\text{equilibrium } Q^\alpha\text{-clathrate-gas} \begin{cases} y_{A1} = \dfrac{C_{A1} p_A}{1+C_{A1} p_A}, \ldots, y_{An} = \dfrac{C_{An} p_A}{1+C_{An} p_A} & (24) \\ \sum_i \nu_i \ln (1-y_{Ai}) = -\Delta\mu/kT. & (25) \end{cases}$$

Equations 24 and 25 constitute $(n+1)$ relations between the $(n+2)$ variables T, p_A, $y_{A1}, \ldots, y_{An}$, thus corresponding to a univariant equilibrium.

By substituting the y_{Ai} from Eq. 24 into Eq. 25 one obtains a relation between p_A, T; by writing

$$Y_A = \sum_i \nu_i y_{Ai} \tag{26}$$

for the total A content of the clathrate (in moles A/mole Q) and again substituting the y_{Ai} from Eq. 24, one obtains a relation between p_A, Y_A, and T (through the C_{Ai}). The pair of relations de-

termines the position of the three-phase line and composition of the equilibrium hydrate in the phase diagram.

Let us explicitly consider the two important cases of hydroquinone clathrates and gas hydrates.

(1) *Hydroquinone Clathrates*

These are characteristic examples of clathrates in which only one type of cavity occurs. The left-hand side of Eq. 25 then contains a single term only and the composition along the three-phase line is completely determined by

$$\nu \ln (1-y_A) = -\Delta\mu(T, P)/kT \qquad (\nu = 1/3) \qquad (25')$$

If there are several solutes the same equation holds when replacing y_A by $\sum_K y_K$. The variation of $\Delta\mu$ with pressure is extremely small (cf. Eq. 27 below) and can be neglected for hydroquinone clathrates, except when speculating about the possible existence of clathrates with light gases such as Ne or H_2. Hence Eq. 25′ implies that the total solute concentration of a clathrate in equilibrium with α-hydroquinone at a given temperature should be independent of the nature of the solute(s). This conclusion has indeed been verified experimentally: the equilibrium clathrates of hydroquinone with argon and krypton both have $y_A = 0.34$ at 25°C (cf. Section III.B.(1). Substituting this result into Eq. 25′ one finds for the difference in Gibbs function between the β- and α-modifications $\Delta\mu = 0.082$ kcal/mole at 25°C.

The equilibrium clathrate of methanol has the much higher value $y_A = 0.47$ at 25°C. This is to be expected since the methanol molecule is so large that it distorts the β lattice contrary to assumption (a) of Section II.A, thereby increasing the value of $\Delta\mu$ to be taken in Eq. 25′. The methyl cyanide molecule distorts the lattice even more, and as already noted by Powell,[24] its equilibrium clathrate must therefore have a value of y_A still higher than that for the methanol clathrate. (The CH_3CN clathrate investigated by Powell, however, was not an equilibrium clathrate, cf. point *B* in Fig. 5).

The variation with temperature and pressure of the composition of the equilibrium clathrate is given by the total differential of Eq. 25′,

$$\nu\, d \ln (1-y_A) = (\Delta H/RT^2)dT - (\Delta V/RT)dP \qquad (27)$$

Here ΔH and ΔV denote the differences between molar heat functions and molar volumes of the β and α modifications ($\beta-\alpha$). The values of ΔH and ΔV for hydroquinone have been collected in Table II. The variation of the equilibrium composition of the argon

TABLE II. Thermodynamic Properties of the Metastable Host Lattice, Relative to the Stable α-Modification

Host lattice		$\Delta\mu$ kcal/mole	ΔH kcal/mole	ΔV ml/mole	V^{α} ml/mole
Hydroquinone, 25°C		0.082 [a]	0.16 [b]	4.6 [c]	82.8 [c]
Hydrates, 0°C	Structure I	0.167 [d]	$\leqq 0$ [e]	3.0 [f]	19.6
	Structure II	0.19 [g]		3.4 [f]	

[a] Waals, J. H. van der, and Platteeuw, J. C., *Rec. trav. chim.* **75**, 912 (1956); this review Section III.B.(1).

[b] Evans, D. F., and Richards, R. E., *Proc. Roy. Soc.* (*London*) **A223**, 238 (1954).

[c] Powell, H. M., *J. Chem. Soc.* (*London*) **1948**, 61.

[d] Platteeuw, J. C., and Waals, J. H. van der, *Mol. Phys.* **1**, 91 (1958); this review Section II.D.

[e] Proposed by Eucken, cf. Stackelberg, M. von, *Naturwiss.* **36**, 361 (1949); this review Section II.F.(2).

[f] Stackelberg, M. von, and Müller, H. R., *Z. Elektrochem.* **58**, 25 (1954).

[g] Approximate; this review Section III.C.(2)(b).

clathrate when going from 25°C ($y = 0.34$, ref. 53) to 60°C ($y = 0.28$, ref. 28) is in good agreement with Eq. 27 if we use the value of ΔH determined by Evans and Richards reported in Table II. The variation with pressure is so small that it can be neglected for the pressures normally encountered.

(2) *Hydrates*

These are characteristic examples of clathrates in which two types of cavities simultaneously occur. The relations 24, 25, and 26 now reduce to

$$y_{A1} = C_{A1}p_A/(1+C_{A1}p_A), \quad y_{A2} = C_{A2}p_A/(1+C_{A2}p_A) \qquad (24'')$$

$$\nu_1 \ln (1-y_{A1})+\nu_2 \ln (1-y_{A2}) = -\Delta\mu/kT \qquad (25'')$$

$$Y_A = \nu_1 y_{A1}+\nu_2 y_{A2} \qquad (26'')$$

For hydrates of Structure I, $\nu_1 = 1/23$, $\nu_2 = 3/23$; for those of Structure II, $\nu_1 = 2/17$, $\nu_2 = 1/17$. It is obvious that Eq. 25'' can be satisfied by an infinite set of (y_{A1}, y_{A2}) values and consequently the concentration Y_A of the solute in an equilibrium gas hydrate is *not* a constant for given T, but depends on the nature of the occluded gas(es). The distribution of the solute molecules over the two types of cavities is determined by the relative values of the functions C_{A1} and C_{A2}. This difference between hydroquinone clathrates and gas hydrates was overlooked by Barrer and Stuart[4] in the discussion of their results. In the special case that the solute molecules are so large that they only fit in the larger cavities ($C_{A1} = 0$) terms with y_{A1} do not occur in Eqs. 24''–26'', and the equations become analogous to those for the hydroquinone clathrates. This has an important practical consequence: although in general no simple relation exists between the composition of an equilibrium gas hydrate and the difference in chemical potential between the empty hydrate lattice and ordinary ice, this difference can yet be found by studying a hydrate with solute molecules of such dimensions that they can only be accommodated in the larger cavities.

The value of $\Delta\mu$ for gas hydrates of Structure I reported in Table II could thus be derived[30] with the aid of Eq. 25' with $\nu = 3/23$ from the composition $Br_2 \cdot 8.47\ H_2O$ of the bromine hydrate following from Miss Mulders' accurate study[19] of the system Br_2+H_2O; cf. Section III.C.(1). It should be possible to derive the value of $\Delta\mu$ for hydrates of Structure II in the same way from the equilibrium composition of the SF_6 hydrate: unfortunately the equilibrium composition of this hydrate is not known. The value of $\Delta\mu$ for hydrates of Structure II reported in the table has been derived from the vapor pressure of the SF_6 hydrate using some further assumptions (cf. Section III.C.(2)(b)).

As Barrer and Stuart[4] have already demonstrated, insufficient data are available to give a quantitative analysis of the change of composition of a hydrate along the three-phase line ice-hydrate-

gas. By differentiating Eq. 25'' one obtains for the total differential of the condition expressing equilibrium between clathrate and Q^{α} (i.e., hydrate and ice)

$$\nu_1 d\ln(1-y_{A1})+\nu_2 d\ln(1-y_{A2})=(\Delta H/RT^2)dT-(\Delta V/RT)dP \quad (28)$$

In this equation, ΔH is not known, but Eucken (as quoted by von Stackelberg[48]) suggested, $\Delta H = 0$, and comparison of experimental and calculated heats of hydrate formation[30] certainly supports a low value of ΔH. The variation of the composition of a gas hydrate along the three-phase line ice-hydrate-gas will therefore be small. (The variation along the three-phase line hydrate-aqueous liquid-gas is larger, cf. Section III.C.(1).)

Barrer's discussion[4] of his analog of Eq. 28 merits some comment. Equation 28 expresses the equilibrium condition between ice and hydrate. As such it is valid for all equilibria in which the two phases coexist and not only for univariant equilibria corresponding with a $P-T$ line in the phase diagram. (It holds, for instance, in the entire ice-hydrateII-gas *region* of the ternary system water-methane-propane considered in Section III.C.(2).)

In addition to Eq. 28 one has Clapeyron's equation

$$dP/dT = \Delta' H/T\Delta' V \quad (29)$$

which is a thermodynamic identity valid for all univariant equilibria, no matter how the compositions of the phases change along the equilibrium line.[14,50] The primed quantities $\Delta' H$ and $\Delta' V$ denote the changes in heat function and volume accompanying the phase transformation possible for the univariant equilibrium considered (at constant P, T). In the present case $\Delta' H$ and $\Delta' V$ might denote the changes in heat function and total volume when one gram of hydrate is formed from ice and gaseous A.

E. Evaluation of the Cell Partition Function by the Method of Lennard-Jones and Devonshire

The partition function Ξ (Eq. 4) and the resulting expressions for the properties of the clathrate contain the cell partition functions h_{Ji} as the only unknowns. If it were possible to construct these parti-

tion functions, the thermodynamic behavior of clathrates relative to the empty β lattice might be predicted.

The theory introduced by Lennard-Jones and Devonshire[13, 17] for the study of liquids provides a powerful method for the quantitative evaluation of the partition function of a solute molecule within its cavity.[51] Because the application of this method to the present problem has been described in detail,[52] we shall restrict ourselves to its most essential features.

As we have seen in Section I.B x-ray analysis of both hydroquinone clathrates and hydrates has revealed that all cavities are approximately spherical and that their walls consist of a relatively large number of atoms. It is therefore plausible to suppose that the field of force acting on a solute molecule in its cage has a spherical symmetry, and, in addition to the aforementioned assumptions (a)–(d), to make the two further assumptions:

(e) The solute molecules can rotate freely in their cavities (i.e., the rotational partition function for the motion in the cavity is the same as that in the perfect gas).

(f) The potential energy of a solute molecule when at a distance r from the center of its cage is given by the spherically symmetrical potential $w(r)$ proposed by Lennard-Jones and Devonshire.

Before proceeding further it should be noted that there is a great difference in severity of the restrictions imposed by the earlier assumptions (a)–(d) and the present ones, (e) and (f). The earlier ones mainly restrict the size of the enclosed molecules to such a range that they neither distort the lattice, nor give rise to multiple occupancies or quantum effects.

By the last two assumptions the theory, strictly speaking, is only applicable to the monatomic gases A, Kr, Xe, to a somewhat lesser extent to the almost spherical molecules CH_4, CF_4, SF_6, and perhaps to nonpolar diatomic molecules. The rotation of even slightly nonspherical molecules like O_2 and N_2 will not be free in the entire cavity: when such a molecule comes close to the wall of its cage it will have to orient itself parallel to this wall. Furthermore, some of the cavities are somewhat oblate (cf. Section I.B), and thus the rotation of relatively large, oblong molecules may be seriously

hindered. These effects will tend to decrease the entropy of the clathrate, that is raise the vapor pressure of the solute relative to that which is calculated assuming free rotation.[30]

The quadrupole effects mentioned in Section I.B.(1) apparently are small, as magnetic susceptibility measurements[18] have revealed that the energy differences between different orientations of an oxygen molecule in a β-hydroquinone cavity become only noticeable at liquid helium temperatures.

The application of the L-J-D method to the present problem amounts to the assumption that the average contribution to the potential energy due to the interaction of a solute molecule with any of the elements constituting the wall of its cage can be described by the familiar force law

$$\varphi(R) = 4\varepsilon\{(\sigma/R)^{12} - (\sigma/R)^{6}\} \tag{30}$$

where R is the distance between the solute molecule and the particular element of the wall considered. In order to be more specific, let us assume that we are dealing with a gas hydrate: the "elements" of the wall of a type i cavity then are its z_i encompassing water molecules, and ε and σ are the energy and distance parameters characteristic for solute-water interaction.

The parameter σ is the distance for which attraction and repulsion are in balance, i.e., $\varphi(\sigma) = 0$. The parameter ε is the value of $-\varphi(R)$, corresponding to the strongest attraction, which occurs at $R = 2^{\frac{1}{6}}\sigma$; the "van der Waals radius"[25] of an atom equals $R/2 = 0.56\,\sigma$.

Lennard-Jones and Devonshire summed the interaction (Eq. 30) over z molecules distributed over the surface of a sphere and so obtained a function $w(r)$ describing the resulting field within the sphere, averaged over all orientations. The precise form of $w(r)$ need not be considered here (cf. ref. 17 or 13), suffice it to say that

$$w(o) = z\varepsilon\{\alpha^{-4} - 2\alpha^{-2}\} \tag{31}$$

$$w(r) - w(o) = z\varepsilon\{\alpha^{-4} l(r^2/a^2) - 2\alpha^{-2} m(r^2/a^2)\} \tag{32}$$

where l and m are rather complicated algebraic functions of the dimensionless variable r^2/a^2. The parameter α measures the cell radius a in terms of the effective molecular diameter σ,

$$\alpha = a^3/\sigma^3\sqrt{2} \tag{33}$$

in Fowler and Guggenheim's notation $\alpha = V/V^*$.

With assumptions (e) and (f) the cell partition function can be written as

$$h = \Phi(T) \exp\left[-\frac{w(o)}{kT}\right] \int_{\text{cell}} \exp\left[-\frac{w(r)-w(o)}{kT}\right] 4\pi r^2 dr$$

omitting the indices J, i for the moment.

The function $\Phi(T)$ is again defined by Eq. 10 and represents the contributions due to translational motion and internal degrees of freedom of the solute molecule.† The second term is related to the potential energy $w(o)$ of the solute molecule at the center of its cage referred to the perfect gas, and the integral is the "free volume" of the solute molecule wandering in the cavity. In order to conform with the customary notation of the L-J-D theory we shall further write the free volume as

$$\int \exp\left[-\frac{w(r)-w(o)}{kT}\right] 4\pi r^2 dr = 2\pi a^3 g \tag{34}$$

where the function g stands for the (dimensionless) integral (cf. Eq. 32)

$$g = \int \exp\left[\frac{z\varepsilon}{kT}\left\{-\frac{l(y)}{\alpha^4} + \frac{2m(y)}{\alpha^2}\right\}\right] y^{\frac{1}{2}} dy \tag{35}$$

Hence,

$$h = \Phi(T) \exp\left[-w(o)/kT\right] 2\pi a^3 g \tag{36}$$

In this expression both $w(o)/kT$ and g are completely determined by the values of the two dimensionless parameters $z\varepsilon/kT$ and α: the first is given by Eq. 31, while the function g cannot be expressed in analytical form but has to be evaluated by numerical integration of Eq. 35. The expression 36 for h evidently enables one to calculate the vapor pressure and energy of formation of a clathrate once the values of the two parameters have been determined.

† This corresponds to the assumption that the electronic and infrared spectra of the occluded solute molecules are the same as in the gas phase, an assumption which can never be strictly true.

By substitution of Eq. 36 into Eq. 11 we obtain for the Langmuir constant

$$C_{Ki} = 1/kT \cdot 2\pi a_i^3 g_{Ki} \exp\left(-w_{Ki}(o)/kT\right) \tag{37}$$

and thence from Eq. 12a for the vapor pressure

$$p_K = \frac{kT}{2\pi a_1^3 g_{K1}} \exp\left[\frac{w_{K1}(o)}{kT}\right] \frac{y_{K1}}{1 - \sum_J y_{J1}}$$

$$= \frac{kT}{2\pi a_2^3 g_{K2}} \exp\left[\frac{w_{K2}(o)}{kT}\right] \frac{y_{K2}}{1 - \sum_J y_{J2}} = \ldots \tag{38}$$

The physical significance of this expression becomes very clear if we replace kT/p_K by the molecular volume v_K^G of K in the gas phase and rewrite Eq. 38 as

$$\frac{y_{Ki}}{1 - \sum_J y_{Ji}} = \frac{2\pi a_i^3 g_{Ki}}{v_K^G} \exp\left[-\frac{w_{Ki}(o)}{kT}\right]$$

The first factor on the right is equal to the ratio of the free volume of a K molecule in the clathrate to its molecular volume in the gas phase, whilst the second is the appropriate Boltzmann factor.

For the energy of the clathrate we have, when substituting Eq. 36 into Eq. 8,

$$\frac{U - U^\beta}{kT^2} = N_Q \sum_{J,i} \nu_i y_i \left\{\frac{\partial \ln \Phi_J(T)}{\partial T} + \frac{w_{Ji}(o)}{kT^2} + \frac{\partial \ln g_{Ji}}{\partial T}\right\}$$

The first term inside the brackets evidently is the energy of a solute molecule J in the perfect gas (cf. Eq. 10); hence we have for the energy of formation of the clathrate from Q^β and the gaseous solute at constant volume per molecule of Q

$$(U - U^\beta)/N_Q = \sum_{J,i} \nu_i y_i \{w_{Ji}(o) + kT^2 \partial \ln g_{Ji}/\partial T\}$$

The first term on the right is the potential energy of the solute molecule at the center of the cavity and the second term is the average of the extra potential energy of the molecule due to its motion in the field $w(r)$. By substituting the values of $w(o)$ and $\partial \ln g/\partial T$ following from the L-J-D theory, one obtains

$$\frac{U-U^{\beta}}{N_Q} = \sum_{J,i} \nu_i y_i \left\{ z\varepsilon \left[-2\left(1+\frac{g_m}{g}\right)\alpha^{-2} + \left(1+\frac{g_l}{g}\right)\alpha^{-4} \right] \right\}_{Ji} \qquad (39)$$

where g_l and g_m are integrals related to g (cf. refs. 17, 13) which likewise have to be calculated numerically.

To conclude this section it may be worthwhile to remark that, although the L-J-D method is generally applied to a face-centered cubic lattice ($z = 12$), it is equally valid for the cavities in a clathrate ($z = 20-28$), as long as one restricts oneself to first-neighbor interactions.

In hydrates with their open structure the relative contribution of second and third neighbor solvent molecules to $w(r)$ is only of the order of $\frac{1}{4}$ of that in the much denser face-centered cubic lattice. It is therefore a better approximation to neglect second and third neighbors altogether than to use the functions derived by Wentorf *et al.*[54] for the face-centered cubic lattice including contributions due to second and third shell neighbors.

The method used by Barrer and Stuart [4] to calculate the potential field within the cavities of gas hydrates is, for a similar reason, open to serious doubt. In their absolute calculations of $w(r)$ these authors replace the summation of the solute-solvent interaction $\varphi(R)$ over the neighbors of a cavity by an integration over the entire crystal. As the number of water molecules per unit volume is relatively low — and the lower limit of their integral does not take account of this — the effective diameter of the cavities becomes far too large. For the smaller cavities of a Structure I hydrate, for instance, the first 20 water molecules are thus taken to lie within a shell between 4.0 and 6.2 A from the center, with an average distance of 5.27 A. The exact distance following from x-ray analysis is 3.95 A. As a result the fields calculated by Barrer and Stuart are completely at variance with the true L-J-D fields. The latter have a deeper minimum, are much narrower, and have no humps for the hydrates of the rare gases (Structure I), except a very small one for argon in the larger cavities.

F. Numerical Calculations

(1) *Hydroquinone Clathrates*

The quantities ε and σ are the force constants of the Lennard-Jones interaction $\varphi(R)$ of a solute molecule K with an element of the wall of the hydroquinone cage (cf. Eq. 30). It is assumed that for this interaction the frequently-used combining rules for the interaction between two unlike particles hold,

$$\varepsilon = (\varepsilon_K \varepsilon_Q)^{\frac{1}{2}} \quad \text{"geometric mean approximation"} \tag{40}$$

$$\sigma = \tfrac{1}{2}(\sigma_K + \sigma_Q) \quad \text{"hard sphere approximation"} \tag{41}$$

Here ε_K, σ_K are the force constants for the pure solute K, which can be determined from measurements of its second virial coefficient, and ε_Q, σ_Q are similar, but as yet unknown, constants characteristic for the β-hydroquinone lattice.

If we use these approximations, together with values of ε_K/k (in °K) and σ_K (in A) reported in the literature, the parameters $z\varepsilon/k$ and α needed to apply the formulas of the preceding section can be obtained in the following manner.

For α one has according to Eqs. 33 and 41

$$\alpha = \frac{a^3}{\sqrt{2}\sigma^3} = \frac{a^3}{\sqrt{2}(\sigma_K/2+\sigma_Q/2)^3} = \frac{(3.95)^3}{\sqrt{2}(\sigma_K/2+1.45)^3} \tag{42}$$

where the value $a = 3.95$ A results from Powell's x-ray analysis (cf. Section I.B.(1)), and $\sigma_Q/2 = 1.45$ A is motivated as follows. For covalently bound oxygen atoms, Pauling[25] suggests a van der Waals radius of 1.40 A; to the half-thickness of an aromatic molecule perpendicular to its plane he assigns the value 1.85 A. As the cavities are surrounded by oxygen atoms and aromatic carbon atoms in equal numbers, σ_Q was chosen equal to the arithmetic mean of the values of σ corresponding to the preceding two equilibrium distances, i.e.,

$$\sigma_Q = 2^{-\frac{1}{2}}(1.40+1.85) = 2.90 \text{ A}$$

For $z\varepsilon/k$ one has, according to Eq. 40,

$$z\varepsilon/k = z(\varepsilon_K \varepsilon_Q)^{\frac{1}{2}}/k = z(\varepsilon_Q/k)^{\frac{1}{2}}(\varepsilon_K/k)^{\frac{1}{2}} \tag{43}$$

For the monatomic gases the values of ε_K/k and σ_K determined by Whalley and Schneider were used,[56] for the other gases, those reported by Hirschfelder, Curtiss, and Bird.[15] To the unknown factor $z(\varepsilon_Q/k)^{\frac{1}{2}}$, the value 294 was assigned in order to fit the theoretical predictions to the aggregate of experimental data at present available.

Table III shows the vapor pressures of some hydroquinone clathrates at 25°C calculated according to Eq. 38, and Table IV

TABLE III. Equilibrium Pressures of Hydroquinone Clathrates at 25°C

Solute	ε_K/k	σ_K	p_K in atm	
			Calc.	Obs.
Argon	119.5	3.408	3.4	3.4 [a]
Krypton	166.7	3.679	0.4	0.4 [a]
Xenon	225.3	4.069	0.06	
Methane	142.7	3.810	0.8	
Nitrogen	95.05	3.698	5.2	5.8 [b]
Oxygen	117.5	3.58	2.6	
HCl	360	3.305	0.02	$\simeq$ 0.01 [c]

[a] Cf. Section III.B.(1).

[b] Unpublished result obtained in this laboratory.

[c] Obtained by extrapolation of $\ln p_K$ as a function of $1/T$ from the vapor pressure measurements by Leech and Richards at 60° and 75°C as reported by Powell [33] in the form of standard Gibbs free-energy changes.

shows their energies of formation following from Eq. 39; experimental results are included for comparison. For y_K the experimental value 0.34 was substituted (cf. Section III.B.(1)).

As the tables show, the agreement between theory and experi-

TABLE IV. Energies of Formation of Hydroquinone Clathrates

Solute	Energy of formation Δ^*U in kcal [a]	
	Calculated from Eq. 39 [b]	Observed ref. 11
Argon	−4.5	−5.4
Krypton	−6.1	
Xenon	−8.0	
Methane	−5.9	
Nitrogen	−4.5	−5.2
Oxygen	−4.8	−4.9
HCl	−7.6	−8.6

[a] Δ^*U is the energy of formation of the clathrate from β hydroquinone and one mole of the gaseous solute at constant volume and 25° C.

[b] The values of the force constants used in the calculation are those reported in Table III.

ment is reasonable. To provide a better test one should measure the heats of formation of the krypton and xenon clathrates and determine the equilibrium pressures lacking in Table III.*

(2) *Hydrates*

Recently[30] results were given of an application of the present theory to some gas hydrates of Structure I. In this case one has to consider two kinds of cavities for which we assumed, again using the approximations 40 and 41,

	Smaller cavities	Larger cavities	All cavities
$\alpha_i = \dfrac{{a_i}^3}{\sqrt{2}(\sigma_K/2+\sigma_Q/2)^3}$	$a_1 = 3.95$ A	$a_2 = 4.30$ A	$\sigma_Q/2 = 1.25$ A
$\dfrac{z_i\varepsilon}{k} = z_i\left(\dfrac{\varepsilon_Q}{k}\right)^{\frac{1}{2}}\left(\dfrac{\varepsilon_K}{k}\right)^{\frac{1}{2}}$	$z_1 = 20$	$z_2 = 24$	$\varepsilon_Q/k = 166.9$°K

$\Delta\mu(273°\text{K}, P)/\text{cal mole}^{-1} = 167+0.073\ P/\text{atm}.$

The radii a_1, a_2 and coordination numbers z_1, z_2 follow from x-ray analysis (cf. Section I.B), and $\sigma_Q/2 = 1.25$ A corresponds to Pauling's van der Waals radius of 1.40 A for a covalently bound oxygen atom.[25] The value of $\varepsilon_Q/k = 166.9$°K was chosen to obtain agreement between calculated and experimental values of the equilibrium vapor pressure of argon hydrate at 0°C.

One important difference between the present and the previous case should be noted. For the hydroquinone clathrates, where the wall of a cavity consists of 12 OH groups, 6 adjacent carbon atoms, and 6 CH groups in ortho position to the OH groups, it seemed best to consider the product $z(\varepsilon_Q/k)^{\frac{1}{2}}$ as *one* unknown. For hydrates one may not do this; the walls of both types of cavities consist exclusively of tetrahedrally-coordinated water molecules. Hence, one should use the same value of $(\varepsilon_Q/k)^{\frac{1}{2}}$—characteristic for a water molecule in a hydrate lattice—for both types of cavities and multi-

* It should be noted that the present values of $\frac{1}{2}\sigma_Q$, $z(\varepsilon_Q/k)^{\frac{1}{2}}$ and y_K are somewhat different from the values used in ref. 52 which were based on preliminary data.

ply this with the appropriate coordination numbers to get the values of $z(\varepsilon_Q/k)^{\frac{1}{3}}$ for the two types.*

The results of the vapor pressure calculations are given in Table V, taken from ref. 30. The occupation numbers y_1 and y_2 are those which simultaneously satisfy Eq. 38 for $i = 1, 2$ and Eq. 25''; the

TABLE V. Dissociation Pressures and Degrees of Occupation of Gas Hydrates at 273°K[30]

Hydrate former	ε_K/k °K	σ_K A	Fraction of cavities occ. L-J-D		Dissociation pressure (atm)		
			y_1	y_2	Obs.	Calc., L-J-D	Calc., sq. wells
Argon	119.5	3.408	0.825	0.841	95.5	95.5	95.5
Krypton	166.7	3.679	0.832	0.830	14.5	15.4	8
Xenon	225.3	4.069	0.813	0.835	1.15	1.0	0.2
Methane	142.7	3.810	0.818	0.836	26	19.0	8.5
CF_4	152.5	4.70	0.282	0.894	$\simeq 1$	1.6	0.2
Ethane	243	3.954	0.837	0.827	5.2	1.1	
Ethylene	199.2	4.523	0.523	0.879	5.44	0.5	
Oxygen	117.5	3.58	0.821	0.839		63	
Nitrogen	95.05	3.698	0.810	0.845		90	

overall composition $Y = \nu_1 y_1 + \nu_2 y_2$ is *not* independent of the nature of the solute. The agreement between calculated and observed equilibrium pressures is remarkably good for the monatomic gases and also for the spherical methane molecule.

For the other solutes the agreement is not as good. The ratio of the equilibrium pressures of the hydrates of oxygen and nitrogen appears plausible, since many investigators[40, 47] have reported that air occluded in gas hydrates is somewhat enriched in oxygen. But, if oxygen and nitrogen indeed form hydrates at the fairly moderate pressures reported in Table V, it is difficult to understand why such hydrates have never been reported.

* In this respect the values of $A^*/kT = z\varepsilon/kT$ used by Barrer and Stuart for the two kinds of cavities in the hydrates of the inert gases show a serious discrepancy (cf. Table V of ref. 4). Their procedure leads to $A_2^*/A_1^* \simeq 1.9$, whereas for a L-J-D field one must have $A_2^*/A_1^* = z_2/z_1 = 1.2$, independent of the combining rules.

For the hydrates of ethane and ethylene, the calculated equilibrium pressures are too low. This is thought to be caused mainly by the hindered rotation of these comparatively large molecules in their cavities, and perhaps also by the fact that the central force field (Eq. 30) does not seem very suitable for large polyatomic molecules; the double bond in ethylene must give rise to anisotropic interaction. In this context it should be noted that although the *a priori* calculation of the dissociation pressures of the hydrates of polyatomic molecules may not be very accurate owing to the failure of the restrictive assumptions (e) and (f), the general formulas of Section II.D should remain applicable. This belief is supported by the precision with which the formulae 24″–26″ with properly chosen constants C_{Ki} can account for the distribution of methane and propane over the gas and hydrate phases as found in an experimental investigation of the phase behavior of the system methane-propane-water at −3°C; cf. Section III.C.(2)(b) and Fig. 7.

In order to see whether the results are sensitive to the exact shape of the potential field, some calculations have been made in which the field $w(r)$ was replaced by a square well. The depth of the well was taken equal to the value (Eq. 31) of $w(o)$ for an L-J-D- field, while the radius was taken equal to the value $(a_i - \sigma)$ valid for hard spheres. In this approximation the free volume is equal to $\frac{4}{3}\pi \cdot (a_i - \sigma)^3$, and hence in formula 38

$$g_{Ki} = \tfrac{2}{3}\{1 - (\sigma_Q + \sigma_K)/2a_i\}^3 \qquad (44)$$

It is clear from the last column of Table V that the agreement is less satisfactory than that obtained with the more realistic L-J-D-field.

For the hydroquinone clathrates it was possible to make a direct comparison between the heat observed for the reaction

$$Q^\alpha + \text{gas} \rightarrow \text{clathrate}$$

and the heat calculated for the process

$$Q^\beta + \text{gas} \rightarrow \text{clathrate}$$

since the difference in heat function between Q^β and Q^α is known to be $\Delta H = 0.16$ kcal/mole from the experiments of Evans and Richards[11] (cf. Table II).

For the gas hydrates it is not possible to make an entirely unambiguous comparison of the observed heat of hydrate formation from ice (or water) and the gaseous solute with the calculated energy of binding of the solute in the β lattice, because $\Delta H = H^{\beta} - H^{\alpha}$ is not known. If one assumes $\Delta H = 0$, it is found that the hydrates of krypton, xenon, methane, and ethane have heats of formation which agree within the experimental error with the energies calculated from Eq. 39; for details the reader is referred to ref. 30.

The fact that both heats of formation and equilibrium pressures of the hydrates of spherical molecules correctly follow from one model must mean that the L-J-D theory gives a good account of the entropy associated with the motions of these solutes in the cavities of a clathrate. That the heat of formation of ethane hydrate is predicted correctly, whereas the theoretical value of its vapor pressure is too low, is a further indication that the latter discrepancy must be ascribed to hindered rotation of the ethane molecules in their cavities.

Nuclear magnetic resonance spectroscopy of the solutes in clathrates and low temperature specific heat measurements are thought to be particularly promising methods for providing more detailed information on the rotational freedom of the solute molecules and their interaction with the host lattice. The absence of electron paramagnetic resonance of the oxygen molecule in a hydroquinone clathrate has already been explained on the basis of weak orientational effects by Meyer, O'Brien, and van Vleck.[18]

III. HETEROGENEOUS EQUILIBRIA

A. General Remarks

As already remarked in the introduction, the formulation of the laws governing heterogeneous equilibria by Bakhuis Roozeboom[1] was partly based on his studies on gas hydrates. Although the general laws he derived are certainly correct, and have marked an important step in the development of physical chemistry, Roozeboom and his contempories were mistaken in the nature of the phase diagram of gas hydrates: gas hydrates are not stoichiometric

compounds, but prove to be solid clathrate solutions. The consequences of this state of affairs for the phase diagram will now be considered. (It should be noted that Bakhuis Roozeboom also investigated the hydrates of HCl and HBr which are not clathrates but indeed stoichiometric compounds.)

When studying heterogeneous equilibria involving clathrates, one is faced with peculiar difficulties owing to the hysteresis effects mentioned in the introduction: the solute in a clathrate crystal of hydroquinone, for instance, will not come to thermodynamic equilibrium with the vapor in which it is placed. Consequently it is impossible, or at least very difficult, to measure the equilibrium vapor pressure of the solute in a clathrate by placing some crystals in a tensometer (cf. the experiments of Wynne-Jones and Anderson,[58] and those of Leech and Richards reported by Powell[33]).

It has proved possible[53] to overcome this difficulty by adding a solvent forming an additional, liquid phase to the system to be investigated. Provided the molecules of the solvent are too large to be encaged in the clathrate, its addition will have no effect on the composition of the solid phase(s); if the solvent further has a low volatility it will also have no effect on the partial pressure(s) of the solute(s) in the gas phase. Hence, the equilibrium conditions of Section II.D and the conclusions derived from them remain valid, exactly as if the solvent were not present; the latter merely acts as a "catalyst" for establishing equilibrium. The function of the solvent is well illustrated by the determination of equilibria in the *binary* system hydroquinone-argon from measurements in the *ternary* system hydroquinone-argon-*n*-propanol discussed below. Likewise the equilibrium ice-hydrate-gas in the *ternary* system water-methane-propane could conveniently be determined in the *quaternary* system resulting from the addition of ethylene glycol (cf. Section III.C.(2)).

B. Hydroquinone Clathrates

(1) *The Binary System Hydroquinone-Rare Gas*

Figure 3 gives the P-T-x diagram for the binary system hydroquinone-argon and shows that at ordinary temperatures the three-

phase equilibria in which clathrate solutions play a role are:

$$\alpha\text{-hydroquinone} + \text{gas} \rightleftarrows \text{clathrate}$$
$$\alpha\text{-hydroquinone} + \text{clathrate} \rightleftarrows \text{liquid}$$
$$\text{liquid} + \text{gas} \rightleftarrows \text{clathrate}$$

In these equilibria the gas phase consists of almost pure argon,

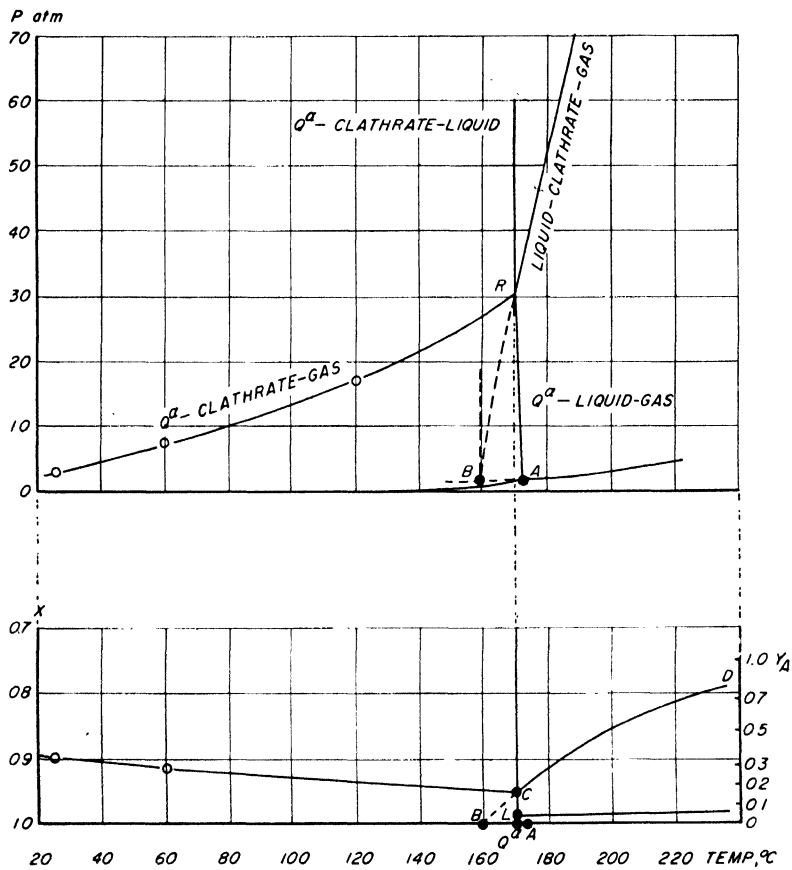

Fig. 3. P-T-x diagram of the system hydroquinone - argon; x = mole fraction of hydroquinone, y_A = fraction of cavities filled by argon ($y_A = 3(1-x)/x$). The pressures of the triple points A and B of the α and β modifications of hydroquinone have been exaggerated in order to make these points visible.

while the liquid phase is liquid hydroquinone in which a small amount of argon is dissolved. The open circles are experimental results (cf. below), while the rest of the diagram is based on the following considerations.

Let us first consider the three-phase equilibrium Q^{α}-clathrate-gas, for which the values of P and $x = 3/(y_A+3)$ were determined at 25°C. When the temperature is raised the argon content in the clathrate diminishes according to Eq. 27, while the pressure can be calculated from Eq. 38 by taking y_A values following from Eq. 27 and the same force constants as used in the calculation of Table III. It is seen that the experimental results at 60°C and 120°C fall on the line so calculated. At a certain temperature and pressure, solid Q^{α} will also be able to coexist with a solution of argon in liquid hydroquinone; at this point (R) the three-phase line Q^{α}-clathrate-gas is intersected by the three-phase line Q^{α}-liquid-gas. At the quadruple point R solid α-hydroquinone (Q^{α}), a hydroquinone-rich liquid (L), the clathrate (C), and a gas phase are in equilibrium; the composition of the latter lies outside the part of the T-x projection drawn in Fig. 3. The slope of the three-phase line AR must be very steep, because of the low solubility of argon in liquid hydroquinone.

Along the three-phase line liquid-clathrate-gas the variation of the composition with temperature is considerable (cf. CD in Fig. 3), because when applying Eq. 27 to this equilibrium, the relatively small quantity $\Delta H = 0.16$ kcal/mole has to be replaced by the much larger difference $H_Q{}^{\beta} - H_Q{}^{L}$ between the partial molar heat functions of β-hydroquinone and the liquid phase, which amounts to about -6 kcal/mole. The argon content of the solid reaches a minimum at the quadruple point.

In the P-T projection the difference in slopes of the three-phase lines Q^{α}-clathrate-gas and liquid-clathrate-gas at the quadruple point R is determined by the heat of fusion of the number of moles of hydroquinone associated with one mole of argon in the clathrate under the conditions prevailing at R. If we extrapolate the three-phase line liquid-clathrate-gas to lower pressures (where it is no longer stable), the value of y_A decreases until it becomes zero when we are dealing with pure β-hydroquinone. Hence, the metastable part of this three-phase line ends in the triple point B of β-hydro-

quinone. A represents the triple point of the stable α-modification.

The occurrence of solid clathrate solutions is clearly seen in Fig. 4, which gives a cross section of the P-T-x diagram at 60°C according to recent results.[28] The two two-phase equilibria clathrate-gas and clathrate-hydroquinone are separated by a one-phase

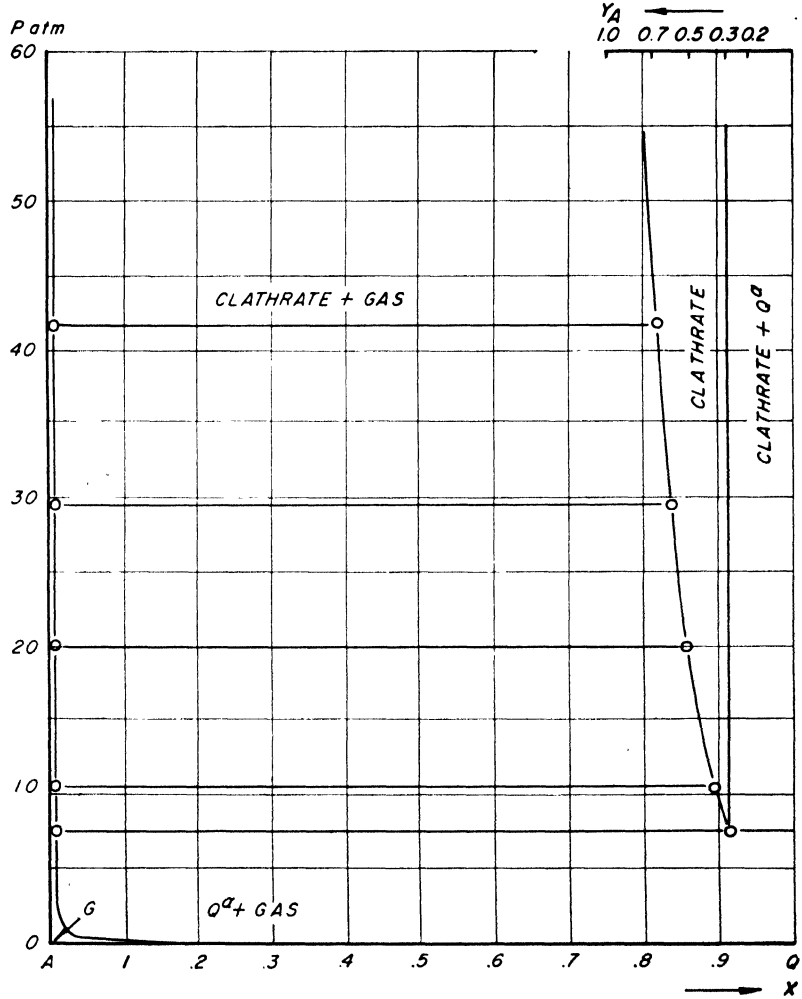

Fig. 4. Cross section through the P-T-x diagram of the system hydroquinone-argon at 60°C (cf. Fig. 3).

area of clathrate solutions. The clathrate compositions in equilibrium with argon indeed obey a Langmuir type isotherm, as predicted by the statistical theory developed in Part II.[28]

The equilibria between clathrate and gas, and Q^{α}, clathrate, and gas could be determined by using *n*-propanol as the auxiliary solvent.[53] In the latter equilibrium, the composition of the clathrate is found from the amount of gas required for the conversion of a given amount of solid α-hydroquinone suspended in the propanol solution into clathrate at constant temperature and pressure. The dissociation pressure of the clathrate is given by the total pressure of the four-phase equilibrium Q^{α}-clathrate-solution-gas, corrected for the vapor pressure of *n*-propanol saturated with α-hydroquinone. Using this technique it was found that the equilibrium clathrates of hydroquinone and argon have $y_A = 0.34$ at 25°C[53] and 0.28 at 60°C.[28]

Recently experiments with the clathrate of hydroquinone and krypton have been carried out in a similar way at 25°C. The result was $p_{Kr} = 0.40$ atm and again $y = 0.34$, thus proving the validity of the generalized form of Raoult's law (Eq. 25').

(2) *The Binary System Hydroquinone-Methanol*

If the component to be encaged is a liquid at the temperature of investigation, the composition of the equilibrium clathrate cannot easily be determined in the way described previously. In this case the pressure of the system is not sensitive enough for detecting phase transformations so that another property has to be used.

An example is given by the system hydroquinone-methanol where *n*-propanol was again added as the auxiliary solvent. Figure 5 shows the result as determined in the following manner. Methanol is added in small portions to a mixture of solid hydroquinone and *n*-propanol of known overall composition (indicated by P_t). The refractive index (any other suitable property might also be used) of the supernatant solution is plotted against the volume of methanol added (cf. lower half of Fig. 5). At first the refractive index gradually decreases, but as soon as the points indicating the overall

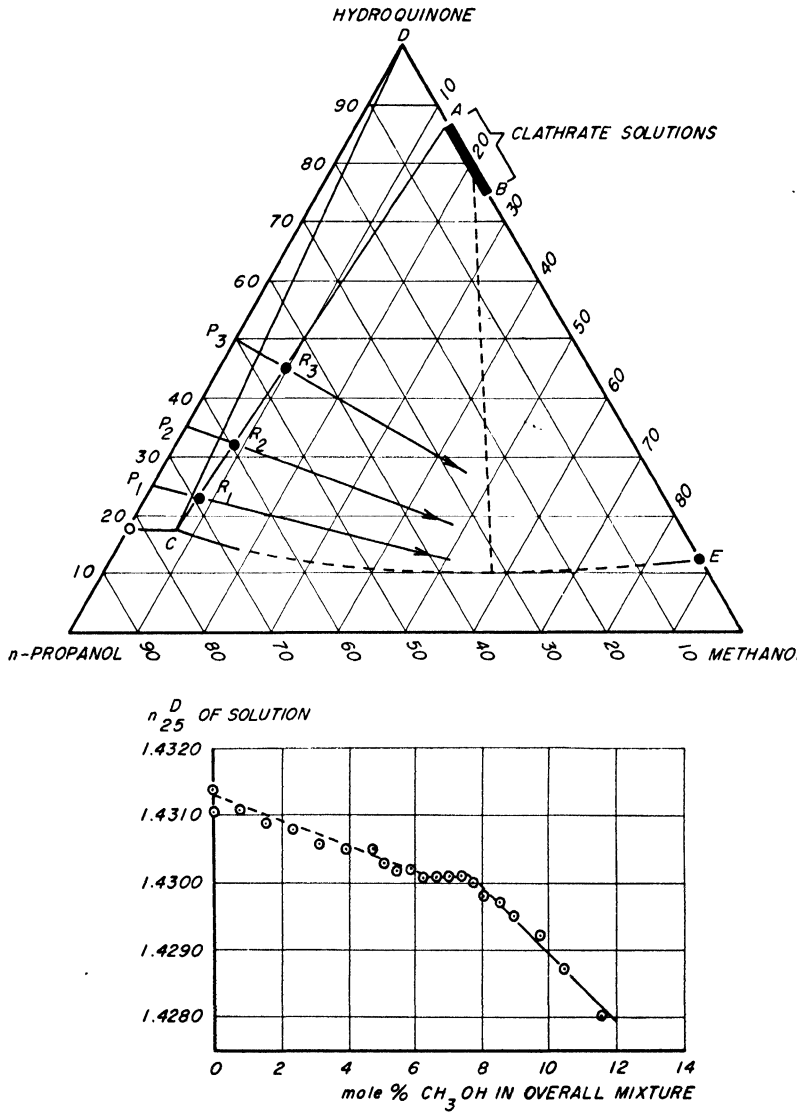

Fig. 5. Determination of the composition of the equilibrium clathrate of hydroquinone and methanol at 25°C with the aid of *n*-propanol as an auxiliary solvent. The figure at the bottom illustrates the method used for determining the position of the side *CA* of the three-phase area *ACD*.

composition fall in the three-phase area ADC, the composition of the liquid phase C, and hence its refractive index remain unchanged. The composition of the liquid and its refractive index start to change again as a function of the methanol content of the system, when the solid α-hydroquinone phase has disappeared. The overall compositions for which the second kink occurs in the refractive index *vs.* methanol content diagram are plotted in the triangle (R_i).

The points R_i have to be on a straight line terminating in the composition of the methanol hydroquinone clathrate (A) in equilibrium with α-hydroquinone at 25°C. The point B roughly corresponds to the composition of the clathrate obtained by Palin and Powell[24] when crystallizing hydroquinone from methanol; points between A and B form a continuous range of solid solutions in equilibrium with liquid phases whose compositions lie on the curve CE. It is found that the equilibrium clathrate has a composition corresponding to $y = 0.474$ at 25°C.

C. Hydrates

In the discussion of phase diagrams involving hydrates, the following nomenclature will be used (if the structure of the hydrate is not specified the subscript is omitted): H_{I} is the hydrate of Structure I, H_{II} is the hydrate of Structure II, L_1 is a nonaqueous liquid, L_2 is an aqueous liquid, and G is a gas.

(1) *Binary Systems*

If the critical temperature of the solute is below room temperature, the phase diagram is similar to the one described for the system hydroquinone-argon. No temperature can then be indicated above which hydrates cannot exist. This situation arises for the following solutes: argon,[48] krypton,[48] xenon,[48] methane,[36] and ethylene.[10]

In most cases the critical temperature of the solute is above room temperature. As can be seen in the binary system H_2S-H_2O drawn in Fig. 6, the three-phase line HL_2G is then intersected by the three-phase line HL_1G. The point of intersection represents the four-phase equilibrium HL_1L_2G and indicates the temperature

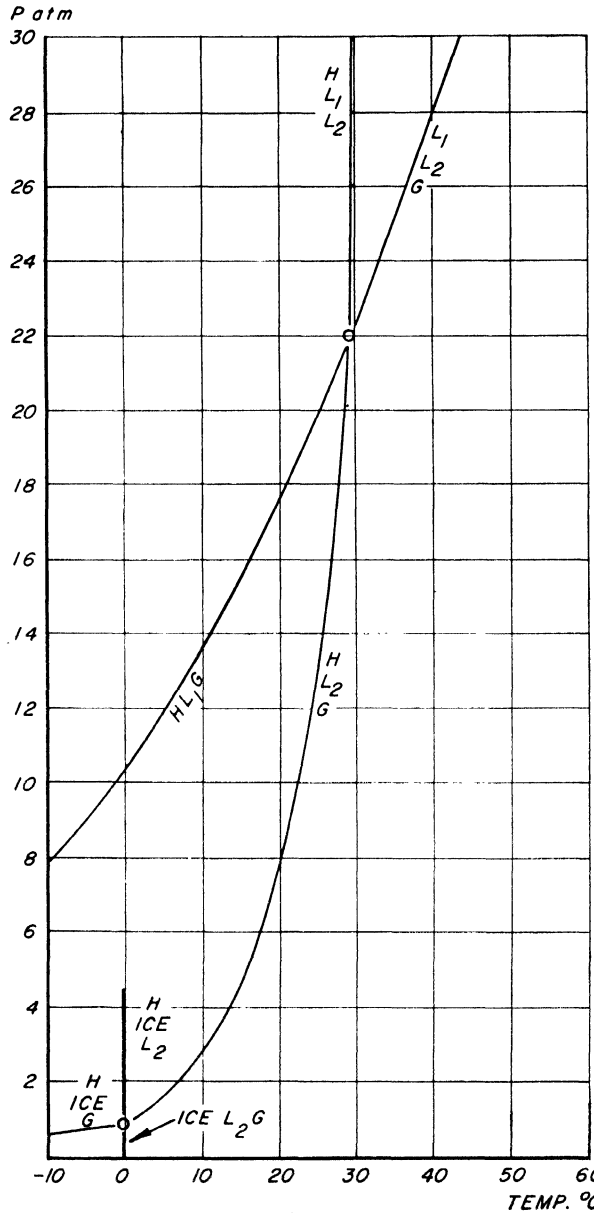

Fig. 6. *P-T* diagram of the system H_2S-H_2O according to Scheffer and Meyer,[38] and Selleck, Carmichael, and Sage.[41]

above which no hydrate exists.* Further examples are given by the systems with carbon dioxide, bromine, ethane, propane, and $CHCl_2F$ (cf. Table I).

The composition of the hydrates varies with temperature along the three-phase lines H ice G and HL_2G in a way similar to that described for the system hydroquinone-argon. But as already noted in Section II.D this variation is smaller than for the hydroquinone clathrates. Accordingly, a cross section through the P-T-x diagram at constant temperature below 0°C would reveal a two-phase area $G+H$ in which the composition of the latter is less sensitive to pressure than found in the corresponding case for the hydroquinone clathrates (cf. Fig. 4).

Since the composition of a hydrate is not constant the method for its determination first suggested by de Forcrand[12] and improved by Scheffer and Meyer[38] gives the composition in the quadruple point only. In this method, which has also been used by von Stackelberg,[42] the heats of formation per mole of solute of the hydrate from pure gas and pure liquid water as well as from pure gas and ice are required. The difference of these heats divided by the molar heat of fusion of water gives the number of water molecules per molecule of the solute in the hydrate. The two heats of formation can be obtained by applying Clapeyron's equation (Eq. 29) to the three-phase lines HL_2G and H ice G, provided certain corrections are made.[38]

Using this method Miss Mulders[19] derived a composition

$$Br_2 \cdot 8.47 \pm 0.05\ H_2O$$

from her painstaking investigation of the system bromine-water. She then was the first to suggest that hydrates might be mixed crystals!

We are convinced that the composition of hydrates along the

* According to Clapeyron's equation (Eq. 29) the line HL_1L_2 must be very steep, because the change in volume ΔV accompanying the formation of the hydrate from the two liquids is quite small. It is conceivable that cases exist where ΔV is negative and the line HL_1L_2 goes to temperatures higher than that of the quadruple point; strictly speaking the temperature of the quadruple point then does not correspond to that above which no hydrate can exist.

three-phase line H ice G might be determined by adding an auxiliary solvent and applying the technique used for the hydroquinone clathrates of argon and methanol mentioned above. This procedure would enable one to find the composition in a straightforward manner at a number of temperatures, and further has the advantage of eliminating the tricky differentiations of the preceding method.

(2) *Ternary Systems*

As mentioned in the introduction, hydrates may crystallize in either of two frameworks. When discussing ternary systems $A+B+H_2O$ it is useful to discriminate between systems in which only hydrates of one structure (I or II) are formed, and those in which hydrates of both structures are formed.

(a) *Systems in which Hydrates of One Structure Occur.* This situation corresponds to complete miscibility of the solid solutions. If hydrates are formed in both binary systems $A+H_2O$ and $B+H_2O$ these two hydrates will be connected by a continuous range of solid solutions.* When considering the three-phase area ice (or aqueous liquid)-hydrate-gas the distribution of the solutes over the gas and hydrate phases should be completely determined by the equations of Section II.D.

The system H_2S-CH_4-H_2O is an example of a ternary system forming a continuous range of mixed hydrates of Structure I. For this system Noaker and Katz[22] studied the H_2S/CH_4 ratio of the gas in equilibrium with aqueous liquid and hydrate. From the variation of this ratio with total pressure at constant temperature it follows that complete miscibility must occur in the solid phase.

Complete miscibility in Structure II was found by von Stackelberg and Meinhold[47] for the systems C_2H_5Cl-CH_3CHCl_2-H_2O and C_2H_5Cl-$CHCl_3$-H_2O. They determined the composition of L_1 (on a water-free basis) as a function of temperature at atmospheric pressure in the three-phase area $H_{II}L_1L_2$. Another example is found in the excellent work of Reamer, Selleck, and Sage[35] who investigated the system propylene-propane-water. The occurrence of complete

* To our knowledge Nikitin [20] was the first to state that mixed hydrates should be described as mixed crystals of two hydrates.

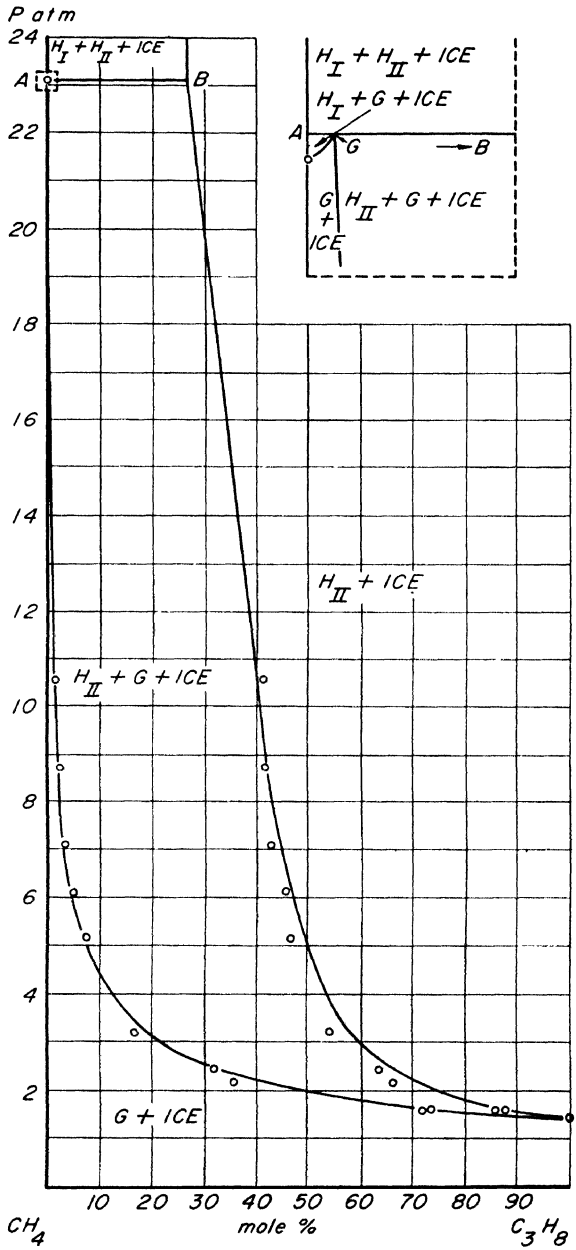

Fig. 7. Isothermal cross section of the system H_2O-CH_4-C_3H_8 on a water-free basis at $-3°$ C. The points represent experimental results and the curves have been obtained from a theoretical analysis. The line AB represents the four-phase equilibrium $H_I H_{II}$ ice G; the gas G consists of almost pure methane, H_I contains only methane. Consequently, the composition of the latter two phases almost coincide in the figure, and the situation around point A has therefore been drawn separately on an enlarged scale.

mixing was clearly demonstrated in the three-phase areas $H_{II}L_2G$ and $H_{II}L_1L_2$. The complete P-T diagram of the ternary system is simple. Both binary systems (propylene-water and propane-water) are similar to H_2S-H_2O (cf. Fig. 6). The ternary diagram is completed by drawing the four-phase lines H_{II} ice L_2G and $H_{II}L_1L_2G$ between the corresponding binary quadruple points.

(b) *Systems in which Hydrates of Both Structures Occur.* If different structures arise in both binary systems, the ternary system must reveal partial miscibility in the solid solutions. This is clearly demonstrated by our investigation of the system methane-propane-water. The experimental results on the equilibrium

$$\text{gas} + \text{ice} \rightleftarrows \text{hydrate}$$

at -3°C are given in Fig. 7. The compositions of the gas phase and those of the coexisting hydrate phase have been plotted on a water-free basis as a function of pressure. In order to establish the equilibria, ethylene glycol was used as auxiliary solvent (cf. ref. 29).

TABLE VI. Composition of the Mixed Hydrate (Structure II) of Methane and Propane, when in Equilibrium with Ice and Gas at -3°C as a Function of Pressure

Pressure atm	Fraction of smaller cavities occupied by CH_4 y_{M1}	Fraction of larger cavities: Occupied by CH_4 y_{M2}	Fraction of larger cavities: Occupied by C_3H_8 y_{P2}	Remarks
35.8	0.8836	0.8522	0	metastable CH_4-hydrate
20	0.8088	0.1795	0.7646	
10	0.6762	0.0309	0.9496	stable "homogeneous" solutions
5	0.4952	0.0060	0.9860	
3	0.3317	0.0017	0.9937	
2	0.1736	0.0005	0.9965	
1.48	0	0	0.99795	C_3H_8-hydrate

Methane hydrate and propane hydrate crystallize in Structures I and II respectively, their dissociation pressures at -3°C have been determined and were found to be 23.1 and 1.48 atm. Above a

certain pressure (in this case slightly above 23.1 atm), the equilibrium H_{II} ice G becomes metastable relative to the equilibrium of both hydrate phases with ice; the two three-phase areas are separated by the four-phase line $H_I H_{II}$ ice G. The extrapolates of gas and hydrate lines intersect on the methane axis at the pressure methane hydrate will exert should it crystallize in Framework II. The curves in Fig. 7, indicating the compositions of gas and hydrate II in equilibrium with each other and ice at -3°C, have been calculated from the pressures of the hydrates of pure methane and pure propane with the aid of the theory developed in Section II.D; they show a remarkably good fit to the experimental data. The compositions of the hydrates as calculated along the hydrate line are given in Table VI.

The curves were determined from Eqs. 24″–26″; in order to apply these in a numerical calculation one first has to know the values of the following functions at -3°C: $\Delta\mu$, the difference in chemical potential between the "empty" Structure II lattice and ice; C_{P2}, the Langmuir constant for propane in the larger cavities of Structure II ($C_{P1} = 0$ for geometrical reasons); C_{M1}, C_{M2}, the Langmuir constants for methane in the two types of cavities of Structure II.

The best method for determining $\Delta\mu$ for Structure II would be to measure the composition of the equilibrium hydrate of SF_6. Since the SF_6 molecules only fit into the larger cavities, the value of $\Delta\mu$ immediately follows from this composition by virtue of Eq. 25″, in the same way as $\Delta\mu$ for Structure I followed from the composition of bromine hydrate. Unfortunately, the composition of SF_6 hydrate has never been measured, and thus it had to be derived in an indirect manner from the vapor pressure of this hydrate.

Molecules of SF_6 are almost spherical, and the results of Section II.F.(2), therefore, lead one to believe that the stability of its hydrate can reliably be calculated from the L-J-D model. If we use the values $\varepsilon_Q/k = 166.9$°K, $\sigma_Q/2 = 1.25$ A (Section II.F.(2)) and $z_2 = 28$ (Section I.B.(2)), together with $\varepsilon_K/k = 200.9$°K, $\sigma_K = 5.51$ A as given for SF_6 in the literature,[18] it follows from Eq. 37 that $C_{K2} = 570$ atm^{-1} for SF_6 hydrate. On the other hand, the vapor pressure of SF_6 hydrate in equilibrium with ice at -3°C was determined to be 0.85 atm, again using ethylene glycol as auxiliary solvent. When substituting these values of C_{K2} and p_K into Eq. 24″ one finds $y_{K2} = 0.9980$, and thence from Eq. 25″ $\Delta\mu/kT = -1/17$ ln $0.0020 = 0.365$; i.e., $\Delta\mu = 0.196$ kcal/mole.

Since the molecules of SF_6 and propane only fit into the larger cavities, their equilibrium hydrates must have identical compositions. From the experimental value of the equilibrium pressure, $p_P = 1.48$ atm for propane

hydrate at $-3°C$ and $y_{P2} = y_{K2} = 0.9980$ it then follows from Eq. 37 that $C_{P2} = 330$ atm^{-1}.

The values of the Langmuir constants C_{M1} and C_{M2} cannot be determined in such a simple manner, since these refer to Structure II, whereas the hydrate of pure methane crystallizes in Structure I. The latter, according to Fig. 7, has an equilibrium pressure of 23.1 atm at $-3°C$. The force constant ε/k for the interaction of methane with a water molecule of the wall of its cage was now adjusted to 147.9°K, in order that the experimental vapor pressure exactly agreed with that calculated from Eq. 38, taking a set of y-values corresponding to $\Delta\mu$ (270°K, 23 atm) = 0.166 kcal/mole and using $\sigma = 3.15$ A, $z_1 = 20$, $z_2 = 24$, as in the calculation of Table V. The values of C_{M1} and C_{M2} for methane in Structure II then immediately follow from Eq. 37 when taking the above values of ε/k and σ, and $z_1 = 20$, $z_2 = 28$.

The actual calculation of the curves in Fig. 7 now is a relatively simple matter. Equation 25'' takes the form (cf. Eq. 12)

$$2/17 \cdot \ln(1+C_{M1}p_M)+1/17 \cdot \ln(1+C_{M2}p_M+C_{P2}p_P) = \Delta\mu/RT$$

Substituting $p_M = (1-x)P$ and $p_P = xP$ for the partial pressures of methane and propane one obtains as equation for the gas branch

$$\{1+C_{M1}(1-x)P\}^2\{1+[C_{M2}(1-x)+C_{P2}x]P\} = \exp(17\Delta\mu/RT) \quad (45)$$

The occupation numbers y_{M1}, y_{M2}, y_{P2} follow from Eq. 24'' with the appropriate values of the constants C_{Ki}. The propane fraction of the gas bound in the hydrate according to Eq. 26'' is then equal to

$$Y_P/(Y_M+Y_P) = \frac{y_{P2}}{2y_{M1}+y_{M2}+y_{P2}}$$

Finally, the following remark may be in order on the situation shown in the inset of Fig. 7. The gas branch of the equilibrium H_I-ice-gas represents a constant partial pressure of methane,

$$p_m = (1-x)P = 23.1 \text{ atm}$$

Its point of intersection G with the gas branch of the equilibrium H_{II}-ice-gas determines the height of the four-phase line AB.

Carson and Katz[5] studied another part of the methane-propane-water system. These authors investigated its behavior when an aqueous liquid, a hydrocarbon liquid, a gas, and some solid were present. It was found that the system was univariant so that the solid consisted of a single phase only. This phase is a hydrate which proved to contain methane and propane in various ratios. They then concluded that these hydrates behaved as solid solutions. It is clear that Carson and Katz measured a part of the four-phase line $H_{II}L_1L_2G$.

The complete P-T diagrams of the ternary systems discussed in this paragraph are more complicated than those of the previous one. This is illustrated by the systems $CHCl_3$-H_2S-H_2O and CCl_4-H_2S-H_2O which were studied by von Stackelberg and Frühbuss.[45] In the light of the theory of heterogeneous equilibria, however, their interpretation of the diagrams does not seem realistic; in particular their Fig. 2 is difficult to understand.

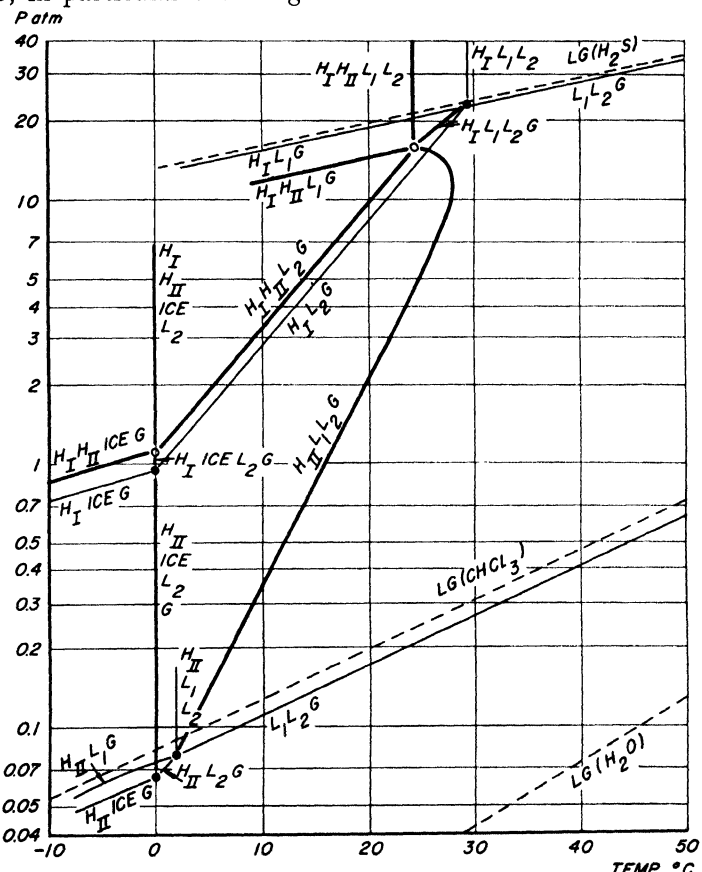

Fig. 8. The system $CHCl_3$-H_2S-H_2O. The univariant equilibria of the single-component systems have been indicated by dotted lines, those of the binary systems by thin lines, and those of the ternary system by heavy lines. The latter are approximate only, except for the lower half of the four-phase line $H_{II}L_1L_2G$ measured by von Stackelberg and Frühbuss.[45]

Figure 8 represents the system $CHCl_3$-H_2S-H_2O, where hydrates occur in the binary systems H_2S-H_2O and $CHCl_3$-H_2O, both of which are known.[41,48] It is assumed that the binary system H_2S-$CHCl_3$ does not show demixing in the liquid phase so that L_1 represents a nonaqueous liquid which changes continuously from pure H_2S to pure $CHCl_3$. All binary equilibria have been drawn with thin lines in Fig. 8.

The main considerations used in the construction of the ternary diagram from the binary diagrams were the following. On addition of $CHCl_3$ to the three-phase equilibrium H_I ice G in the system H_2S-H_2O the total pressure will increase until a mixed hydrate of Structure II (H_{II}) is formed. Hence, the four-phase line H_IH_{II} ice G must lie *above* H_I ice G. (Cf. the inset in Fig. 7, where methane is the analog of H_2S and propane that of $CHCl_3$.) Above the melting point of ice the same reasoning holds for the position of $H_IH_{II}L_2G$ *versus* H_IL_2G.

It is known that the three-phase line H_IL_1G in the binary system H_2S-H_2O lies below the liquid vapor line (LG) of pure H_2S. Likewise, after addition of $CHCl_3$ the four-phase line $H_IH_{II}L_1G$ lies *below* H_IL_1G. The reason for this is that both H_2O and $CHCl_3$ are much less volatile than H_2S. Consequently, the quintuple point where the two four-phase lines $H_IH_{II}L_2G$ and $H_IH_{II}L_1G$ intersect lies at a lower temperature and pressure than the binary quadruple point $H_IL_1L_2G$. (The exact location of the quintuple point is not known.)

The most interesting part of Fig. 8 is the four-phase line $H_{II}L_1L_2G$, the lower half of which has been determined experimentally by von Stackelberg and Frühbuss.[45] It must begin in the binary quadruple point of the system $CHCl_3$-H_2O, where the same four phases are in equilibrium, and it can only end in the quintuple point previously mentioned. If the compositions of the five phases in equilibrium at the quintuple point are plotted in a triangular concentration diagram, whose vertices represent pure $CHCl_3$, H_2S, and H_2O, the points form a pentagon. As Bakhuis Roozeboom has shown,[2] this has as a necessary consequence, that each angle subtended by two neighboring four-phase lines at the quintuple point contains the metastable extrapolate of one other four-phase line.

As a result the situation at the quintuple point must approximately be that shown in Fig. 8. In the four-phase line $H_{II}L_1L_2G$ there

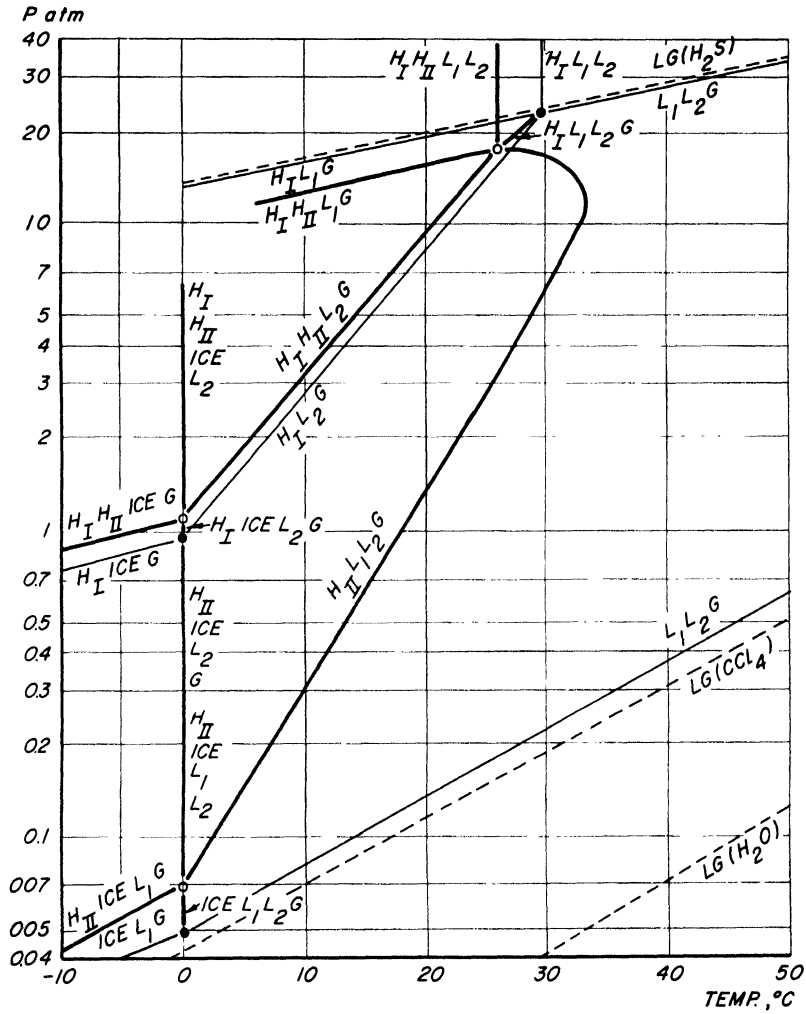

Fig. 9. The system CCl_4-H_2S-H_2O. The univariant equilibria of the single-component systems have been indicated by dotted lines, those of the binary systems by thin lines, and those of the ternary system by heavy lines. The latter are approximate only, except for the lower half of the four-phase line $H_{II}L_1L_2G$ measured by von Stackelberg and Frühbuss.[45]

occurs a temperature maximum, above which no hydrates of Structure II can exist.

Figure 9 represents the system CCl_4-H_2S-H_2O, where no hydrates occur in the binary system CCl_4-H_2O. In the ternary system von Stackelberg and Frühbuss again determined the lower half of the four-phase line $H_{II}L_1L_2G$. As the binary quadruple point $H_{II}L_1L_2G$ does not exist in the system CCl_4-H_2O, the four-phase line must necessarily begin in the quintuple point H_{II} ice L_1L_2G (cf. Fig. 9). The rest of the diagram is completely analogous to the diagram of $CHCl_3$-H_2S-H_2O described above. The authors mentioned carried out an experiment in which they filled a glass tube with the mixed hydrate of CCl_4 and H_2S. The tube was then sealed with a minimum of dead space and slowly heated. The hydrate phase disappeared at 33°C. Probably, this temperature approximately indicates the maximum of the four-phase line $H_{II}L_1L_2G$ in the CCl_4-H_2S-H_2O system.

In his discussion of hydrates of Structure II containing two types of solutes, von Stackelberg[44] makes a distinction between double hydrates ("Doppelhydrate") and mixed hydrates ("Mischhydrate"). Double hydrates are those hydrates of Structure II which contain either H_2S or H_2Se, together with relatively large molecules which can only occupy the larger cavities. (The systems of Figs. 8 and 9 would belong to this class.) When putting such a double hydrate in a tube which is subjected to intermittent pumping at constant temperature, von Stackelberg and Frühbuss[45] found that its vapor pressure remains constant until all the hydrate has been decomposed, i.e., the equilibrium is a univariant one. The other hydrates containing more than one solute investigated by von Stackelberg and Meinhold[47] showed a different behavior: when subjected to similar pumping at constant temperature the pressure decreases gradually and the system, therefore, must have more than one degree of freedom.

Von Stackelberg and Frühbuss[45] explain this difference by assuming that double hydrates are stoichiometric compounds with a fixed composition, e.g., $CHCl_3 \cdot 2H_2S \cdot 17H_2O$. In the light of the present solution theory, this explanation seems highly improbable.

Note added in proof

Recent experiments[29] on the equilibrium H_{II} ice gas at $-3°C$ in the system H_2S-propane-water confirm that these two gases also form mixed hydrates of variable composition, as shown in Fig. 10. In this respect the present system is similar to the system methane-propane-water of Fig. 7, but unlike the latter it exhibits a minimum pressure (azeotrope). It was further shown that the solution theory of clathrates can account for this interesting phenomenon. For details the reader is referred to ref. 29.

The difference in behavior reported by Von Stackelberg is not thought to be an essential one. Whether decomposition of a hydrate containing two solutes by removal of its vapor through pumping will be a univariant process depends on the number and compositions of the phases formed. In the system of Fig. 10, for instance, a mixed H_2S-propane hydrate will exhibit a constant decomposition pressure on pumping at $-3°C$ if it contains H_2S and propane in the "azeotropic" ratio of approximately 3 : 1.

Alternatively, a constant pressure on decomposition will also result if such a hydrate decomposes into 3 phases, e.g., $H \rightarrow L_1+L_2+G$, cf. ref. 29.

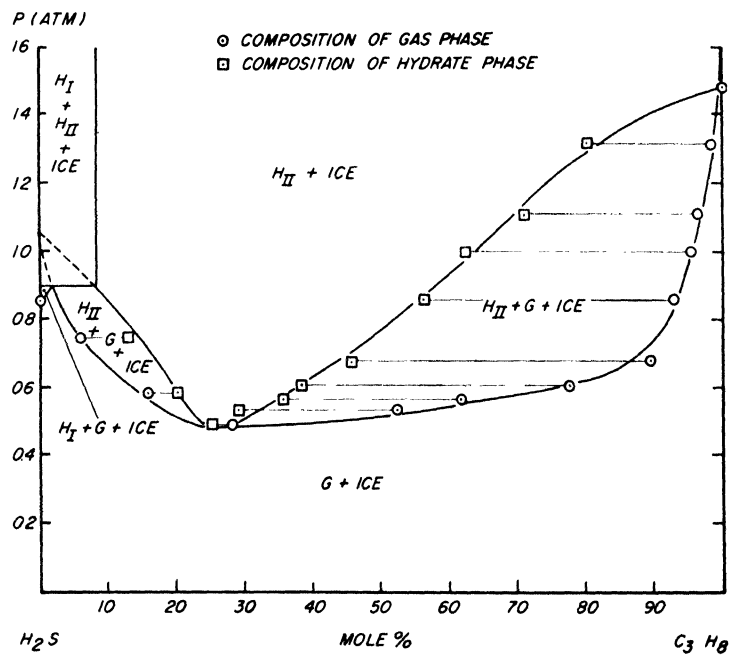

Fig. 10. Isothermal cross-section of the system H_2S-C_3H_8-H_2O on a water-free basis at $-3°C$.

In contrast to the ternary systems just discussed, the four-phase line $H_{II}L_1L_2G$ investigated by Carson and Katz in the system

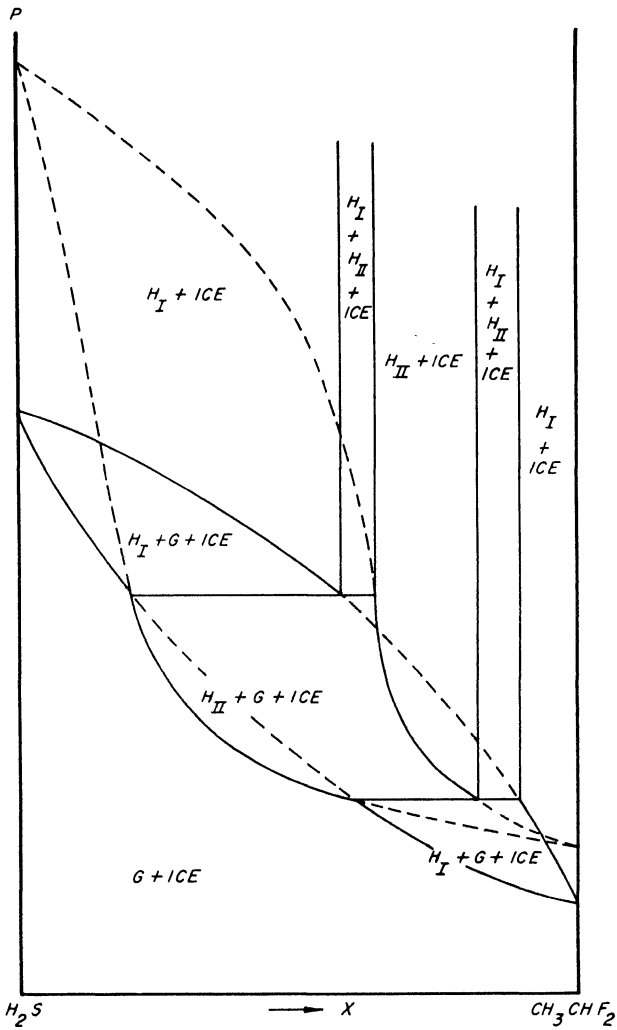

Fig. 11. Tentative isothermal cross section of the system H_2O-H_2S-CH_3CHF_2 on a water-free basis below 0°C. In the two binary systems H_2O-H_2S and H_2O-CH_3CHF_2 only hydrates of Structure I occur, but in the ternary system mixed hydrates of Structure II have been reported.[46]

CH_4-C_3H_8-H_2O does not end in a quintuple point but proceeds to high pressures until two phases (L_1 and G) become critically identical. This arises from the fact that the critical temperature of methane is below room temperature (cf. Section III.C.(1)).

An interesting complication is shown by the system H_2S-CH_3CHF_2-H_2O. The pure components both form hydrates of Structure I. According to von Stackelberg and Jahns,[46] however, hydrates of Structure II occur in the ternary system! This phenomenon must arise from the fact that the dissociation pressure exerted by CH_3CHF_2-hydrate should it crystallize in Framework II is not much higher than that of the stable hydrate of Structure I at the corresponding temperature. Figure 11—drawn on a water-free basis—illustrates a situation in which this state of affairs would occur. The large number of small cavities in the Structure II hydrate, which can be occupied by H_2S but not by CH_3CHF_2, must favor this curious effect.

The authors are grateful to Messrs. J. H. de Baas, D. Kok, and H. J. van Haren for the patience with which they helped in measuring equilibria involving clathrates. They further wish to thank Ir. C. M. van Battum and Prof. Dr. L. J. Oosterhoff for valuable suggestions concerning the presentation of this review.

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INTER- AND INTRAMOLECULAR FORCES AND MOLECULAR POLARIZABILITY

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I. INTRODUCTION

The correlation of electron motion in molecular systems is responsible for many important effects, but its theoretical treatment has proved to be very difficult. Thus many quantum valence calculations use wave functions which are adjusted to optimize kinetic energy effects and the potential energy of interaction of nuclei and electrons but which do not adequately allow for electron correlation and hence yield excessive electron repulsion energy. This problem may be subdivided into cases of overlapping and nonoverlapping electron distributions. Both are very important but we shall concern ourselves here with only the nonoverlapping case.

F. London opened this field with his classic treatment[24] of the

* This paper was prepared under the auspices of the U. S. Atomic Energy Commission.

attractive intermolecular forces which arise because of correlation of electron motion in the two molecules. These are commonly called London forces or dispersion forces. This work explained the previously unaccounted for attraction between nonpolar molecules and rare gas atoms. The importance of this qualitative success obscured for a time discrepancies from quantitative agreements for molecules larger than H_2 and He. Recognition of the need for improved quantitative prediction of London forces[34, 17] led to additional work to be reviewed in this paper.

The key element in London's approach is the expansion of the electrical potential energy in multipole series. Since neutral molecules or portions of molecules are involved, the leading term is that for dipole-dipole interaction. While attention has been given to higher-order terms, these are usually small, and the greater need seems to be for improved treatment of the dipole-dipole terms. London used second order perturbation theory in his treatment, but Slater and Kirkwood[38, 21] soon followed with a variation method treatment which yielded similar results. Other individual papers will be mentioned later, but the excellent review of Margenau[26] should not be overlooked.

In the first approximation London forces in complex systems may be taken as the sum over all interacting pairs. Higher-order corrections for triple interactions have been given by Axilrod and Teller[2, 3] and by Jansen and McGinnies.[18]

We shall consider only forces between systems of moderate size which are in their ground electronic states. Dahler and Hirschfelder[8] have discussed the additional complications when excited states are introduced. Yos, Bade, and Jehle[42] gave special consideration to London forces between macromolecules but found it difficult to determine the magnitude of the special effects they noted.

In polyatomic molecules there are separate regions of essentially nonoverlapping electron clouds whose interaction may be treated by London's methods. This was recognized by many authors, but relatively few calculations have emphasized this factor. Indeed sometimes it may have been erroneously dismissed as of negligible magnitude. Born and Mayer[5] considered London forces in their

treatment of ionic crystals and Davydov[9] and Simpson[37] have considered these effects in conjugated π electron systems. Pauling and Simonetta[28a] included London energy terms in calculations on phosphorous. Pitzer[33] suggested that the anomalous sequence of bond energies in the halogens might be explained on this basis and Pitzer and Catalano[32] showed that the isomerization energies of the lighter paraffin hydrocarbons were predicted satisfactorily by the London theory. This work will be reviewed and some further considerations discussed.

II. THEORY FOR MANY-ELECTRON SYSTEMS

It was mentioned in the introduction that theoretical and experimental values of London energies agree reasonably well for He and H_2. But for larger molecules serious diagreement (frequently about a factor of two) arises between various theoretical formulas and between theory and experiment. Let us review the theory for many-electron systems with particular attention to approximations which may become increasingly important as the number of electrons increases. This discussion follows largely that of Donath[11] and, in part, that of Buckingham.[6]

Atomic units are used throughout this section; the most important formulas are rewritten in other terms at the beginning of Section III.

We write for the ground state wave function of the closed shell atom or molecule a Slater determinant for the N electrons

$$\Psi = (N!)^{-\frac{1}{2}} \det \{\psi_1 \psi_2 \ldots \psi_N\} \tag{1}$$

It is presumed that this function is optimized in the Hartree-Fock approximation.

A. Polarizability

Consider first the polarization of the system in an electric field F along the z axis. The perturbing potential is

$$V = F \sum_{p=1}^{N} z_p \tag{2}$$

and the variational wave function is taken to be

$$\Psi' = \Psi + \sum_{\lambda=1}^{N} a_\lambda \Phi_\lambda \tag{3a}$$

$$\Phi_\lambda = (N!)^{-\frac{1}{2}} \det \{\psi_1 \psi_2 \ldots \phi_\lambda \ldots \psi_N\} \tag{3b}$$

$$\phi_\lambda = z_\lambda \psi_\lambda f_\lambda \tag{4}$$

where f_λ is either unity or a function such as $(1+c_1 r+c_2 r^2+\ldots)$ adjusting ϕ slightly from $z\psi$. A variation method adjustment of the parameters in f_λ is possible in principle.

Next we define the three quantities

$$h_\lambda = \langle \Psi^* | \sum z_p | \Phi_\lambda \rangle \tag{5}$$

$$Q_{\lambda\mu} = \langle \Phi_\lambda^* | H | \Phi_\mu \rangle - E_0 g_{\lambda\mu} \tag{6}$$

$$g_{\lambda\mu} = \langle \Phi_\lambda^* \Phi_\mu \rangle \tag{7}$$

Where H is the complete Hamiltonian operator for the unperturbed system and the usual quantum-mechanical integrals over all space are indicated.

The energy change upon imposition of the field is

$$h' = 2F \sum_\lambda a_\lambda h_\lambda + \sum_\lambda \sum_\mu a_\lambda a_\mu Q_{\lambda\mu} \tag{8}$$

which is to be minimized with respect to each a_λ.

$$\frac{\partial h'}{\partial a_\lambda} = 0 = 2Fh_\lambda + 2 \sum_\mu a_\mu Q_{\lambda\mu} \tag{9}$$

From determinant theory the solution is

$$a_\lambda = -A_\lambda F \tag{10}$$

$$A_\lambda = \frac{\begin{vmatrix} Q_{11} & \cdots & h_1 & \cdots & Q_{1N} \\ \vdots & & & & \\ Q_{\lambda 1} & \cdots & h_\lambda & \cdots & Q_{\lambda N} \\ \vdots & & & & \\ Q_{N1} & \cdots & h_N & \cdots & Q_{NN} \end{vmatrix}}{\begin{vmatrix} Q_{11} & \cdots & Q_{1\lambda} & \cdots & Q_{1N} \\ Q_{\lambda 1} & \cdots & Q_{\lambda\lambda} & \cdots & Q_{\lambda N} \\ Q_{N1} & \cdots & Q_{N\lambda} & \cdots & Q_{NN} \end{vmatrix}} \tag{11}$$

and the minimized energy is

$$h' = -F^2 (2 \sum_\lambda A_\lambda h_\lambda - \sum_\lambda \sum_\mu A_\lambda A_\mu Q_{\lambda\mu}) \tag{12}$$

After several steps this simplifies to

$$h' = -F^2 \sum_{\lambda} A_\lambda h_\lambda \tag{13}$$

and the polarizability is

$$\begin{aligned} \alpha &= -2h'/F^2 \\ &= 2 \sum_{\lambda} A_\lambda h_\lambda \end{aligned} \tag{14}$$

While it is not beyond the realm of possibility to evaluate the g's, h's, and Q's for appropriate wave functions, some further simplification is necessary for our present arguments. We assume that the ϕ's are orthogonal to all ψ's. This is not necessarily true although the f_λ's can be selected to make it true. Even without specific selection of f_λ's it is probably a good approximation for those ϕ's which contribute substantially to the polarizability. Then

$$g_{\lambda\mu} = 0 \qquad \text{if } \lambda \neq \mu \tag{15}$$

$$h_\lambda = \langle \psi_\lambda^* \, z_\lambda \phi_\lambda \rangle \tag{16}$$

The calculation of the Q's is more complex. If f_λ in equation (4) is unity and Hartree wave functions are used, $Q_{\lambda\lambda} = \frac{1}{2}$. This value was taken by Slater and Kirkwood[38] and by Buckingham,[6] and is probably a reasonable approximation. Buckingham gives values for other simple f_λ's. Donath[11] points out, however, that the off-diagonal terms which have been neglected previously are not without significance. They reduce to

$$\begin{aligned} Q_{\lambda\mu} = \Bigg[&\left\langle \phi_\lambda^*(2)\, \psi_\lambda(2) \left| \frac{1}{r_{12}} \right| \psi_\mu^*(1)\, \phi_\mu(1) \right\rangle \\ &- \left\langle \phi_\lambda^*(2)\, \phi_\mu(2) \left| \frac{1}{r_{12}} \right| \psi_\mu^*(1)\, \psi_\lambda(1) \right\rangle \Bigg], \quad \text{for } \lambda \neq \mu \end{aligned} \tag{17}$$

in the present approximation.

The importance of the off-diagonal $Q_{\lambda\mu}$ terms is most easily demonstrated in the case of a shell of N equivalent orbitals. Then A_λ may be reduced to

$$A_\lambda = h_\lambda / \left(\sum_{\mu} Q_{\lambda\mu} \right) \tag{18}$$

and

$$\alpha = 2\sum_{\lambda} h_\lambda^2/(\sum_{\mu} Q_{\lambda\mu}) = 2Nh^2/\sum_{\mu} Q_{\lambda\mu} \tag{19}$$

In the noble gas atoms the outermost electron subshell is most important for the polarizability and may be arranged in a fashion to make all orbitals equivalent. Donath[11] calculated approximately the net effect of the off-diagonal terms for the $2p$ shell for Ne with Slater orbitals. Two effective Z values were used,[25] 6.31 and 4.77, and the resulting values of the sum of off-diagonal Q's are 0.325 and 0.430, respectively. These are to be compared with a value of about $\frac{1}{2}$ for the diagonal term. It is evident that, if the approximate results for neon are typical, the use of all Q's will substantially reduce the calculated polarizability of many-electron systems. Earlier calculations[6] yielded too large values; consequently, the improved theory will yield better agreement. More extensive numerical calculations are now being made to test the improved theory and to eliminate certain approximations.

B. London Forces

Since the polarizability is so closely related to the London force, all approximate formulas for the latter are obtained by replacing arrays of unevaluated terms which approximate the polarizability by that quantity itself. We shall examine the several ways in which this has been done with reference to the magnitude of error which may have been introduced.

If we limit ourselves to spherically symmetric systems, the perturbing potential for the interaction of atoms A and B is

$$H' = 6^{\frac{1}{2}} R^{-3}(\sum_{i} z_{A,i})(\sum_{j} z_{B,j}) \tag{20}$$

where R is the distance between the two atom centers. The wave function generalized for two nonoverlapping atoms is

$$\Psi' = \Psi^A \Psi^B + \sum_{\lambda}\sum_{\mu} b_{\lambda\mu} \Phi_\lambda^A \Phi_\mu^B \tag{21}$$

where the various quantities were defined in Eqs. 1 and 3b.

It is an assumption to use the same Φ_λ functions, or more specifically, the same f_λ of Eq. 4, for London forces and for polariza-

bility. It is easy to check this point for hydrogen atoms. Let ψ be the regular 1s function and $f = e^{cr}$. If c is adjusted for the polarizability, one finds $c = 0.204$, $\alpha = 4.438$ (as compared to the exact value 4.500), and the London energy $E_L = -6.19R^{-6}$. But if c is adjusted to optimize the London energy directly, $c = 0.134$ and $E_L = -6.45R^{-6}$ (as compared to the exact value $-6.50R^{-6}$). If $c = 0$, $f = 1$, $E_L = -6.00R^{-6}$.

This result indicates that in strictly theoretical calculations, the f_λ functions may almost as well be omitted unless they can be optimized for the London energy itself. For the purpose of semiempirical calculations, however, the f_λ functions from the polarizability must be retained for the substitution in the London energy. The error for hydrogen atoms is only about 4 per cent, however, and there does not appear to be any reason that it would increase greatly in more complex systems.

We now proceed to write out the London energy with the same symbols and approximations as were made before. In particular we retain the approximation that the ϕ's are orthogonal to the ψ's.

$$E_L = \frac{2\sqrt{6}}{R^3} \sum_{k,p} b_{kp}\, h_k{}^A\, h_p{}^B + \sum_{k,p} \sum_{l,q} b_{kp}\, b_{lq}\, R_{kl,pq} \tag{22}$$

$$R_{kl,pq} = Q_{kl}{}^A\, g_{pq}{}^B + Q_{pq}{}^B\, g_{kl}{}^A \tag{23}$$

The variational treatment follows similar steps to those given above and yields

$$E_L = -\frac{6}{R^6} \sum_{k,p} B_{kp}\, h_k{}^A\, h_p{}^B \tag{24}$$

$$B_{kp} = \det |R_{kl,pq} + (h_k{}^A\, h_p{}^B - R_{kl,pq})\, \delta_{kl}\, \delta_{pq}| \,/ \det |R_{kl,pq}| \tag{25}$$

Again it is a useful approximation to consider just the set of equivalent orbitals of the outermost subshell. Then

$$B_{kp} = h_k{}^A\, h_p{}^B \Big/ \sum_{l,q} R_{kl,pq} = h_k{}^A\, h_p{}^B \Big/ \left(g_{pp}{}^B \sum_l Q_{kl}{}^A + g_{kk}{}^A \sum_q Q_{pq}{}^B\right) \tag{26}$$

where the sums are now limited to the orbitals of the outer subshell. Equation 24 may be rearranged to

$$E_L = -\frac{6}{R^6}\left\{\sum_k \frac{(h_k{}^A)^2}{\sum_l Q_{kl}{}^A}\right\}\left\{\sum_p \frac{(h_p{}^B)^2}{\sum_q Q_{pq}{}^B}\right\}\frac{[\sum_l Q_{kl}{}^A/g_{kk}{}^A]\cdot[\sum_q Q_{pq}{}^B/g_{pp}{}^B]}{[\sum_l Q_{kl}{}^A/g_{kk}{}^A]+[\sum_q Q_{pq}{}^B/g_{pp}{}^B]} \tag{27}$$

The quantities in braces are $\frac{1}{2}\alpha_A$, $\frac{1}{2}\alpha_B$, respectively, and, if we define the energies in brackets, for example,

$$U_A = \sum_l Q_{kl}{}^A/g_{kk}{}^A \tag{28}$$

then the London energy takes the familiar form

$$E_L = -\frac{3\alpha_A\alpha_B}{2R^6}\cdot\frac{U_A U_B}{U_A+U_B} \tag{29}$$

This is, of course, just a formula first presented by London but with a new meaning to the characteristic energies U_A, U_B.

If in Eq. 28 only $Q_{kk}{}^A$ were important, then U_A would be approximately the ionization energy, which was London's interpretation. For many-electron systems, however, we have seen that the off-diagonal Q's make a substantial contribution. Consequently, Donath has suggested that the value of U for a typical many-electron atom may be about twice the ionization energy and that this accounts for the fact that observed London energies are about double those calculated by the London formula. Donath also suggests that U be regarded as an empirical parameter for a semi-empirical system for estimation of London forces. We shall return to this system in the next section.

In many electron atoms the maximum contributions to the polarizability and to London forces arise from configurations with more than one electron contributing to the net dipole moment of the atom. But in such configurations the electronic repulsion is especially high. The physical meaning to be attributed to the Q_{kl} terms is just the additional electron repulsive energy which these configurations require.

At this point let us introduce throughout the approximation $f_\lambda = 1$ which we have used in part heretofore. Then

$$g_{\lambda\lambda} = h_\lambda = \langle \psi_\lambda{}^* z_\lambda{}^2 \psi_\lambda \rangle \tag{30}$$

and for just a subshell of equivalent orbitals

$$\begin{aligned} \alpha_A &= 2 \sum_{\lambda} h_{\lambda}^{A} / U_A \\ &= 2Nh^A / U_A \end{aligned} \tag{31}$$

We shall use these results in various derivations to follow.

There is another effect[31] leading to an increase in the effective energy U_i above even the value of Eq. 28. The treatment for that equation considered only the outer subshell of electrons. Other, more tightly bound electrons must make some contribution to both the polarizability and the London energy. But Eqs. 11, 14, 28, and 30 show that the polarizability depends on terms of the type $(h^2/Q) \cong (h/U)$ while the London energy terms from Eqs. 24 and 25 are of the order $(h^4/gQ) \cong (h^2/U)$. Thus, if other electrons still have large h values but larger Q values than the outer subshell electrons do, they contribute more to the London energy than the product $\alpha_A \alpha_B$ predicts. This has the effect of yielding a higher effective excitation energy or raising U_i even more above the ionization energy.

Let us now derive the Slater-Kirkwood[38] formula in terms of our present quantities. A single subshell of equivalent electrons is assumed. Equation 29 may be rearranged to

$$E_L = -3\alpha_A \alpha_B / 2R^6 \cdot (U_A^{-1} + U_B^{-1})^{-1} \tag{32}$$

where from Eqs. 28 and 30

$$U_A^{-1} = h^A / \sum_{l} Q_{kl}^{A} = (\alpha_A / 2N \sum_{l} Q_{kl}^{A})^{\frac{1}{2}} \tag{33}$$

and Eq. 19 was used in the last transformation. Then adoption of the value $\frac{1}{2}$ for $\sum Q$ yields the Slater-Kirkwood formula

$$E_L = -3\alpha_A \alpha_B / 2R^6 \left[(\alpha_A / N_A)^{\frac{1}{2}} + (\alpha_B / N_B)^{\frac{1}{2}} \right] \tag{34}$$

Our earlier discussion of off-diagonal Q's, however, indicated that $\sum Q$ would substantially exceed $\frac{1}{2}$ in many-electron systems. Consequently, if Eq. 34 is used with N an empirical factor,[31] we may expect the N values to exceed substantially the actual number of electrons of the outer subshell.

Another generally useful equation for the London energy is that

of Kirkwood and Müller[27] which uses the diamagnetic susceptibility as well as the polarizability of the individual atoms or molecules. The *susceptibility* per atom or molecule of a *spherically symmetrical* system is given by

$$\chi = -(2mc^2)^{-1} \sum_k \langle z_k^2 \rangle \tag{35}$$

where c is the velocity of light and m the electronic mass. But in view of Eq. 30 and for a subshell of equivalent electrons

$$\chi_A = -Nh^A/2mc^2 \tag{36}$$

and with Eq. 31

$$U_A^{-1} = \alpha_A/2Nh^A = -(4mc^2)^{-1}(\alpha_A/\chi_A) \tag{37}$$

Then the London energy becomes

$$E_L = 6mc^2\alpha_A\alpha_B/R^6\,[(\alpha_A/\chi_A) + (\alpha_B/\chi_B)] \tag{38}$$

Margenau[26] thought that the cancellation of the errors of various approximations would be poor for Eq. 38, but the Kirkwood-Müller formula does have the great advantage that $\sum Q$ has been eliminated and the result does not depend on any assumptions about the off-diagonal Q_{kl} type integrals. On the other hand, as Müller emphasized, the diamagnetic susceptibility of nonspherical systems contains terms in addition to those in Eq. 35, the second-order paramagnetic terms. Consequently, great care must be used in applying Eq. 38 to nonspherical systems.

This completes the discussion of the theory for many-electron systems from which we believe we have elucidated the reason for the failure of earlier approximate formulas for London forces. Many approximations remain and we summarize a few that seem most important.

(*1*) In Eq. 4 the use of the same perturbing function for both polarizability and London energy and in some cases the further assumption $\phi_\lambda = z_\lambda\psi_\lambda$, or $f_\lambda = 1$. In hydrogen the former assumption yields about 4 per cent error and the latter 12 per cent in polarizability and 9 per cent in London energy.

(*2*) The assumption of orthogonality of all ϕ_λ with all ψ_λ.

(*3*) The assumption that only the outermost subshell of electrons contributes to either α or E_L.

(*4*) The use of Hartree-Fock wave functions for the unpolarized atoms (or molecules). The principal deficiency is the lack of correlation terms for electrons of unlike spin in the wave function. The inclusion of such terms will be necessary before purely theoretical calculations yield quantitative agreement with experiment. For example, Buckingham's calculation[6] including exchange of α for Cl^- from Hartree-Fock wave functions yielded 6.9 ($\times 10^{-24}$ cm^3) as compared to the range 3.0 to 3.6 from experimental sources. Donath[11] found that angular correlation for the $3p$ shell approximately halved the polarizability which yields good agreement. Donath also explored the effect of correlation on the semi-empirical formulas for London energy in terms of polarizability, etc. His results indicate that the net effect in various cases is probably of the order of assumptions (*1*), (*2*), and (*3*) preceding and smaller than that of the omission of off-diagonal Q_{kl} terms. Further study of electron correlation is much to be desired.

III. EXPERIMENTAL INTERMOLECULAR ENERGIES

In this section the several theoretical or semi-empirical formulas for the prediction of London energies are compared with experimental values. The formulas to be tested are summarized in conventional units both for unlike atom pairs and in the simplified form for pairs of like atoms as follows:

London, Eq. 29

$$E_L = (3\alpha_A\alpha_B/2R^6)\, U_A U_B/(U_A + U_B) \tag{29}$$

$$E_L = -3\alpha^2 U/4R^6 \qquad \text{if } A = B \tag{29a}$$

London theory: $U = I$ = ionization energy; empirical: evaluate U from E_L and correlate (U/I) with number of electrons in system.

Slater-Kirkwood, Eq. 34

$$E_L = -(3e\hbar/2m^{\frac{1}{2}}R^6)\ \alpha_A\alpha_B/[(\alpha_A/N_A)^{\frac{1}{2}} + (\alpha_B/N_B)^{\frac{1}{2}}] \tag{39}$$

$$E_L = -3e\hbar\alpha^{\frac{3}{2}}N^{\frac{1}{2}}/4m^{\frac{1}{2}}R^6 \quad \text{if } A = B \tag{39a}$$

Slater-Kirkwood theory: N = no. of electrons of outer subshell; empirical: evaluate N from E_L and correlate with actual number of electrons of both outer subshell and of whole system.

Kirkwood-Müller (valid only for *spherical* systems, i.e., atoms)

$$E_L = 6mc^2\alpha_A\alpha_B/N_0 R^6 \left[(\alpha_A/\chi^A_{\text{mol}}) + (\alpha_B/\chi^B_{\text{mol}})\right] \tag{40}$$

$$E_L = 3mc^2\alpha\chi_{\text{mol}}/N_0 R^6 \quad \text{if } A = B \tag{40a}$$

where N_0 is Avogadro's number and χ_{mol} is a molal susceptibility in cm^3. This equation does not adapt itself so well to empirical use although a correction factor could be introduced and correlated with the number of electrons in the system.

Intermolecular potential functions have been fitted to various experimental data, such as second virial coefficients, viscosities, and sublimation energy. The use of data from dense systems involves the additional assumption of the additivity of pair interactions. The viscosity seems to be more sensitive to the shape of the potential than the second virial coefficient; hence data from that source are particularly valuable. These questions are discussed in full by Hirschfelder, Curtiss, and Bird[17] whose recommended potentials based primarily on viscosity data are given in the tables of this section.

Another problem arises from the presence of higher terms in the multipole expansion of the electrostatic interaction. While theoretical formulas exist for these also, they are even more approximate than those for the dipole-dipole term. Also, there is the uncertainty about the exact form of the repulsive interaction. Quite arbitrarily we shall group the higher multipole terms with the true repulsive interaction and assume that the empirical repulsive term accounts for both. The principal merit of this assumption is simplicity; the theoretical and experimental coefficients of the R^{-6} term are compared without adjustment. Since the higher multipole terms are known to be attractive and have been estimated to amount to about 20 per cent of the total attractive potential at the minimum, a rough correction for their possible effect can be made if it is believed that this is a preferable assumption.

The polarizability, ionization potential, and magnetic susceptibility data from the last edition of the Landolt-Börnstein tables are given in Table I for the inert gases and for H_2, N_2, Cl_2, and CH_4. The coefficients of the dipole-dipole or R^{-6} potential term are

given in Table II; Table III gives effective U values and U/I ratios; while Table IV gives effective N values for Eq. 39 and a comparison with both the number N_{os} of outer shell electrons and the total number of electrons Z.

TABLE I. Properties of Atoms and Molecules[a]

Subst.	$\alpha \times 10^{24}$ cm^3	$\chi_{mol} \times 10^6$ cm^3	I, ev
He	0.21	1.94	24.56
Ne	0.40	7.2[b]	21.56
Ar	1.63	19.4	15.76
Kr	2.48	28	14.0
Xe	4.01	43	12.13
H_2	0.79	4.0	15.43
N_2	1.76	12.0	15.51
Cl_2	4.61	42	13.2
CH_4	2.60	12.2	13.04

[a] Source, Landolt-Börnstein, 6. Auflage, I, 1 and 3.

[b] This value was based upon the discordant values 7.77 ± .01 and 6.62 ± .18.

TABLE II. Theoretical and Empirical R^{-6} Potential Coefficients (units: erg cm$^6 \times 10^{-60}$; all are negative)

Subst.	Exp.	London Eq. 29	S. and K. Eq. 39	K. and M. Eq. 40
He	1.57[a]	1.30	1.71[b]	1.66
Ne	9.50	4.14	7.8	12.8
Ar	109.2	50.3	64	129
Kr	232	103	120	283
Xe	561	235	247	703
H_2	12.6	11.6	12.5	(12.9)
N_2	125.6	58	72	(86)
Cl_2	957	337	394	(790)
CH_4	258	106	150	(130)

[a] Experimental potentials are from Hirschfelder, Curtiss, and Bird;[17] of the several potentials given there for He the Lennard-Jones potential fitted by DeBoer, Michels, and Lunbeck was selected.

[b] The N values used in Eq. 39 are 2 for He and H_2, 6 for Ne, Ar, Kr, Xe, and N_2, 8 for CH_4, and 10 for Cl_2.

Table II shows clearly the large differences between various theories for many-electron systems. The Kirkwood-Müller equation always yields somewhat too large coefficients for the atoms which are the only spherical systems; but the London equation deviates by a greater amount on the low side. The Slater-Kirkwood equation gives a high value for He but yields coefficients smaller than the empirical ones for all other cases.

TABLE III. Effective U Values for Equation 29

Subst.	U, ev	U/I
He	29.6	1.20
Ne	49.	2.27
Ar	34.2	2.17
Kr	31.4	2.24
Xe	29.0	2.39
H_2	16.8	1.09
N_2	33.7	2.17
Cl_2	37.5	2.84
CH_4	31.8	2.44

The results in Table III give promise of a useful method of prediction and at the same time confirm the importance of the off-diagonal Q_{kl} terms discussed in the previous section. It appears that U/I may be taken as about 1.15 for two-electron systems and about 2.25 for systems with sp closed shells. The latter value is also satisfactory for N_2 and CH_4. Treatment of Cl_2 as a spherical system is such a poor approximation that the U/I value should not be given much significance in that case.

The discussion in the previous section indicated that N_{eff} values would be expected to exceed substantially the actual number of outer shell electrons. Table IV amply confirms this conclusion. Since N appears to the $\frac{1}{2}$ power in the Slater-Kirkwood equation, the deviations are exaggerated. Thus, in making a very similar treatment a few years ago in which slightly different empirical potentials were used, the writer[31] found substantially smaller effective N values. For the same reason a relatively crude effective

N will yield a fair estimate of the potential coefficient. Selection of the mean of the total number of electrons and of the number in the outer shell would appear to be a reasonable formula for the rare gas atoms.

TABLE IV. Effective N Values in Equation 39

Subst.	N_{eff}	N_{os}	Z
He	1.7	2	2
Ne	8.8	6	10
Ar	17.3	6	18
Kr	22.2	6	36
Xe	30.6	6	54
H_2	2.0	2	2
N_2	18.1	6	14
Cl_2	59	10	34
CH_4	24	8	12

The empirical potentials for the molecules were obtained on the assumption of single attraction centers. This assumption is probably good for H_2, fair for CH_4 and N_2, and very poor for Cl_2. Even for molecules such as CH_4 which are relatively spherical in shape, the fact that some atoms are near the outer surface rather than the center has an important effect. The closest interatomic distances are emphasized by the R^{-6} dependence of the potential. This point has been considered by several authors who worked out examples showing the net intermolecular potential for several models.

Kihara[20] used a core model in which the Lennard-Jones potential is assumed to hold for the shortest distance between the molecular cores instead of molecular centers. By use of linear, tetrahedral, and other shapes of cores, various molecules can be approximated. Thomaes,[41] Rowlinson,[35] Hamann, McManamey, and Pearse,[14] Atoji and Lipscomb,[1] Pitzer,[30] and Balescu,[4] have used other models of attracting centers and other mathemtical methods, but obtain similar conclusions. The primary effect is to steepen the potential curve so that in terms of inverse powers of the inter-

molecular distance the effective exponent exceeds six. Depending on the shape of the molecule, angular dependency of the potential may or may not be important.

In view of the complications of the intermolecular potential (as compared to the interatomic potential of the rare gas atoms) the comparisons for molecules in Tables II, III, and IV should be judged with caution. The apparent discrepancies from the theories for single atoms can be misleading. An example is the calculation for CH_4 on the Slater-Kirkwood theory where Table IV shows the absurd value of 24 for the effective number of electrons. Pitzer and Catalano[32] have applied the Slater-Kirkwood equation to the intermolecular potential of CH_4 by addition of all the individual atom interactions and, with $N = 4$ for carbon and 1 for hydrogen, obtained agreement within 5 per cent for the London energy at the potential minimum.

IV. INTRAMOLECULAR APPLICATIONS

Since electrostatic forces propagate through a molecule as through space, the motion of electrons in different parts of the same molecule will interact in at least the same way as electrons in different molecules. There may be additional intramolecular interactions arising from effects propagated through the bonding system of the molecule, such as in conjugated or mesomeric systems. *But we wish particularly to emphasize that the electron correlation energy effects of nonoverlapping portions of molecules can be treated by the same methods as intermolecular energies.*

A. Saturated Hydrocarbons

A relatively unambiguous intramolecular application of London energy theory is that of Pitzer and Catalano[32] to the paraffin hydrocarbons. They assumed that C—H and C—C single-bond energies were constant and that the time average polarity of these bonds was negligible. Since there are no multiple bonds in the paraffins, no conjugation or first-order hyperconjugation effects are possible. The London interaction energies were summed for all pairs of nonbonded atoms. These nonbonded atoms are far enough separated to make the nonoverlapping approximation satisfactory

in all cases except a very few where steric repulsion must also be recognized. Then any correction to the London energy can be included with the repulsive energy which is treated empirically.

The Slater-Kirkwood equation (Eq. 39) was selected with $N = 4$ for carbon and $N = 1$ for hydrogen. The success of the equivalent calculation for the intermolecular interaction of CH_4 molecules was mentioned in the previous section. Atoms, rather than bonds, were chosen as the basis for the calculation because the location of the atom centers is unambiguous and the approximation of isotropic polarizability is better for an atom than for a bond. Possible deviations from isotropic polarizability are discussed in Section V. Ketelaar[19] gives for the atomic polarizabilities of hydrogen and carbon: $\alpha = 0.42$ and 0.93×10^{-24} cm^3, respectively. The resulting equation for the London energy is

$$\Delta E_L = -[22.6 \Sigma R_{C-C}^{-6} + 8.68 \Sigma R_{C-H}^{-6} + 3.42 \Sigma R_{H-H}^{-6}] \times 10^{-60} \text{ ergs} \tag{41}$$

Pitzer and Catalano compared calculated heats of formation of the various paraffins through the pentanes with experimental values corrected to 0°K. The known vibrational frequencies were used to calculate the zero-point vibrational energy. The agreement in most cases was well within the experimental error of the heat of formation although the difference did reach 1 kcal/mole in one case and 0.8 in another. It is particularly interesting to consider the energies of isomerization from *n*-butane to isobutane and from *n*-pentane to neopentane because these differences arise exclusively from the London energy and the zero-point vibrational energy. The results are given in Table V.

TABLE V. Isomerization Energies for Butane and Pentane (units: kcal/mole)

Isomerization	ΔE_L	ΔE_{vib}	ΔE_{calc}	ΔE_{exp}
Iso- to *n*-butane	1.28	0.24	1.52	1.63
Neo- to *n*-pentane	3.8	1.0	4.8	4.1

Donath[11] has extended these calculations to cyclohexane and cyclopentane and obtained comparably good agreement. It seems safe to conclude that these long-range electron correlation effects account for the isomerization energies of the paraffins which had heretofore remained unexplained.

B. Unsaturated Hydrocarbons

The application of these methods to unsaturated hydrocarbons involves certain complications. Unsaturated hydrocarbons show an additional polarizability[19] of 0.58×10^{-24} cm^3 per double bond and 0.86×10^{-24} cm^3 per triple bond in the molecule. Similarly the polarizability of a molecule containing a benzene ring exceeds that computed for the atoms present by about 1.28×10^{-24} cm^3. These results are most readily explained on the basis that oscillations of charge from atom to atom are significant when double bonds are present.

The concept of an *extra* polarizability associated with a double bond can be checked from the spectrum of ethylene. The transition at 61,000 cm^{-1} for that substance seems clearly to be associated with the presence of the double bond. Hammond and Price[15] found the intensity of this transition to yield an f value of 0.29. The component of polarizability at low frequency associated with this transition is given by the formula[26,31]

$$\alpha_k = (e^2/4\pi^2m)\, f_k/\nu_k^2 \qquad (42)$$

This yields 0.51×10^{-24} cm^3 which agrees approximately with the value 0.58×10^{-24} ascribed to the double bond on an empirical basis. Also we may note that this f value corresponds to a transition dipole of 3.16×10^{-18}, if a one-dimensional charge oscillation is assumed, and that this dipole yields an apparent charge of 0.49 times the electronic charge for a C=C distance of 1.34 A.

The usual multipole expansion is inappropriate for the treatment of London energies associated with the interatomic charge oscillation. However, London[23] has given an appropriate method, known as the monopole method. Coulson and Davies[7] and Haugh and Hirschfelder[16] have applied the monopole method to the inter-

molecular forces between molecules containing large amplitude oscillators.

Simpson[37] discussed the conjugated polyenes in terms of internal London interactions and showed that the results from this theory alone gave a self-consistent explanation of both the conjugation energy of the ground state and the pattern of low lying excited electronic states in terms of a single empirical parameter. Since these phenomena had been previously ascribed to resonance with different bond structures, it became of interest to try to determine the magnitude of each effect.

We assume that the double bonds in 1,3-butadiene would be the same as in ethylene if they did not interact with one another. Introduction of the known geometry of 1,3-butadiene in the *s-trans* conformation and the monopole charge of 0.49 *e* on each carbon yields an interaction energy $\delta = 0.48$ ev between the two double bonds. Simpson found the empirical value $\delta = 1.91$ ev from his assumption that only a London interaction was present. Hence it appears that only a small part of the interaction between double bonds in 1,3-butadiene is a London type of second-order electrical effect and the larger part is a conjugation or resonance associated with the structure with a double bond in the central position.

The London interaction of saturated portions of a hydrocarbon with a double bond may also be calculated by the use of equations given by Haugh and Hirschfelder.[16] The writer has made exploratory calculations for simple olefins by this method; the results do not fit the observed heat of formation values on the assumption of constant bond energies. The extra stability of alkyl groups adjacent to double bonds, which is commonly attributed to hyperconjugation, is somewhat increased after London energies have been consistently included. There are aspects of this calculation, however, which are on less firm ground than those already described, hence the conclusion should be regarded as somewhat tentative.

C. Halogens

Possible explanations of the peculiarly low heat of dissociation of fluorine as compared to the other halogens have been discussed

by Mulliken[28] and the writer.[29,33] The electron correlation or London energy of interaction between the unshared pairs of electrons on the two halogen atoms is a very substantial term. While the assumption of lack of overlap of the electron distributions and the dipole-dipole approximation are both subject to question in this case, nevertheless, the simple formulas should indicate whether the trend down the halogen series is anomalous or not. A simple calculation[33] using the London equation (Eq. 29) indicated that this trend was indeed anomalous with a low energy for F_2. Calculations which are revised to use a recently observed polarizability value for F_2 [13] and which use the (U/I) value of 2.25 recommended above are given in Table VI.

TABLE VI. Intramolecular London Energies for the Halogens

Calculation	F_2	Cl_2	Br_2	I_2
$\alpha_X = \frac{1}{2}\alpha_{X_2}$, 10^{-24} cm^3	0.64	2.30	3.34	5.11
$R(X-X)$, 10^{-8} cm	1.435	1.988	2.284	2.667
$U = 2.25\ I$, ev	39.0	29.1	26.6	23.9
$-E_L$ (dipole-dipole), kcal/mole	32.	43.	36.	30.
ΔE_{dissoc}, kcal/mole	39.	57.1	45.4	35.6

In addition to the calculations in Table VI which are based upon Eq. 29, one may use the Slater-Kirkwood equation (Eq. 39). If one takes effective N values less by one than those given in Table IV for the rare gas atom adjacent to each halogen, the resulting London energies are very nearly the same as those in Table VI.

The departure of the E_L values from a smooth trend is somewhat over half as large as that of the dissociation energy values in the last row of Table VI. Until the London energy calculations are refined to eliminate the dipole-dipole approximation and other uncertainties, it is not possible to say whether that effect accounts for the entire anomaly or not. In any event a substantial portion of the anomaly may be ascribed to the correlation of the motion of the unshared electron pairs in the valence shell.

V. ANISOTROPIC EFFECTS

The rare gas atoms are strictly spherical but other systems which have been considered, such as hydrogen, carbon, or halogen atoms, may be anisotropic. These have been treated in preceding sections as isotropic and it is one purpose of the present section to consider the magnitude of possible error.

A. Polarizability

We consider first the polarizability of a molecule consisting of two or more polarizable parts which may be atoms, bonds, or other units. When the molecule is placed in an electric field the effective field which induces dipole moments in various parts is not just the external field but rather the local field which is influenced by the induced dipoles of the other parts. The classical theory of this interaction of polarizable units was presented by Silberstein[36] and others and is summarized by Stuart in his monograph.[40] The writer has examined the problem in quantum theory and finds that the same results are obtained to the order of approximation being considered.

Let us take the problem of a diatomic molecule, such as Cl_2, with the two atoms as the two polarizable parts. Each atom has a polarizability α_1 parallel to and α_2 perpendicular to the interatomic axis, respectively. The Silberstein theory yields for the effective polarizability of the molecule the values b_1 and b_2, respectively, parallel and perpendicular to the axis.

$$b_1 = 2\alpha_1\left[\frac{1+(2\alpha_1/R^3)}{1-(2\alpha_1/R^3)^2}\right] \tag{43a}$$

$$b_2 = 2\alpha_2\left[\frac{1-(\alpha_2/R^3)}{1+(\alpha_2/R^3)^2}\right] \tag{43b}$$

The mean polarizability b is

$$b = \tfrac{1}{3}b_1 + \tfrac{2}{3}b_2 = 2\left(\frac{\alpha_1}{3} + \frac{2\alpha_2}{3}\right) + \frac{2(\alpha_1{}^2 - \alpha_2{}^2)}{3R^3} + \ldots \tag{44}$$

where the expansion is made on the assumption that (α_i/R^3) is less

than unity. We note that the first-order term is just the appropriate sum of component polarizabilities and that the second-order term is very small if either $\alpha_1 \cong \alpha_2$ or if (α_i/R^3) is small. Thus interactions have much less effect on the mean polarizability than on the anisotropy.

The values for Cl_2 are $b_1 = 6.60$, $b_2 = 3.62$, both $\times 10^{-24}$ cm^3. When these values are substituted in Eq. 43 together with $R = 1.99 \times 10^{-8}$ cm, one obtains $\alpha_1 = 1.79$ and $\alpha_2 = 2.36$, both $\times 10^{-24}$ cm^3. Thus, although the polarizability of the chlorine molecule is almost twice as great parallel than perpendicular to the axis, the atom is nearly isotropic with slightly greater polarizability perpendicular to the axis.

Recently this important interaction of polarizable parts of a molecule seems to have been forgotten. Denbigh[10] and Le Fèvre and Le Fèvre[22] have presented extensive tables of bond polarizabilities which are so selected that simple addition of the polarizability components for the various bonds yields the components of the polarizability of the entire molecule. These schemes have been surprisingly successful in an empirical sense and may have considerable value on that basis. But it is evident from the theory of Silberstein that the anisotropy of these bond polarizabilities cannot be directly interpreted as properties of the bonds. In particular the nearly zero transverse polarizability reported for the C—C single bond must be spurious. It seems most likely that there is some fortuitous cancellation of conflicting factors which allows the Denbigh-Le Fèvre scheme to succeed over a limited range of substances, and the failure of the scheme to fit an additional array of molecules may not indicate any error in the assumed structures of the molecules but only that the range of this accidental cancellation has been exceeded. The failure of Stein[39] to obtain good agreement with the anisotropy of *n*-paraffin polarizabilities may be an example of this sort, since certain of the structures that he considered fit all theoretically sound experimental criteria.

Unfortunately the complete calculation of the principal polarizabilities of a polyatomic molecule including the Silberstein interactions is very complex. Possibly electronic calculators will make this computation feasible for an array of molecules such as the

saturated hydrocarbons. Fortunately, however, these interactions drop out of the first approximation to the mean polarizability of the entire molecule. Consequently simple sum rules for the mean polarizability of a molecule in terms of component atoms or bonds are sound to that approximation.

B. London Forces

London[23] has treated the case of the attractive force between anisotropic molecules on the dipole-dipole interaction basis as well as on the monopole basis mentioned above. The small anisotropy found for the chlorine atom makes the dipole-dipole formulation appropriate. For the symmetrical orientation in the Cl_2 molecule the London formula is

$$-E_L = \frac{2\alpha_1^2 U_1 + \alpha_2^2 U_2}{4R^6} \tag{45}$$

where U_1 and U_2 are the characteristic energy quantities for polarization parallel to and perpendicular to the axis, respectively. In London's theory these were thought to be approximately the ionization potential but we have found that both theory and experiment indicate much larger values, possibly about 2.25 times I for many electron systems.

There is no reason to believe that the off-diagonal Q integrals which yield this increase in U over I should be equal for longitudinal and transverse polarization but neither is there at present any basis for selecting different values. Hence we assume $U_1 = U_2$ and by use of the α values given above for the chlorine atom, the value of $-E_L$ is calculated to be about 30 per cent smaller than was obtained in Table VI. Since the effect of anisotropy would be expected to be about the same for all of the halogens, the qualitative conclusions drawn from the results in Table VI are not affected. It is clear that anisotropy may be important, however, and must be considered in quantitative work.

In the more complex case of the saturated hydrocarbons, the anisotropic equations have not been solved. Rough estimates from approximate solutions indicated that the anisotropy of hydrogen and of saturated carbon atoms is small but an accurate check on this matter would be desirable.

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THE SOLUBILITY OF SOLIDS IN COMPRESSED GASES

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I. INTRODUCTION

If a solid is placed in contact with a liquid then it is most usual for an equilibrium state to be reached in which there are three phases present—a gas phase composed of one of the pure components, a liquid phase which contains both components, and a solid phase which contains only the second pure component. A system of two components and three phases has one degree of freedom, and so the solubility of the solid in the liquid phase is a function only of temperature. A change of pressure at a given composition and temperature removes one of the phases. At low temperatures a reduction of pressure leads to the evaporation of the liquid phase, and so gives a system of two phases each formed of one pure component. There is little of interest in such a system. An increase of pressure leads to the condensation of the gas phase, but, in general, has little effect on the concentration of the solid in the remaining fluid phase. However, there may be marked changes of concentration if the temperature is above the normal boiling point of the fluid component, which, for convenience, will always be called component 1. The solutions discussed in this review are those of a pure solid, component 2, in a fluid phase at temperatures near and above the critical temperature of pure component 1. First, the general form of the phase diagrams of such systems is described, second, examples are quoted of some of the more recent studies of simple systems, third, the application of statistical thermodynamics to the theory of such solutions is described, fourth, it is shown how the study of such solutions can add to our scant knowledge of the physical forces between unlike molecules, and finally it is shown that the far-from-negligible solubility of many solids in compressed gases must often be taken into account when interpreting physical measurements on compressed gases.

Booth and Bidwell,[6] in an earlier review, have described the experimental methods used in this field and have given a qualitative account of much of the work that is of interest to geologists and engineers.

II. PHASE EQUILIBRIA

The solubility of a solid in a liquid at its saturation vapor pressure is usually represented as a (T, x_2) graph, where x_2 is the mole

fraction of the solid component. Such a curve starts from the triple point of the second component, where the two liquids are assumed to be completely miscible, and moves to lower temperatures with a continuously decreasing x_2 until it cuts a similar curve starting from the triple point of component 1. The point of intersection is called the eutectic point. Many of the solids discussed in this review are appreciably volatile and a complete representation of the phase equilibria needs therefore a three-dimensional (p, T, x)

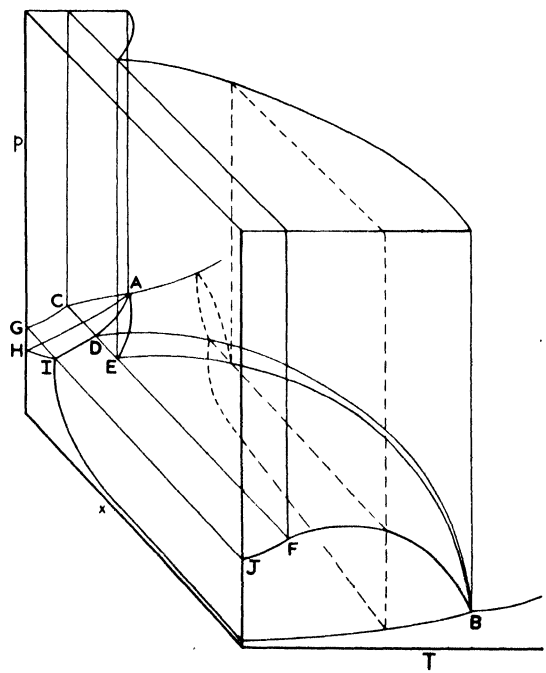

Fig. 1. The pressure-temperature-composition surfaces for the equilibrium between two pure solid phases, a liquid phase, and a vapor phase.

graph, such as that shown in the classic work of Roozeboom.[64] Figure 1 is a simplified version of this diagram for the equilibrium between a substance of low volatility and high melting point and one of high volatility and slightly lower melting point. The two side planes of the diagram ($x_2 = 0$, $x_2 = 1$) show the usual solid-gas, solid-liquid and liquid-gas boundary curves for the two pure

substances which meet, three at a time, at the two triple points, A and B. The eutectic line, C, D, E, F, is an invariant state of four phases—solid 1 (C), solid 2 (F), saturated liquid (E) and saturated vapor (D). The (p, T) projection of this line gives the quadruple point of the binary system. The projection of A, B, C, E, and F on the (T, x) plane gives the familiar solubility diagram of two immiscible solids and a miscible liquid phase, and a eutectic point that is the projection of point E. This solubility diagram is essentially the same as the "cut" shown at the top of the figure, since

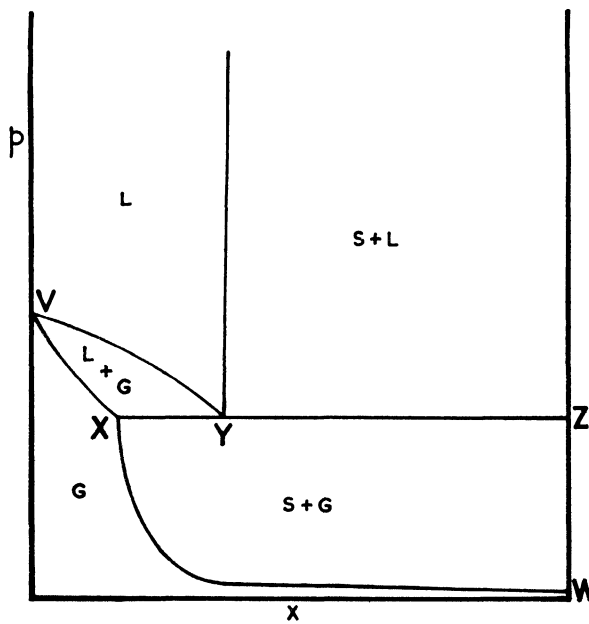

Fig. 2. A section of Fig. 1 at a constant temperature lying between the melting points of the pure components.

pressure has little effect on the equilibrium between condensed phases. However, it is the (p, x) projections that are here of greater interest. Below the eutectic (or quadruple) temperature the (p, x) projection is given by G, H, I, J, and K. The vapor pressures of the two pure solids are represented by H and K and the total vapor pressure of the two solids in equilibrium with the mixed vapor by

G, I, and J. The total will be very close to the sum of the vapor pressures of the two pure components and the ratio GI/IJ will be very close to the ratio of their vapor pressures. Above the melting point of component 1, the (p, x) section has the shape shown by the dashed lines in Fig. 1 and is drawn in more detail in Fig. 2. This section is formed of two homogeneous regions, liquid and gas, and three heterogeneous regions, liquid + gas, solid 2 + gas, and solid 2 + liquid. As the temperature is raised towards the melting point of the second component, points W and Y move towards Z and the liquid + gas region expands, until the usual (p, x) diagram for two liquids is reached at the melting point (Fig. 3). At still

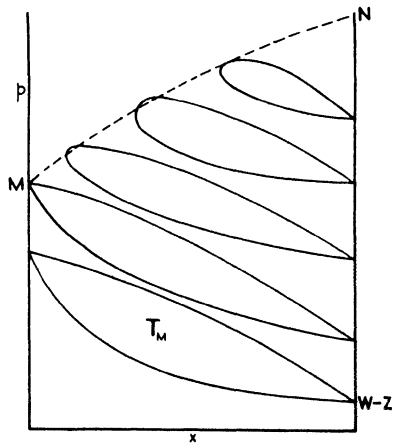

Fig. 3. Sections of Fig. 1 at temperatures at and above the melting point of the second component.

higher temperatures the critical point of the first component will be reached (M, see Fig. 3) and then the (p, x) loop contracts until it finally vanishes at the critical point of the second component, N. The locus (M—N) of the maxima of the (p, x) loops is the plait-point line, or gas-liquid critical-point line, of the binary mixture.

The behavior described by Figs. 1–3 is that of a mixture of two similar substances. The only curves that represent the equilibrium of a solid with a gaseous mixture are HI and KI in Fig. 1 and WX in Fig. 2. Here the total pressure is low, and the gas mixture will

be almost a mixture of perfect gases. However, consider the course of the vapor pressure curve of the saturated liquid mixture, EB, when the melting point B is as high or higher than the critical point of the first component. The vapor pressure curve will first rise with temperature. The solution will be weak in the second component and the predominant effect of temperature will be to increase the vapor pressure, exactly as for a pure substance. However, as the mole fraction of the second component increases towards unity, the vapor pressure curve must pass through a

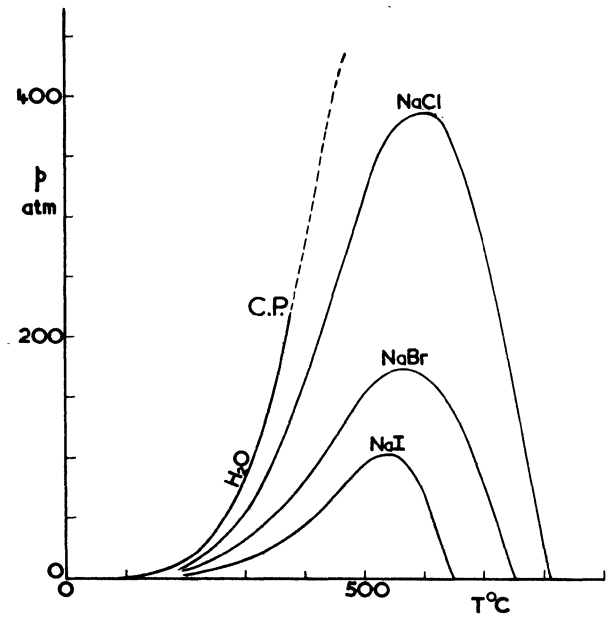

Fig. 4. The vapor pressure curves of pure water and of saturated aqueous solutions of the sodium halides. The dashed curve (– – – – – –) is the (p, T) projection of the critical line of the system water + sodium chloride.

maximum until it finally falls to the triple point of component 2. Such maxima have been demonstrated for several solutions of which the best known is, perhaps, the system water + silver nitrate.[17] The maximum is here at 1.32 atm and 169°C. The melting point of silver nitrate is 210°C. Solutions of organic solids in water often show even lower maxima, since their melting points are

lower. For example, water + resorcinol[16] has a maximum vapor pressure of 0.18 atm at 87°C. High maxima are shown by solids of low solubility and high melting point. Keevil[40] has found maxima from 100–400 atm for the alkali halides. His results for sodium chloride, bromide, and iodide are shown in Fig. 4. Ölander and Liander[51] have studied again the sodium chloride system from 350–475°C and obtain results that are about 10 atm higher, but which would doubtless have shown a similar maximum if they had carried their measurements to a high enough temperature. The melting points of these salts are all above the critical temperature

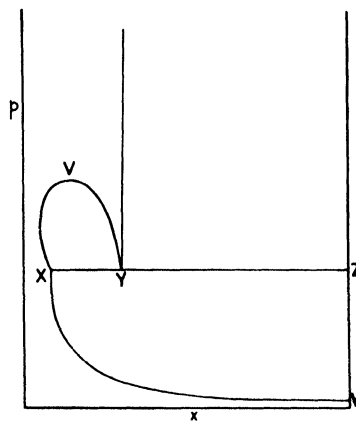

Fig. 5. A (p, x) section at a constant temperature lying above the critical point of the first component and below the melting point of the second.

of water and the (p, x) sections near the maxima of the vapor pressure curves must be of the type shown in Fig. 5. The (p, T) curves of Fig. 4 are the locus of the univariant system solid + liquid + gas, that is, of line X, Y, Z of Fig. 5. The point W is the vapor pressure of the pure solid and is here virtually zero. Point V is the critical point of the mixture where liquid and gas become identical. Outside the region VXY it is meaningless to distinguish between liquid and gaseous states, and other areas of Fig. 5 are therefore described as fluid or as fluid + solid, where the fluid is a solution in supercritical steam. Figure 6 shows the mole fraction of sodium chloride in the saturated liquid phase and in the critical phase, that is Y and V of Fig. 5, as functions of temperature.[40, 51]

The mole fraction in the saturated gas phase (X in Fig. 5) is too small to represent on Fig. 6. Ölander and Liander estimate it at

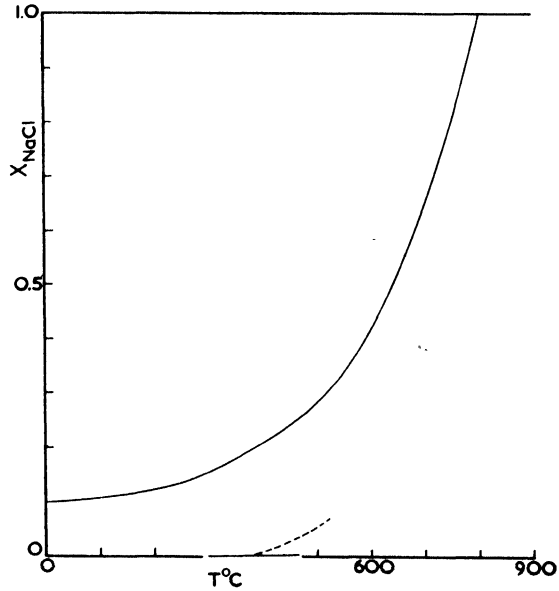

Fig. 6. The composition of the saturated liquid phase in the system water + sodium chloride. The dashed line (- - - - - - -) shows the mole fraction of the salt at the critical points. The mole fraction in the vapor is too small to be shown in this diagram.

1.6×10^{-5} at the critical temperature of water, 374°C, and at 6.2×10^{-5} at 475°C.

The only parts of Fig. 5 which can meaningfully be described as "solubility in a compressed gas" are WX and XV. However, a very different situation arises if the saturated vapor pressure curve cuts the critical curve (M—N of Fig. 3). Figure 4 shows that this does not happen for the three sodium halides. The complete course of the critical curve is not known, but enough is known in the case of the sodium chloride system[51, 75] for it to be clear that it rises well above the maximum of the saturated vapor pressure curve. However, it is cut by the vapor pressure curves of less soluble salts such as sodium carbonate and sodium sulphate.[40, 87] The (p, T) projection of a system of the type water + sodium chloride is

shown in Fig. 7 and of a system of the type water + sodium sulphate in Fig. 8. In the latter diagram the saturated vapor pressure curve has been broken into two unconnected parts, EO and PB.

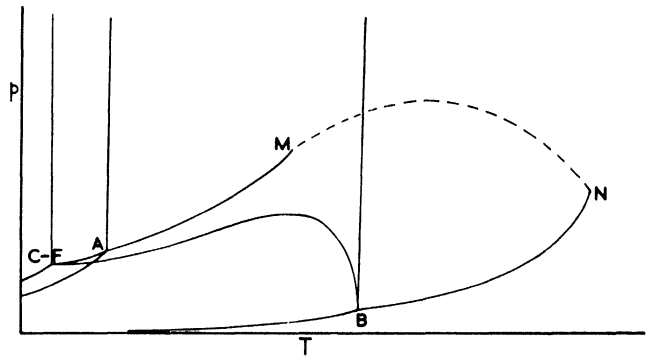

Fig. 7. The (p, T) projection of a system in which the saturated vapor pressure curve does not cut the critical line, MN.

The critical line is similarly broken into MO and PN. Between O and P there is no critical point and no saturated vapor pressure

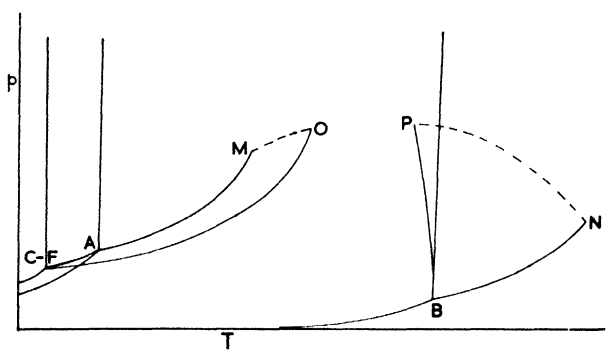

Fig. 8. The (p, T) projection of a system in which the saturated vapor pressure curves cut the critical line at lower and upper critical end points, O and P.

for the mixture. Such points are called, respectively, lower and upper critical end points, since they mark the limits of pressure and temperature in which critical states may be found. The (p, x) projections of the lower end of Fig. 8 are shown in Fig. 9, where it is seen that the liquid + gas loop decreases to zero at the critical

end point, O. Beyond O, the isotherm is continuous; that is, equilibrium is established between two phases only, solid + supercritical fluid, at all pressures and temperatures in this region. There have recently been quantitative studies of several systems in

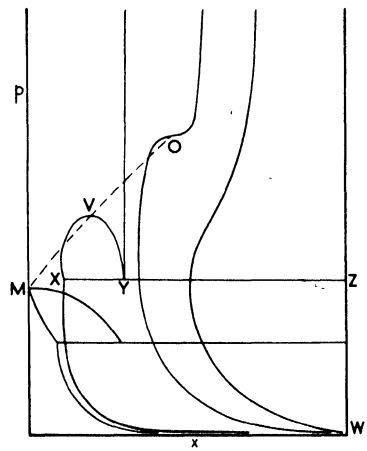

Fig. 9. Sections at constant temperatures lying between the critical point of the first component M, and the lower critical end point, O.

this region, and it is with the interpretation of such results that this review is chiefly concerned. Most of the systems have been nonaqueous, as solutions of salts in supercritical steam are extremely corrosive.

Smits first established experimentally that phase behavior of the type shown in Fig. 8 is possible, with his classic investigation of the system ethyl ether + anthraquinone.[76–81, 83, 84] The temperature and pressure of the principal points of the phase diagram are

TABLE I. The System Ethyl Ether (1) + Anthraquinone (2)

		T°C	p atm	x_2
A	Triple pt. of (1)	−116	0.00	0.0
B	Triple pt. of (2)	286	0.14	1.0
M	Crit. pt. of (1)	194	35.6	0.0
O	Lower crit. end pt.	203	43	0.009
P	Upper crit. end pt.	247	64	0.11

shown in Table I. It is seen that here the gap between O and P is quite small compared to the total gap between the critical point of ether, 194°C, and that of anthraquinone which must lie above 500°C.

III. RECENT WORK ON SIMPLE SYSTEMS

In this section we review the measurements that have been made recently on simple systems, that is, on mixtures where one or both of the components is composed of simple molecules for which something is known of the intermolecular forces. In each system the gaseous component is listed first.

A. Helium + Xenon

Ewald[22] measured the amount of xenon in the gas phase at 155°K for pressures of helium up to 108 atm. The vapor pressure of pure xenon is 0.50 atm at this temperature and so its concentra-

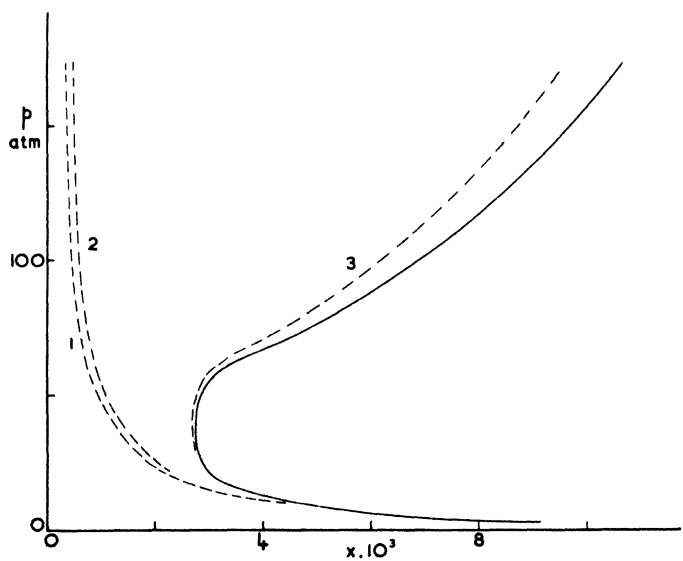

Fig. 10. The mole fraction of carbon dioxide in saturated solutions in air at −110°C (above the lower critical end point). The full line is the experimental curve of Webster and the dashed curves are: 1, an ideal gas mixture; 2, an ideal gas mixture with Poynting's correction; and 3, the solubility calculated from Eq. 8 and the principle of corresponding states.

tion in the gas phase is appreciable at all pressures. The isotherm probably resembles the experimental isotherm of Fig. 10, but the part studied lies very close to that for a perfect gas mixture and has not reached the minimum in x_2 at 108 atm. However, at this temperature the system is almost certainly above the lower critical end point.

B. Hydrogen + Xenon

This system is very similar.[22]

C. Nitrogen + Xenon

Ewald[22] studied this system at 150° and 155°K. These temperatures are above the critical temperature of pure nitrogen, 126°K, but he found that they are below the lower critical end point of the mixture. The saturated vapor pressure of the system was 50 atm at 150°K and 57 atm at 155°K. The mole fraction of xenon in the saturated gas (X in Figs. 5 and 9) was 0.035 and 0.045 at these temperatures, respectively.

D. Hydrogen + Nitrogen

Dokoupil, van Soest, and Swenker[18] have examined this system in detail from 25° to 70°K and at pressures up to 50 atm. The critical points of the pure substances are at 33° and 126°K and the lower and upper critical end points are at about 37° and 61°K. The majority of their measurements lie between the critical end points.

E. Hydrogen + Carbon Monoxide

This system is very similar.[18]

F. Helium + Carbon Dioxide

Ewald[22] studied this system at 190°K where the vapor pressure of pure carbon dioxide is 0.66 atm. He took his measurements to 143 atm without finding a minimum mole fraction of carbon dioxide.

G. Hydrogen + Carbon Dioxide

This system is very similar.[22]

H. Air + Carbon Dioxide

Air is itself a mixture but may be treated here as a pure substance, since the constituents have similar physical properties. Webster[90] measured the concentration of carbon dioxide in air from 77° to 163°K and at pressures up to 200 atm. The critical point of air (133°K, 37 atm) lies in this range and so his results cover both liquid and homogeneous states. He did not determine exactly the lower critical end point but showed that it lay between the critical temperature of air and 140°K and at a pressure a little below 37 atm. Three of his isotherms (143°, 152° and 163°K) are therefore wholely in the homogeneous region and one is shown as the experimental isotherm in Fig. 10. The minimum mole fraction of carbon dioxide increases from 3×10^{-4} at 143°K and 20 atm, to 3×10^{-3} at 163°K and 40 atm. Gratch[29] has obtained some similar results in the same temperature range.

I. Methane + Carbon Dioxide

Donnelly and Katz[19] have made a very thorough study of this system from −79° to 31°C, the critical point of carbon dioxide. The triple point of carbon dioxide is at −56.6°C. They found that

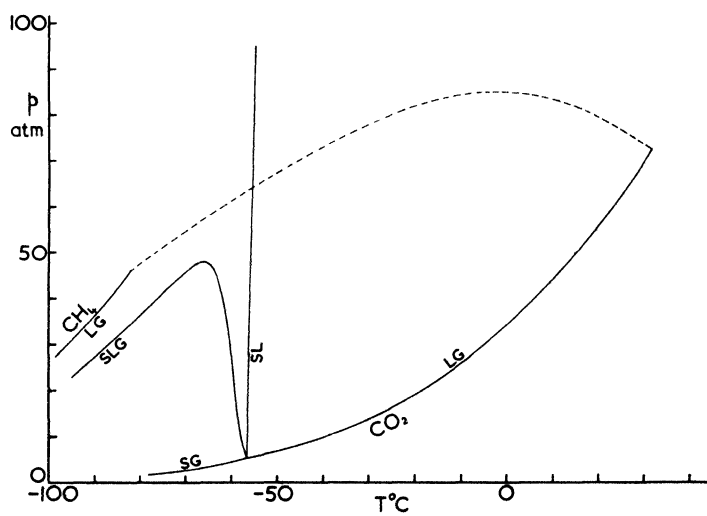

Fig. 11. The (p, T) projection of the system methane+carbon dioxide.

the system is of the same kind as water + sodium chloride, that is, the saturated vapor pressure curve does not cut the critical curve. Figure 11 is a (p, T) projection of their results.

J. Carbon Dioxide + Iodine

Braune and Strassman[8] measured the concentration of iodine in gaseous carbon dioxide at pressures up to 50 atm from 32° to 98°C. They passed the carbon dioxide over an excess of solid iodine and analyzed the effluent mixtures. Their pressures were too low to find the saturation vapor pressures or to show whether or not critical end points were formed.

The solubility of iodine in many organic vapors behaves similarly at moderate pressures, but at pressures below atmospheric the concentration of iodine is much less than in the pure saturated vapor. Jepson and Rowlinson[38] suggested that this is due to strong absorption of the vapors on the surface of the iodine. The effect is most marked with vapors of substances such as pyridine which are known to form strong electron-transfer complexes with iodine.

K. Nitrogen + Ammonia

Lurie and Gillespie[44] used the solid ammine $BaCl_2 \cdot 8NH_3$ in order to study the nitrogen + ammonia system at 45°C. The system $BaCl_2 + BaCl_2 \cdot 8NH_3$ is univariant and has a vapor pressure of ammonia of 7.12 atm at 45°C. They used nitrogen pressures up to 54 atm. More recently Field[24] has studied similarly the hydrogen + ammonia system at 32°C, and Perkins[52] has studied the equilibrium between the ammine and helium, argon, hydrogen, and nitrogen also at 32°C.

L. Air + Ice

Webster[89] has measured the amount of water vapor in air that is in equilibrium with ice from −35° to 0°C, and at pressures up to 200 atm. No critical states were found. McHaffie[45] had previously added air to the system $Na_2SO_4 + Na_2SO_4 \cdot 10H_2O$ at room temperature, but his results are internally inconsistent—sometimes showing an increase and sometimes a decrease in the water concentration with increasing pressure of air.

M. Propane + Iodoform, Methyl Ether + Iodoform

Ewald[20, 23] made a few measurements on these systems at 80°C in order to show that the formation of a hydrogen bond between iodoform and an ether leads to an enhanced solubility in the gas phase as well as in the liquid phase. In the absence of such a bond, the solubility in methyl ether would be expected to be about the same as that in propane. Ewald found solubilities that were up to four times greater.

N. Nitrogen + Phenanthrene

Robin[57, 59] studied this system up to 1000 atm. He measured the concentration of phenanthrene from its light absorption—a method that can only be used where a careful study has been made of the direct effect of pressure on the spectrum. He studied the direct effect in separate experiments with unsaturated solutions.

O. Steam + Quartz

This system has been studied both by geologists and by engineers who use high-pressure steam. Much of the work is only qualitative, but quantitative studies of the solubility of silica (quartz) have been made by van Nieuwenberg and van Zon[50] and, more recently, by Kennedy.[41, 42] The system is an extreme case of Fig. 8 in which the lower critical end point almost coincides with the critical point of pure water. The behavior at higher temperatures is complicated by the allotropy of quartz but Smits[82] has sketched the probable behavior up to the melting point of quartz in a (p, T) projection. Kennedy[42] claimed to have shown that the lower critical end point was within 0.4°C of the true critical temperature of water, but it is difficult to say what measurement has ever been made of the true critical point if so inert and involatile a substance as quartz can change it by half a degree. The solubility of quartz in the liquid phase (Y of Figs. 2 and 9) reaches a maximum of 0.075 % by weight at 332°C. It falls at higher temperatures until it is only 0.023 % at the critical end point, when it meets the gas-solubility curve. The upper critical end point has not been found. Kennedy's measurements go to 560°C and pressures up to 1700 atm.

P. Ethane + Hexachlorethane

Holder and Maass[34] found that the lower critical end point was at 44.85°C, that is, 12.5°C above the critical temperature of pure ethane. They did not measure the pressure and their claim of having detected different solubilities in different parts of the fluid at temperatures above this point probably does not apply to a system at equilibrium in the absence of a gravitational field.[66]

Scheffer and his colleagues[13–15, 31, 71–74] have studied a wide range of systems in which the first component was ethane, ethylene, or

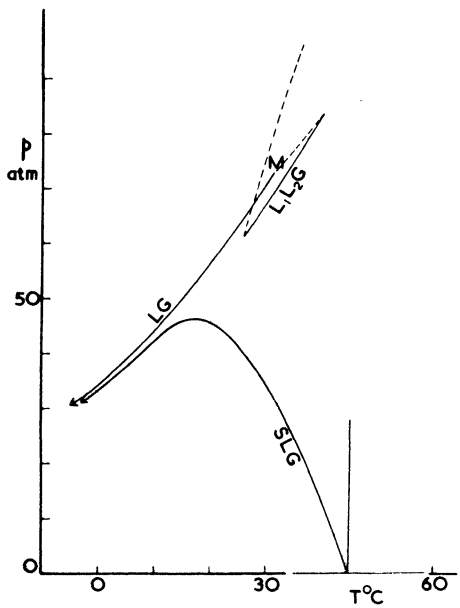

Fig. 12. The (p, T) projection of the system carbon dioxide + o-nitrophenol.

carbon dioxide and in which the second was an organic solid, often a derivative of benzene, with a melting point above 35°C. Their systems may be classified as follows.

(*1*) Systems in which the saturated vapor pressure curve does not cut the critical curve (as in Figs. 7 and 11). Example, ethane + p-dichlorobenzene.[74]

(*2*) Systems in which the phases in equilibrium with the solid

behave as in Fig. 7 but in which the course of the critical curve is interrupted by a region of immiscibility of liquid + liquid + gas, as in Fig. 12. Examples, ethylene + *p*-dichlorobenzene,[13] ethane + 1,3,5-trichlorobenzene,[74] carbon dioxide +*o*-nitrophenol.[72]

(*3*) Systems in which the saturated vapor pressure curve cuts a three-phase line of liquid + liquid + gas at a second quaternary point (solid + liquid + liquid + gas). Such systems have the first (or normal) quaternary point (solid + solid + liquid + gas) at lower temperatures and pressures (Fig. 13). Examples, ethane +

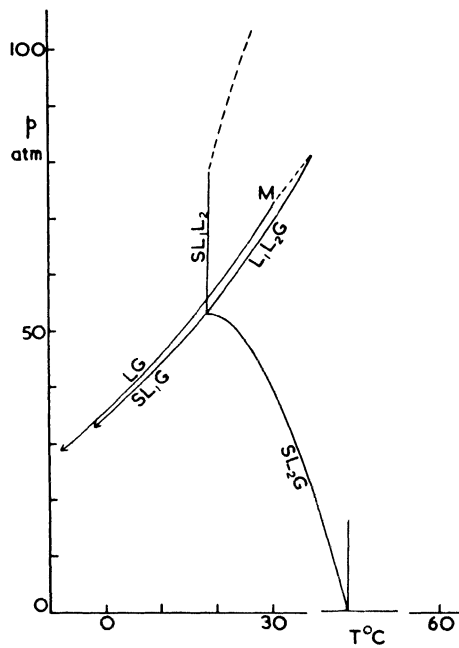

Fig. 13. The (p, T) projection of the system carbon dioxide+*m*-nitrochlorobenzene.

p-bromochlorobenzene[74] ethane + *p*-iodochlorobenzene,[74] carbon dioxide + *m*-nitrochlorobenzene,[72] carbon dioxide + *o*-nitrochlorobenzene,[72,73] carbon dioxide + *p*-toluidine,[71,73] carbon dioxide + 3,4-xylidine.[71]

(*4*) Systems which are formally similar to ethyl ether + anthra-

quinone (Fig. 8) but in which the two parts of the critical curve, MO and NP, do not appear, from their (p, T) projections, to be part of one smooth hypothetical curve $MOPN$. Figure 14 shows the

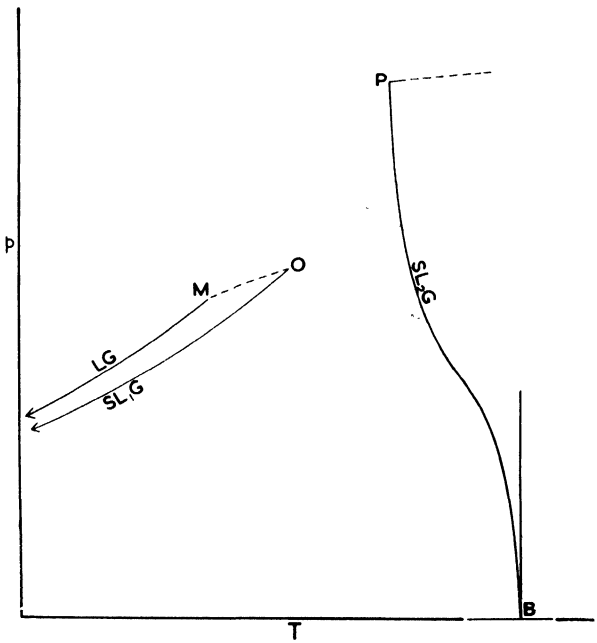

Fig. 14. The (p, T) projection of a system of the type of ethylene + naphthalene (schematic).

upper and lower critical end points for a system such as ethylene + naphthalene[31] and it is seen that no smooth curve could join the two critical points of the pure substances and the two critical end points of the mixture. The following substances all behave similarly in solutions of ethylene, hexachlorethane,[31] diphenyl,[13] anthracene,[31] stilbene,[31] hexamethyl benzene,[31] hexaethyl benzene,[31] n-$C_{28}H_{58}$,[13] n-$C_{36}H_{74}$,[13] p-dibromobenzene,[13] p-bromochlorobenzene,[13] p-iodochlorobenzene,[13] m-dinitrobenzene,[31] and 1,3,5-trichlorobenzene.[13] The explanation of this behavior is almost certainly that these pairs would be immiscible in the liquid state if the melting point of the second component was not so far above the critical point of the first. Indeed, if ethane is substituted for ethy-

lene then some of these solutes do form immiscible liquid pairs, as was mentioned previously. Thus in these systems, as in those whose behavior is described by Figs. 12 and 13, there would not be a continuous curve joining the critical points of the pure substances, but a curve which would be broken into two segments connected by a three-phase line of liquid + liquid + gas. It may seem strange that hydrocarbons such as naphthalene or n-$C_{28}H_{58}$ should be partially immiscible with ethylene and ethane, and that this immiscibility often ends at a *lower* critical solution point. However, there is known to be similar immiscibility in other systems of this type. Francis[25] has shown that liquid carbon dioxide is only partially miscible at 25°C with decalin (mp below −31°C), with n-hexadecane (mp 20°C) and with n-octadecane (mp 28°C), and it has recently been found that cyclo-$C_6H_{11} \cdot CH_2 \cdot CH(n\text{-}C_{10}H_{21})_2$ (mp −4°C) shows a lower critical solution point with liquid ethane at 13°C, of the type shown in Fig. 12 but below the critical temperature of ethane at 32°C.[27] The immiscibility in all these systems is undoubtedly due in some way to the approach of the more volatile component to its critical point. A fuller discussion is given elsewhere.[67]

Detailed measurements of the solubility between the lower and upper critical end points have been made only for the solutions in ethylene of naphthalene,[14] hexachlorethane,[30] and p-iodochlorobenzene.[21] Atack and Schneider[2] have used dilute solutions of the last-named substance to study the formation of clusters near the gas-liquid critical point of ethane.

Q. Propane + Mercury, n-Butane + Mercury

The equilibrium between a compressed gas and a liquid is outside the scope of this review, since such a system has, in general, two mixed phases and not one mixed and one pure phase. This loss of simplicity makes the statistical interpretation of the behavior of such systems very difficult. However, it is probable that liquid mercury does not dissolve appreciable amounts of propane and butane so that these systems may be treated here as equilibria between a pure condensed phase and a gaseous mixture. Jepson, Richardson, and Rowlinson[39] have measured the concentration of

mercury in the gas phases from 184° to 256°C and at pressures up to 30 atm. More recent work on *n*-butane has extended the temperature range to 300°C and the pressure range to 400 atm.[56]

IV. THEORY

The equilibrium between a pure solid and a gaseous mixture is one of very few classes of solution for which an exact treatment can be made by the methods of statistical mechanics. The earliest work on the theory of such solutions was based on empirical equations, such as those of van der Waals,[45] of Keyes,[44] and of Beattie and Bridgemann.[3] However, the only equation of state of a gas mixture that can be derived rigorously is the virial expansion,[46, 66]

$$\frac{pV}{nRT} = 1 + \sum_{l=2} \frac{J_l n^{l-1}}{V^{l-1}} \tag{1}$$

where p is the pressure, V the volume, n the number of moles, R the molar gas constant, T the absolute temperature, and where J_l is the lth virial coefficient of the mixture. It is a function of temperature and composition only. In general,

$$J_2 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta B_{\alpha\beta} \tag{2}$$

$$J_3 = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} x_\alpha x_\beta x_\gamma C_{\alpha\beta\gamma} \quad \text{etc.} \tag{3}$$

where α, β, γ, etc. are dummy suffixes which are to be equated to all the components 1, 2, 3, etc. in the multicomponent mixture, and where B, C, etc. are single terms in the virial coefficients which are functions only of the temperature and of the intermolecular forces between the components indicated by the suffixes. The chemical potential of component 2 in such a mixture is given by the equation,[66]

$$\mu_2(\text{gas}) = \mu_2^{\dagger}(\text{gas}) + RT \ln\left(\frac{n_2 RT}{V}\right) + RT \sum_{l=2} \frac{l}{l-1} \frac{J_l^2 n^{l-1}}{V^{l-1}} \tag{4}$$

where $\mu_2^{\dagger}(\text{gas})$ is a standard potential that is a function only of temperature, and where

$$J_2^2 = \sum_{\alpha} x_\alpha B_{2\alpha} \tag{5}$$

$$J_3^2 = \sum_{\alpha} \sum_{\beta} x_\alpha x_\beta C_{2\alpha\beta} \quad \text{etc.} \tag{6}$$

The chemical potential of the same component in the solid is given by

$$\mu_2(\text{solid}) = \mu_2^{\dagger}(\text{solid}) + pv_2^{s} \tag{7}$$

where $\mu_2^{\dagger}$(solid) is another standard potential, and where v_2^{s} is the molar volume of the solid. It is assumed, in writing this equation, that none of the gas dissolves in the solid and that the solid is incompressible. The equilibrium concentration of component 2 in a binary gas mixture in equilibrium with pure solid 2 may now be found, (a) by equating μ_2(gas) and μ_2(solid) in the absence of component 1 at the saturation vapor pressure of component 2, and (b) by equating the potentials in the presence of component 1 at a total molar density of (n/V). Subtraction of these equations eliminates the difference between the standard potentials in the two phases, and gives the following equation in the limit $x_2 \ll x_1$,

$$\ln\left(\frac{c_2}{c_2^{i}}\right) = \ln\left(\frac{x_2}{x_2^{i}}\right) = \frac{v_2^{s}-2B_{12}}{v} + \frac{v_2^{s}B_{11}-\frac{3}{2}C_{112}}{v^2} + \frac{v_2^{s}C_{111}-\frac{4}{3}D_{1112}}{v^3} + \cdots \tag{8}$$

where v is the molar volume of the mixture, where c_2 is the concentration of component 2 in the mixture, where c_2^{i} is the concentration of component 2 in its pure saturated vapor, and so the concentration to be expected in an ideal mixture, and where x_2 and x_2^{i} refer similarly to the mole fractions. The right-hand side of this equation gives, as an expansion in the gas density, an expression for the enhancement of the concentration of component 2. There are two types of terms, first those with v_2^{s} as a factor which express the direct effect of hydrostatic pressure on the chemical potential of the solid, as in Eq. 7, and second, the terms with the virial coefficients B_{12}, C_{112}, D_{1112}, etc. These coefficients represent the interaction of successive molecules of component 1 with one molecule of component 2 in clusters in the gas phase. The coefficient B_{12} is often large and negative and it is this term which represents the greater part of the enhancement of concentration shown by many of the solutions described above. The higher coefficients are probably positive in almost all cases.[68] Figure 10 represents x_2^{i}, x_2^{i} as

augmented by the effects of hydrostatic pressure, and the course of x_2 with increasing pressure of added gas.

Equation 8 has a long history. Poynting[54] first showed that a hydrostatic pressure would increase the activity (or potential) of a solid by the amount shown in Eq. 7, and for many years the "Poynting effect" was invoked to explain the increased volatility of solids in the presence of added gases. However, the molar volumes of most solids are small, and, as is shown in Fig. 10, the enhancement due to this effect alone is only a small part of the total effect. The terms in Eq. 8 containing the virial coefficients B_{12}, etc. were added independently by Perkins[52] in 1937 (second coefficient only), by Robin, Vodar, and Bergeon[58,61-63] in 1951–53 (second coefficient only), by Ewald, Jepson, and Rowlinson[23] in 1953 (complete expansion), and by Dokoupil, van Soest, and Swenker[18] in 1955 (complete expansion and its inversion to a pressure expansion). Ewald[21] has given the more complete form of Eq. 8 in which x_2 is not assumed to be very small.

Like all virial expansions this equation converges satisfactorily only at low and moderate gas densities. In practice it can usually be used to gas densities up to about 10 mole/l with coefficients up to C_{112}, as long as the temperature is not too close to the critical end points of the system. Franck[26] has suggested semiempirical modifications to this equation, based upon association according to the law of mass action, which extend its validity to higher densities. There are two ways of using Eq. 8. First, the coefficients in it can be calculated from what knowledge we have of the relevant intermolecular forces, the calculated solubilities can then be compared directly with experiment. This may be done by (a) assuming that nonpolar molecules have Lennard-Jones 12-6 potentials, (b) assuming that the characteristic energy (ε_{12}) and collision diameter (σ_{12}) of this potential for a pair of unlike molecules are related to those for like molecules by the equations

$$\varepsilon_{12} = \varepsilon_{11}^{\frac{1}{2}} \varepsilon_{22}^{\frac{1}{2}} \tag{9}$$

$$\sigma_{12} = \tfrac{1}{2}\sigma_{11} + \tfrac{1}{2}\sigma_{22} \tag{10}$$

and, (c) calculating B_{12} from published tables[33] and C_{112} by some suitable approximation.[68] Figure 10 shows a successful example of

such an *ab initio* calculation for the system air + carbon dioxide.[23] The second, and perhaps more profitable way of using Eq. 8 is to use the experimental results as a direct source of values of the coefficient B_{12}. These values may then be combined with others at much higher temperatures that have been derived from conventional p-V-T measurements on gas mixtures. The combined values will usually determine B_{12} over unusually wide ranges of temperature and so may be used to derive values of ε_{12} and σ_{12} that can be compared both with Eqs. 9 and 10 and with values derived from the interdiffusion coefficient D_{12}. This course is followed here.

V. THE SECOND VIRIAL COEFFICIENT AND THE FORCES BETWEEN UNLIKE MOLECULES

Equation 8 may be fitted to those results just described for which the vapor pressure of the pure solid is known. We show graphically the second virial coefficients derived from such fitting and those derived from conventional p-V-T measurements.

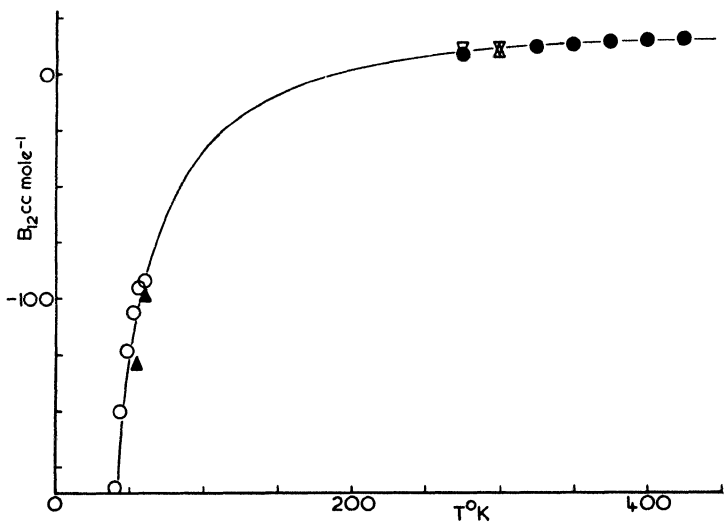

Fig. 15. The coefficient B_{12} for hydrogen+nitrogen. ○, calculated by Reuss and Beenakker from the results of Dokoupil, *et al.*; ▲, calculations by us from the same results; ●, measurements of Michels and Wassenaar; △, Michels and Boerboom; ▽, Verschoyle. The line is calculated from the parameters in the text.

A. Hydrogen + Nitrogen

Figure 15 shows the second virial coefficients derived independently by us and by Reuss and Beenakker[55] from the measurements of solubility by Dokoupil, van Soest, and Swenker,[18] and the coefficients at room temperature from the conventional measurements of Verschoyle,[86] Michels and Wassenaar,[49] and Michels and Boerboom.[47] These results are sufficient to give unambiguously the parameters of a 12-6 potential

$$\varepsilon_{12}/k = 53°\text{K} \ (59°\text{K}); \qquad \sigma_{12} = 3.31 \text{ A} \ (3.31 \text{ A})$$

The values in brackets are those calculated from Eqs. 9 and 10 by using the parameters for the pure substances recommended by Hirschfelder, Curtiss, and Bird[33] (with the quantum corrections for the hydrogen-hydrogen interaction).

The interdiffusion coefficient has been measured for this mixture by Boardman and Wild,[5] by Waldmann,[88] and by Schäfer and his colleagues.[69, 70] Figure 16 shows that the coefficient calculated

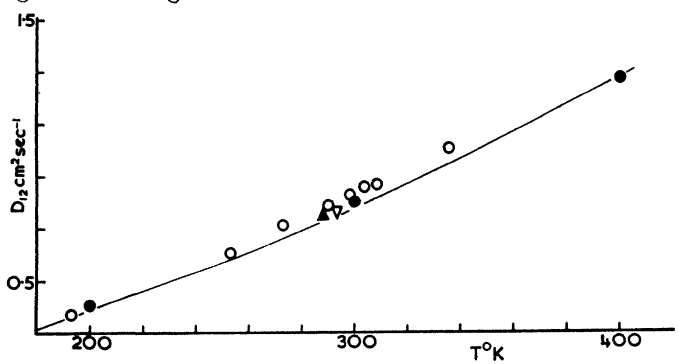

Fig. 16. The diffusion coefficient D_{12} for hydrogen + nitrogen. ▲, measurement of Boardman and Wild; ▽, Waldmann; ○, Schäfer, Corte, and Moesta; ●, Schäfer and Moesta. The line is calculated from the same parameters as the line in Fig. 15.

from the preceding parameters is close to the experimental results over a range of 210°K.

B. Hydrogen + Carbon Monoxide

Figure 17 shows two sets of virial coefficients—derived by us and by Reuss and Beenakker[55] from the measurements of Dokoupil,

van Soest, and Swenker.[18] The virial coefficient has been measured at room temperature by Townend and Bhatt,[85] and some approximate values have been derived at intermediate temperatures by van Itterbeek and van Doninck[36] from measurements of the velocity of sound. Figure 17 shows that their results lie a little above

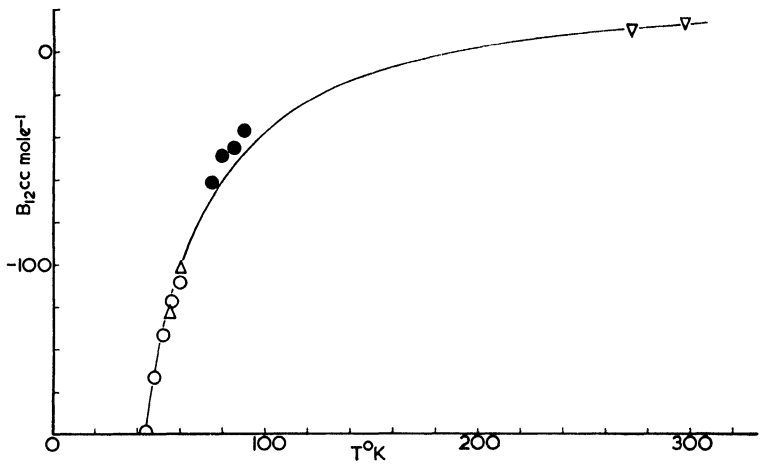

Fig. 17. The coefficient B_{12} for hydrogen+carbon monoxide. ○, calculated by Reuss and Beenakker from the results of Dokoupil, *et al.*; △, calculated by us from the same results; ▽, measurements of Townend and Bhatt; ●, derived from the velocity of sound by van Itterbeek and van Doninck. The line is calculated from the parameters in the text.

the curve and are probably in error. The calculation of a second virial coefficient from the velocity of sound cannot be done directly, since the velocity is a function not only of B but of its first and second temperature derivatives. The parameters that give the curve in Fig. 17 are

$$\varepsilon_{12}/k = 55°\text{K} \ (61°\text{K}); \qquad \sigma_{12} = 3.34 \text{ A} \ (3.35 \text{ A})$$

These parameters give a calculated diffusion coefficient of 0.649 cm^2/sec at 0°C which compares well with some old experimental values[35] of 0.651 cm^2/sec.

C. Helium + Carbon Dioxide, Hydrogen + Carbon Dioxide

The virial coefficients at 190°K have been calculated from Ewald's results[22] and may be combined with the measurements at room temperature of Michels and Boerboom,[47] of Cottrell and his colleagues,[11,12] and of Harper and Miller,[32] to give the parameters for helium + carbon dioxide

$$\varepsilon_{12}/k = 48°\text{K}; \qquad \sigma_{12} = 3.73 \text{ A}$$

and for hydrogen + carbon dioxide

$$\varepsilon_{12}/k = 90°\text{K}; \qquad \sigma_{12} = 3.68 \text{ A}$$

These parameters cannot be compared with Eqs. 9 and 10, since pure carbon dioxide cannot be adequately represented by a spherical potential. Figure 18 shows that they give only a moderate

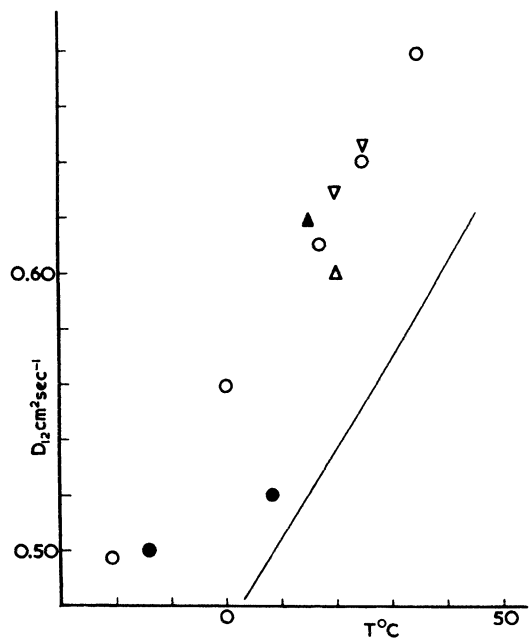

Fig. 18. Diffusion coefficient D_{12} for hydrogen + carbon dioxide. ▲, measurement of Boardman and Wild; △, Waldmann; ▽, Boyd, *et al.*; ○, Schäfer, Corte, and Moesta; ●, Lonsdale and Mason. The line is calculated from the parameters in the text.

fit of the diffusion coefficient for hydrogen + carbon dioxide, which has been measured experimentally by Boardman and Wild,[5] by Boyd and his colleagues,[7] by Schäfer and his colleagues,[69, 70] and by Lonsdale and Mason.[43]

D. Air + Carbon Dioxide

Figure 19 shows B_{12} calculated from the observations of Webster[90] and Gratch,[29] and for nitrogen + carbon dioxide at room temperature from the result of Michels and Boerboom,[47] of

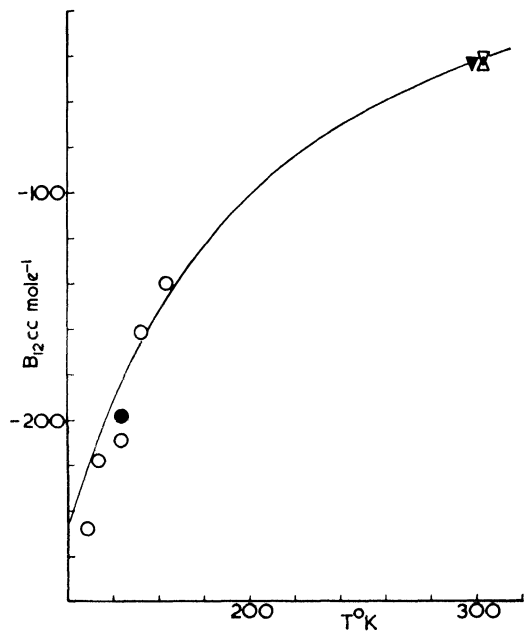

Fig. 19. The coefficient B_{12} for nitrogen (air)+carbon monoxide. ○, measurements of Webster; ●, Gratch; ▼, Michels and Boerboom; ▽, Pfefferle, *et al.*; △, Cottrell, *et al.*

Pfefferle, Goff, and Miller, [53] and of Cottrell and his colleagues.[12] It is impossible to get a perfect fit of these results with a spherical 12-6 potential but the best is for

$$\varepsilon_{12}/k = 150°\text{K}; \qquad \sigma_{12} = 3.76\ \text{A}$$

The discrepancy may be due to the difference between pure nitrogen and air, but is more probably due to the nonsphericity of carbon dioxide. A slightly better fit can be obtained by using a nonspherical potential.[65] However, the parameters above give good agreement with the diffusion coefficients for nitrogen + carbon dioxide of Boardman and Wild,[5] of Waldmann,[88] of Boyd and his colleagues,[7] of Schäfer and his colleagues,[69] and of Andrew.[1] (See Fig. 20.)

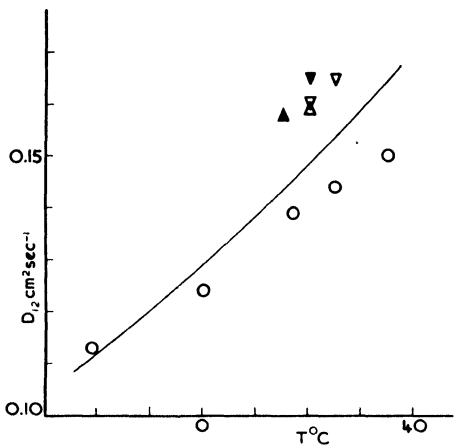

Fig. 20. Diffusion coefficient D_{12} for nitrogen+carbon dioxide. ▲, measurement of Boardman and Wild; △, Waldmann; ▽, Boyd, *et al.*; ○, Schäfer, Corte, and Moesta; ▼, Andrew.

E. Helium + Xenon, Hydrogen + Xenon, Nitrogen + Xenon

The second virial coefficients at 155°K are, respectively, +15, −9, and −19 cm³/mole for these three systems.[22] There are no measurements at room temperature.

The parameters obtained here from measurements of B_{12} and D_{12} over wide ranges of temperature are probably as reliable as any that have been proposed for the interaction of molecules of different species. Unfortunately they do not provide an adequate test of Eqs. 9 and 10, since each of the systems has as one of its components either helium or hydrogen (for which there are significant quantum corrections) or carbon dioxide (which does

not have a spherical potential). However, the method could clearly be extended to more suitable mixtures, such as argon + xenon or nitrogen + xenon, by making measurements both at room temperature and at low temperatures in equilibrium with a solid phase.

VI. THE EFFECTS OF SOLUBILITY ON OTHER PHYSICAL MEASUREMENTS

It has been known for nearly eighty years that compressed gases can dissolve solids to give mixtures in which the concentration of the solid component is very large compared to that in the pure saturated vapor. Nevertheless, this effect has not always been appreciated by those working with compressed gases in other fields. Here we discuss briefly two types of measurement in which the enhanced concentration of the second component may have introduced unsuspected errors.

The first field is that of the accurate measurement of p-V-T relations of a compressed gas at temperatures above 100°C and at pressures up to several thousand atmospheres, when mercury is used to confine the gas to the measured volume. It has been customary to assume that the amount of mercury in the gas phase is that present in the pure vapor at the same temperature and that the mixture obeys Dalton's law of partial pressures. Jepson and Rowlinson[37] suggested that both of these assumptions were incorrect and that the concentration of mercury, as estimated from Eq. 8, might greatly exceed that in the pure vapor. Subsequent measurements have confirmed qualitatively these calculations.[39,56] The greatest enhancement factor so far observed is for n-butane + mercury at 215°C and 7.1 moles/l (approx. 220 atm) where the amount of mercury in the gas phase was 3.7 times that in the pure vapor.[56] The pure saturated vapor pressure is 28 mm Hg at this temperature. The factor increases with pressure and falls with rising temperature, although, of course, the absolute amount of mercury in the gas increases with temperature because of the rapid rise of the saturated vapor pressure. The effects of such amounts of mercury on the measured gas isotherms cannot be estimated very accurately but they are certainly significant in the best modern measurements. The calculations of Jepson and Rowlinson sug-

gested that at high concentrations the presence of mercury might cause the pressure of the mixture to be less than that of the pure gas—that is, that the partial molar volume of mercury might be negative. The expansion in powers of the pressure for the partial molar volume of component 2 at infinite dilution is

$$v_2 = RT/p + (2B_{12} - B_{11}) + O(p) \qquad (11)$$

and the right-hand side of this equation can easily become negative at moderate pressures when B_{12} is large and negative and (RT/p) has become small. Negative partial molar volumes, down to -4 l/mole, have been found experimentally for sodium chloride in supercritical steam.[4]

A second type of measurement whose accuracy may be affected by an enhanced solubility is that of the effect of added gases on the oscillator strengths of the electronic transitions in metallic vapors. For example, Fürchtbauer, Joos, and Dinkelacker[28] studied the effect on the mercury spectrum of added argon, hydrogen, nitrogen, and carbon dioxide up to 40 atm; Ch'en[9] studied the effect of helium and argon on rubidium up to 100 atm; and Michels and de Kluiver[48] the effect of helium on mercury up to 500 atm. In each case they found shifts of the lines, changes of shape and changes of integrated intensity. The last of these was ascribed to changes of the oscillator strengths with the pressures of added gases. However, all their measurements were carried out in the presence of excess metal, and it is pertinent to ask how much of their measured effects were due to changes of concentration. We estimate B_{12} for helium + mercury to be $+3$ cm^3/mole at 350°K, the mean temperature of the results of Michels and de Kluiver, but such an estimate may not be very accurate. For argon + mercury we estimate a coefficient of about -90 cm^3/mole. The observed changes of oscillator strength are all decreases, and so cannot be explained as enhancement of concentration.* In fact a diminution of concentration corresponding to B_{12} of about $+40$ cm^3/mole

* *Note added in proof.* J. C. Strijland and A. J. Nanassy (*Physica* **24**, 935 (1958)) have shown recently that there are no changes of oscillator strength in argon + mercury. Increases in spectral intensity are entirely accounted for by increases in mercury concentration.

would be required to fit the observed curve of Michels and de Kluiver. These calculations suggest, however, that the observed effects may not give the true size of the change of oscillator strength with polarizable gases such as argon, nitrogen, and carbon dioxide. It appears that the true change may be twice or thrice that observed. The only system in which the two effects have been properly separated is nitrogen + phenanthrene[57–59] where the effect of pressure is to increase the oscillator strength, but this increase is much less than that due to the increase in concentration when measurements were made in the presence of excess solid phenanthrene. Robin and Robin[60] and Ch'en and Takeo[10] have recently reviewed these and other effects of pressure on electronic spectra.

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THERMODYNAMICS OF METALLIC SOLUTIONS

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I. INTRODUCTION

A. Early History of the Theory of Metal Solutions

The incentive for much of the early work in the thermodynamics of alloys arose from the desire to rationalize the general features of metallic phase diagrams beyond what is possible by systematic studies of the sequence of phases that occur in some types of binary systems. The high points for this kind of approach were the recognition by Hume-Rothery[18] of the importance of large atom size disparity for limiting the extent of solid solubility, the importance of the electronegativity difference for the stability of some kinds of intermetallic compounds, and the relevance of the valence electron/atom ratio to the position of the phase boundary for some types of alloys ("electron compounds"), together with Jones's explanation[20] of the relevancy of the electron/atom ratio in terms of the filling up of rigid electron energy bands. These concepts, as well as Laves's[27] space-geometrical principles for certain types of intermetallic compounds, have dominated the thinking in the field of alloys for a long time.

However, the discovery[64] in 1919 of the existence of superlattices (i.e., solid solutions characterized not only by periodicity of the positions of the atoms but by a periodicity in the atomic species as well), served to focus attention on the properties of the metallic solutions themselves, as distinguished from a consideration of the relative stability of various possible phases. This came about because the development of the treatments of Bragg-Williams, of Bethe, and of Guggenheim[12] for the order-disorder transformation led to prediction of correlations between the kind of short-range order found in the solid solution with the signs of the thermodynamic excess functions of the solution. The amazing success which such statistical theories encountered in their first applications has led to an inordinate preoccupation with a few of the characteristics of metallic solutions and a concomitant neglect of other more important features. It is only very recently that metallic solutions have been looked at from a broader point of view.

This paper will be concerned only with work on the thermodynamic properties of primary metallic solutions, i.e., those which

are contiguous to the pure component and include it as a limiting case. Work in fields other than thermodynamics will be only briefly touched upon as needed. For summaries of information on metallic phases other than primary solutions the reader is directed to reviews of Massalski,[30] Laves,[27] Duwez,[7] and Raynor.[55]

B. Experimental Techniques

Trustworthy thermodynamic data for metal solutions have been very scarce until recently,[25] and even now they are accumulating only slowly because of the severe experimental difficulties associated with their measurement. Thermodynamic activities of the component of a metallic solution may be measured by high-temperature galvanic cells,[44] by the measurement of the vapor pressure of the individual components, or by equilibration of the metal system with a mixture of gases able to interact with one of the components in the metal.[26] Usually, the activity of only one of the components in a binary metallic solution can be directly measured; the activity of the other is calculated via the Gibbs-Duhem equation if the activity of the first has been measured over a sufficiently extensive range of composition.

The partial molar entropy of a component may be measured from the temperature dependence of the activity at constant composition; the partial molar enthalpy is then determined as a difference between the partial molar Gibbs free energy and the product of temperature and partial molar entropy. As a consequence, entropy and enthalpy data derived from equilibrium measurements generally have much larger errors than do the data for the free energy. Calorimetric techniques should be used whenever possible to measure the enthalpy of solution. Such techniques are relatively easy for liquid metallic solutions, but decidedly difficult for solid solutions. The most accurate data on solid metallic solutions have been obtained by the indirect method of measuring the heats of dissolution of both the alloy and the mechanical mixture of the components into a liquid metal solvent.[65]

The deviation of the heat capacity of a solid solution from the heat capacity calculated by the additivity hypothesis (Kopp-Neumann rule), a quantity of importance for the evaluation of the

nonconfigurational entropy of solution, may be measured by the temperature dependence of the enthalpy of formation in the high-temperature range. At low temperatures, however, only direct measurements of the heat capacity may be made.

II. THERMODYNAMIC CHARACTERISTICS OF SUPERLATTICE SYSTEMS

A. The Quasi-Chemical Theory

Because much experimental work has been stimulated by the quasi-chemical theory, it is important to gain proper perspective by first describing the features of this theory.[12] The term, quasi-chemical will be used to include the Bragg-Williams approximation as the zeroth-order theory, the Bethe or Guggenheim pair-distribution approximations as the first-order theory, and the subsequent elaborations by Yang,[69] Li,[28] or McGlashan[31] as theories of higher order.

The quasi-chemical theory assumes that the energy of a solution is given by the sum of interaction energies, ε_{ij}, between nearest neighbors i and j, and that the interaction ε_{ii} between atoms of the same species in the solution is the same as in the pure component. All of the ε_{ij} are taken as being independent of composition and of phase, the concomitant assumptions being that the coordination number Z (the number of nearest neighbors) is taken as independent of composition or phase, and that volume changes of solution are zero. Furthermore, changes in the vibrational spectrum upon formation of the solution are neglected.

The simplest form of the quasi-chemical theory that is of interest in the present connection is the first-order approximation, which considers the distribution of nearest-neighbor pairs as affected by nonzero values of the linear combination,

$$w = \varepsilon_{12} - \tfrac{1}{2}(\varepsilon_{11} + \varepsilon_{22})$$

the assumption is made that the relative probabilities for a pair of neighboring sites to be occupied in the several possible ways are independent of the manner of occupation of all other sites. The ε_{ij} being measured relative to the gaseous state, a negative w

means that a bond between dissimilar atoms is of lower energy than the average of bonds between similar atoms, so that there will be found a larger than random number of 1—2 bonds (positive short-range order). The enthalpy of solution and the excess partial molar free energies of solution are then negative quantities, as is also the excess entropy of solution. At temperatures below a critical temperature, T_c, which bears a definite relationship to $|w|$ and which depends on the crystallography, a superlattice becomes stable relative to the parent solid solution.

On the other hand, if w is positive, there will be a smaller than random number of 1—2 bonds (negative short-range order, or clustering), positive enthalpy of solution, positive excess partial molar free energies of solution, and again, negative excess entropy of solution. Below a critical temperature, a two-phase mixture becomes stable relative to a homogeneous solution. If one employs a lattice model of the liquid state, the machinery of the quasi-chemical theory can be applied equally well to liquid solutions in all respects, except that the concept of a superlattice does not apply. Higher approximations of the quasi-chemical theory produce no changes in the foregoing qualitative correlations.

B. Characteristics of Ordering Systems at Temperatures Above T_c

(1) *The Copper-Gold System*

Historically, the copper-gold binary system furnished the first examples of superlattices,[4] and has been most actively studied ever since. It was fortunate for the development of the quasi-chemical theories that this system served as the prototype for ordering alloys, because by and large, fair agreement is found between theory and experiment for the copper-gold system. For example,[41] very good agreement exists between the experimentally measured degree of short-range order and that calculated by first-order theory from the experimental free energy of solution, ΔG. Furthermore, the enthalpy of solution, ΔH, calculated from the theory and the experimental ΔG checks very well with the experimental ΔH. More qualitatively, the ΔH is negative, as it should be for positive short-range order, the excess partial molar free energies

of both components are negative over the whole range of composition, and the excess entropy of solution is also negative, at least over most of the range of composition.[41]

On the other hand, upon closer examination even the copper-gold solid solutions evince serious discrepancies with the quasi-chemical theory. There is a composition range where the entropy of solution is larger than that for random mixing (see Fig. 1) where

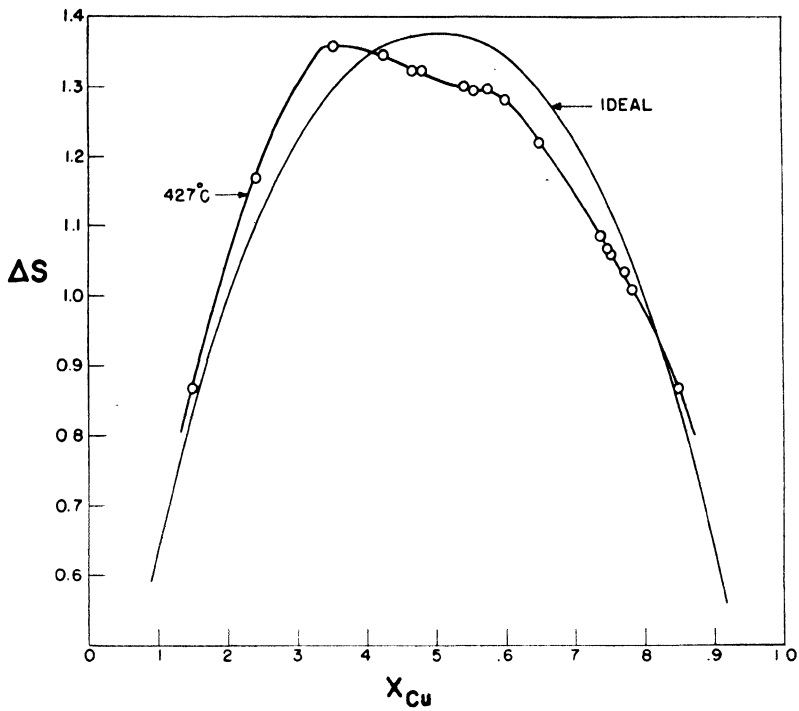

Fig. 1. The entropy of solution of face-centered cubic solid solutions of Cu-Au at 427°C, from reference 41.

at lower temperatures the superlattice $CuAu_3$ exists. The low critical temperature of 250°C,[14] compared with the 394°C for the T_c of the homologous Cu_3Au superlattice is probably associated with the lattice vibrations[57] which increase the vibrational entropy in the solid solutions about the $CuAu_3$ superlattice. Furthermore, Guttman[13] has pointed out that, although the measured total free

energy and enthalpy of solution are fairly consistent with the observed short-range order[5, 56] when the connection is made by the quasi-chemical theory,[37, 41] the individual activity coefficients calculated by the same theory do not agree so well with the observed values (see Table I). Guttman[13] has also shown that it is impossible

TABLE I.[a] Comparison of Observed Activity Coefficients of Cu and Au with Values Calculated from Observed Short-Range Order Parameters by the First-Order Quasi-Chemical Theory

	$-\log_{10} \gamma_{Au}$		$-\log_{10} \gamma_{Cu}$	
Composition	Observed	Calculated	Observed	Calculated
$Cu_{.75}$ $Au_{.25}$	0.92	1.57	0.125	0.133
$Cu_{.5}$ $Au_{.5}$	0.51	0.34	0.20	0.34

[a] By courtesy of L. Guttman, taken from reference 13.

to fit either the observed activity coefficients or the observed short-range order parameters with the same value of w over the whole composition range.

(2) *Other Ordering Systems*

A dependence of w upon composition must also be adduced in the case of the Fe-Ni solid solutions. Over the range from 0 to 56 at. per cent Ni, these solid solutions exhibit essentially ideal behavior,[39] so that $w \approx 0$. Since the $FeNi_3$ superlattice appears at lower temperatures, either w is markedly different at compositions about 75 at. per cent Ni than at lower Ni contents, or $w \approx 0$ for the solid solutions about the superlattice. Either possibility represents a deviation from the requirements of the quasi-chemical theories.

Other ordering systems show striking discrepancies with the predictions of the quasi-chemical theories. Cu-Pt,[67] Co-Pt,[38] and Pb-Tl[36] are binaries the solid solutions of which exhibit a positive partial excess free energy for one of their components, as well as positive excess entropies of solution. Co-Pt goes even further in deviating from theory in that it has a positive enthalpy of solution,

despite the fact that at lower temperatures superlattices appear. It should be noted that the ordering systems Cu-Au, Cu-Pt, Co-Pt, and Pb-Tl form solid solutions with a positive volume change.

In short, we see that the existence of a superlattice at lower temperatures is not a sufficient indication of the thermodynamic characteristics of the solid solutions at higher temperatures; this is in opposition to the expectations of the quasi-chemical theories. The only characteristic that solid solutions of ordering systems have in common, as far as is known now, is that all such solid solutions exhibit a positive short-range order,[2] i.e., a preference for dissimilar atomic species as nearest neighbors. An analogous statement cannot be made for solid solutions bearing miscibility gaps, where theory predicts negative short-range order, since the gold-nickel system has been shown[10] to exhibit positive short-range order.

C. Characteristics of the Order-Disorder Transitions

(1) *Change of w with Phase*

In the quasi-chemical theories, the driving force for the formation of the superlattice from the parent solid solution is taken to be the tendency to increase the number, n_{12}, of dissimilar nearest neighbors, leading to a lower energy for the superlattice. However, there are some instances where the formation of the superlattice is not accompanied by an increase in n_{12}. The CuPt superlattice may be described[66] as made up of (111) planes alternately populated by Cu and by Pt atoms, so that n_{12} is six for any one atom, a slightly smaller number than in the parent solid solution because of the positive short-range order therein. The orthorhombic CuAu superlattice[19] is another instance where the n_{12} does not increase in going from the solid solution to the superlattice. Such cases must be understood either from a consideration of neighbors beyond the first coordination shell, or from a change in w with phase.

That w changes with phase has been shown[49] for the tetragonal CuAu superlattice and the face-centered cubic solid solution from measurements of the enthalpies of formation of these two phases. Such measurements for the f.c.c. phase lead to $|w| = 373$ cal/g atom, in good agreement with the 350 cal/g atom derived by

Guttman[13] as giving the best fit with measurements of the activity coefficients[41] and of short-range order.[5, 56] However, the enthalpy of formation[49] of the tetragonal superlattice leads to $|w| = 463$ cal/g atom for that phase. Another connection can be made between $|w|$ and the quasi-chemical theory, by means of the critical temperature. The higher-order theory of Yang[69] and Li,[28] which utilizes the tetrahedron instead of the pair as the local configurational unit, yields $RT_c/|w| = 0.823$ for a Ll_2 superlattice (viz. Cu_3Au) and 0.731 for Ll_0 structure (viz. AuCu). Table II presents the values of $|w|$ calculated from the known critical temperatures of three of the superlattices of the CuAu system. It will be noticed that not only is $|w|$ thus calculated dependent on phase, but also its magnitude is very different from that calculated above from the properties of any one phase.

TABLE II. Comparison Between Experimental E_0/RT_c with the Value Given by the Yang-Li Quasi-Chemical Theory for Cu-Au Superlattices. Interaction Parameter, w, Calculated from T_c and the Yang-Li Theory

Superlattice	E_0/RT_c		Calc. $\|w\|$, cal/g atom
	Exp.	Theor.	
Cu_3Au	.4–.7	.91	1610
CuAu	.59–1.1	1.37	1860
$CuAu_3$	.3–?	.91	1300

Table II also demonstrates the discrepancy existing between E_0/RT_c calculated by the Yang-Li quasi-chemical theory and the experimental ratio. E_0 is the energy difference between a fully ordered superlattice and the corresponding solid solution with an ideally random atom species distribution. It is a quantity that can only be estimated from existing experimental information, but the disparity between theory and experiment is beyond question.

(2) *Order of the Superlattice Reaction*

A question that has given much trouble, both experimentally

and theoretically, is that of the thermodynamic order of the transition between a superlattice and its parent solid solution.[13] On the experimental side, the difficulties are associated with securing equilibrium at any stage of the experiment despite the sluggishness with which many of these transformations proceed. From the theoretical point of view, the difficulty lies in the necessity of taking a large enough group of atoms as the local unit in order to calculate the combinational factor in the partition function.[70] For example, only the work of Yang and Li and that of McGlashan, who have taken a tetrahedral group of atoms as the local unit in the quasi-chemical theory can account for a superstructure arising from a face-centered cubic solid solution.

At the present time, several superlattices are known to be Gibbsian phases distinct from the corresponding solid solutions. Two general classes of experiments have been performed towards this end. The first class deals solely with the alloy composition having the highest critical temperature, and endeavors to investigate the manner of the disappearance of the superlattice as the temperature is raised. Sykes and Jones[63] and Hirabayashi, Nagasaki, and Kono[17] have succeeded in demonstrating a finite latent heat for the disordering of Cu_3Au; Hirabayashi has done a similar thing for CuAu.[15] The long-range order as a function of temperature has been measured for the superlattices CuPt by Walker,[66] for Cu_3Au by Cowley,[5] and for tetragonal CuAu by Roberts;[56] in each case, it was found that the curve of long-range order *vs.* temperature has a sharp discontinuity at the critical temperature, so that the transition is of first order.

The second class of experiments has to do with demonstrating the equilibrium coexistence of both superlattice and solid solution at one temperature at various overall compositions about the maximum critical temperature. By very careful x-ray diffraction investigations the superlattices NiPt,[9] CoPt,[35] $MgCd_3$,[8] and orthorhombic CuAu[34] have been shown to be true Gibbsian phases. The writer[41] has demonstrated that both the orthorhombic CuAu and the tetragonal CuAu (see Fig. 2), as well as the Cu_3Au superlattice, are true Gibbsian phases. This was done by the measurement of equilibrium thermodynamic activities. The same principle has been

used by Assayag and Dode[1] to establish the existence of two-phase fields about the CuPt superlattice. On the other hand, the superlattices at CuZn,[21] AgZn,[32] Mg_3Cd,[68] and $CuAu_3$[14,16] have been shown to disorder via a second-order transition; this means that the superlattice and the solid solution cannot be considered as

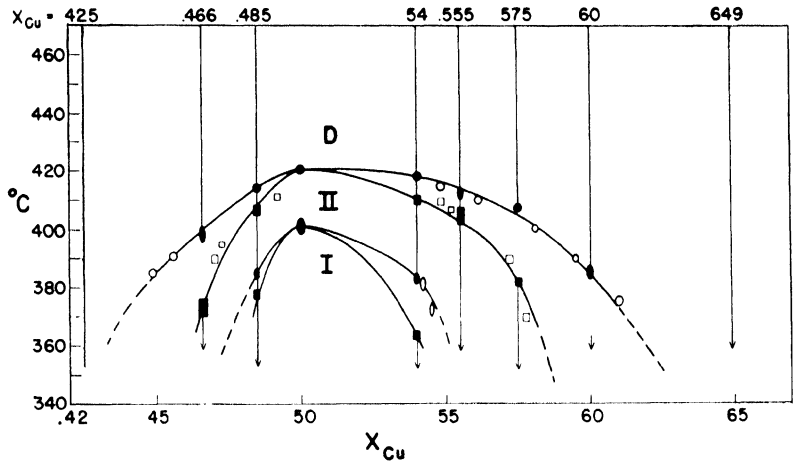

Fig. 2. Equilibrium phase relations about the Cu-Au superlattices, from reference 41.

distinct phases.[13] It should be pointed out, however, that it is even more difficult to prove that a transition is of second order than it is to prove it to be of first order, and that the foregoing results may be a consequence of not achieving equilibrium in the experiments. The reasons for one superlattice disordering via a first-order transformation and another superlattice via a second-order transition are not clear.

(3) *Possible Correlation between Melting Temperature and* T_c

Because the appearance of a superlattice is usually well characterized qualitatively in terms of an interaction parameter w which has nothing to do, in the usual treatments, with the melting of the parent solid solution, one does not expect to find a simple relationship between the critical temperature for disordering of the superlattice, and T_s, the solidus temperature of the corresponding solid

solution. Nevertheless, a simple correlation does appear to exist[40] between these two temperatures in the absolute scale. The ratio T_c/T_s for all the 1 : 1 superlattices has the value $0.63 \pm .06$, and the value of $0.55 \pm .10$ for the 1 : 3 superlattices. The clustering of T_c at about the same fraction of the melting temperature of the solid solution indicates that the disordering and melting phenomena have something in common that is not reflected in the usual formal treatments accorded to each one separately.

III. NONCONFIGURATIONAL FACTORS OF SOLUTION FORMATION

A. Introduction

We have seen that the quasi-chemical theories concern themselves chiefly with the configurational aspect of solutions, that is, the degree of order in the atomic species distribution. However, from the point of view of the intrinsic properties of a solution not in relation to the formation of a superlattice, the degree of order is of minor importance[53] compared with the effect of the changes in the nonconfigurational properties accompanying the solution process and which are neglected by these theories. Such factors include electronic properties both magnetic and translational, and changes in the vibrational characteristics upon solution formation.

It is simplest to consider these factors as they are reflected in the entropy of the solution, because it is easy to subtract from the measured entropy of solution the configurational contribution. For the latter, one may use the ideal entropy of mixing, $-\Sigma \chi_i \ln \chi_i$, since the correction arising from usual deviation of a solution (not a superlattice) from randomness is usually less than -0.1 cal/deg-g atom. (In special cases, where the degree of short-range order is known from x-ray diffuse scattering, one may adequately calculate this correction from quasi-chemical theory.) Consequently, the excess entropy of solution, ΔS^e, is a convenient measure of the sum of the nonconfigurational factors in the solution.

The ΔS^e may be obtained from equilibrium measurements of the free energy and its dependence upon temperature, or more directly, by measuring the $\Delta C_P(T)$ of a solution of frozen-in atomic configuration. The ΔC_P at any one temperature is the

change in the heat capacity at constant pressure and per gram-atom accompanying the reaction

$$\chi_1 A + \chi_2 B = A_{\chi_1} B_{\chi_2}$$

The

$$\Delta S^e \approx \int_0^T \Delta C_P(T)\, d \ln T$$

the symbol for approximate equality has been used because the $\Delta C_P(T)$ is measured for a solution of fixed configuration, at least in the low-temperature region, whereas what is wanted is the ΔS^e for the solution the atomic configuration of which is really a function of temperature, though having a very weak functional dependence. In some rare instances, $\overline{\Delta S_i^e}$, the partial excess entropy of solution of component i, may be obtained from phase diagram data for dilute solutions.

B. Excess Entropy of Concentrated Solutions

(1) *Vibrational Entropy*

Table III presents integral excess entropies of formation for some solid and liquid solutions obtained by means of equilibrium techniques. Except for the alloys marked by a letter b, the excess entropy can be taken as a measure of the effect of the change of the vibrational spectrum in the formation of the solution. The entropy change associated with the electrons, although a real effect as shown by Rayne's[54] measurements of the electronic specific heat of α-brasses, is too small to be of importance in these numbers. Attention is directed to the very appreciable magnitude of the vibrational entropy contribution in many of these alloys, and to the fact that whether the alloy is solid or liquid is not of primary importance. It is difficult to relate even the sign of the excess entropy to the properties of the individual constituents.

(2) *Magnetic Disordering Entropy*

Four of the solid solutions of Table III have excess entropies of solution which include contributions from magnetic disordering in both the alloy and in one or both of the pure components. These contributions can be quite large, and since there is no assurance

TABLE III. Integral Excess Entropies of Formation of Concentrated Solutions [a]

Solution	ΔS^e cal/deg-g atom	Ref.
$Ag_{.5}$ $Au_{.5}$ (S)	−0.2	43
β-$Ag_{.5}$ $Zn_{.5}$ (S)	0.1	25
$Au_{.5}$ $Fe_{.5}$ (S) [b]	0.8	59
$Au_{.5}$ $Ni_{.5}$ (S) [b]	1.4	25
$Co_{.5}$ $Pt_{.5}$ (S) [b]	1.1	38
$Cu_{.5}$ $Pt_{.5}$ (S)	1.3	67
β-$Cu_{.5}$ $Zn_{.5}$ (S)	−0.4	25
γ-$Fe_{.5}$ $Ni_{.5}$ (S) [b]	0.1	39
$Pb_{.5}$ $Tl_{.5}$ (S)	−0.3	25
$Ag_{.5}$ $Au_{.5}$ (l)	−0.3	43
$Au_{.5}$ $Bi_{.5}$ (l)	1.0	25
$Au_{.5}$ $Cu_{.5}$ (l)	−0.4	43
$Au_{.5}$ $Pb_{.5}$ (l)	0.8	25
$Au_{.5}$ $Tl_{.5}$ (l)	0.5	25
$Bi_{.5}$ $Cd_{.5}$ (l)	0.4	25
$Bi_{.5}$ $Mg_{.5}$ (l)	−2.0	25
$Bi_{.5}$ $Pb_{.5}$ (l)	0.1	25
$Bi_{.5}$ $Zn_{.5}$ (l)	0.5	25
$Cd_{.5}$ $Pb_{.5}$ (l)	0.2	25
$Cd_{.5}$ $Sb_{.5}$ (l)	0.2	25
$Cd_{.5}$ $Sn_{.5}$ (l)	0.3	25
$Hg_{.7}$ $Tl_{.3}$ (l)	−0.2	25
$Pb_{.5}$ $Tl_{.5}$ (l)	−0.1	25
$Pb_{.8}$ $Zn_{.2}$ (l)	0.2	25
$Sb_{.5}$ $Sn_{.5}$ (l)	−0.2	25
$Sb_{.5}$ $Zn_{.5}$ (l)	0.3	25
$Sn_{.5}$ $Tl_{.5}$ (l)	0.3	25
$Sn_{.5}$ $Zr_{.5}$ (l)	0.5	25

[a] Adapted from reference 50.

[b] These solid solutions have magnetic contributions to the measured excess entropy of formation.

that the magnetic entropy of the solution will equal that of the pure component, one cannot conclude that the measured ΔS^e reflects only vibrational effects. DeSorbo[6] and Oriani[42] measured the deviation of the heat capacity of $Au_{.52}Ni_{.48}$ solid solution from the Kopp-Neumann rule from 13° to 1190°K and attempted to

evaluate the vibrational portion of the ΔS^e by correcting for the magnetic heat capacity of Ni by the method of Stoner.[62] They obtain $\Delta S_v^e = 1.07 \pm 0.2$ cal/deg-g atom for the vibrational portion of the ΔS^e. The difference between the ΔS^e of 1.4 cal/deg-g atom measured[58] by Seigle, Averbach, and Cohen and the ΔS_v^e is to be ascribed to the difference at 1173°K between the magnetic entropy of the alloy and the mole fraction of Ni times the magnetic entropy of the pure nickel. This assertion has not yet been confirmed by measurements of the heat capacity of the alloy in the neighborhood of its magnetic transformation point below 13°K.

The case of γ-Fe-Ni is very interesting in that the small deviations[39] from ideality in the entropy and in the other thermodynamic functions of solution at all concentrations from zero to 56 at. per cent Ni imply either one of two possibilities.[52] The vibrational entropy change of solution is equal and of opposite sign to the magnetic entropy change of solution, or each of these contributions to the entropy change of solution is itself zero. Because it seems very unlikely that the first possibility is true at all the compositions examined, the second possibility appears more probable. This means that the entropy of magnetic disordering of [χ_1Fe (f.c.c.)+ χ_2Ni] is equal to the entropy of magnetic disordering of the $Fe_{\chi_1}Ni_{\chi_2}$ (f.c.c.), and this in turn implies that the magnetic moment of any one atom is unchanged in the alloying process.

C. Vibrational Entropy in Dilute Solutions

Vibrational contribution to the entropy of solution is important in dilute as well as in concentrated solutions. Kleppa[23] has calculated the partial excess entropy of solution, $\overline{\Delta S_2^e}$, of solutes in moderate dilution in liquid alloys from solubility data and galvanic cell measurements. He finds that for solutions of the noble metals in liquid Tl, Pb, or Bi, $\overline{\Delta S_2^e}$ is a positive 1 to 2 cal/deg-g atom, bearing no relation to the sign or magnitude of the partial molar enthalpy of solution, $\overline{\Delta H_2}$. Larger positive values of $\overline{\Delta S_2^e}$ are found for extremely dilute solid solutions of metals in the semiconductors germanium and silicon.[48] The $\overline{\Delta S_2^e}$ are about 4 to 15 cal/g atom, and for any one solvent, increase with increasing $\overline{\Delta H_2}$ as the solute is varied. In the case of the semiconductor solid solutions then, an

increase in the vibrational entropy appears to be caused by a decreased bonding between solute and solvent.

By measuring the partial molar heat of solution as a function of temperature for infinitely dilute concentrations of Cu, Ag, and Au in liquid tin, Oriani and Murphy[51] have determined $\overline{\Delta C_P}$ for the liquid solutes to be 1.0, 0, and 3.0 cal/deg mole respectively. These numbers bear no relationship to the sign of the heat of solution, or to atom-size disparity, but seem to be related to the deviation from unity of the ratio of the masses of the components.

It is clear that nonconfigurational factors are of great importance in the formation of solid and liquid metal solutions. Leaving aside the problem of magnetic contributions, the vibrational contributions are not understood in such a way that they may be embodied in a statistical treatment of metallic solutions. It would be helpful to have measurements both of ΔC_P and $\Delta\alpha$ (where α is the thermal expansion coefficient) for the solution process as a function of temperature in order to have an idea of the relative importance of changes in the harmonic and the anharmonic terms in the potential energy of the lattice.

IV. STATISTICAL MODELS OF SOLUTIONS

A. Introduction

By a statistical model of a solution we mean a model which does not attempt to describe explicitly the nature of the interaction between solvent and solute species, but simply assumes some general characteristic for the interaction, and presents expressions for the thermodynamic functions of the solution in terms of an assumed interaction parameter. The quasi-chemical theory is of this type, and we have noted that a serious deficiency is its failure to consider the vibrational effects in the solution. It is of interest, therefore, to consider briefly the average-potential model which does include the effect of vibrations.

B. The Average-Potential Model

This model, developed by Prigogine and collaborators,[53] depends on the premise that the pure components obey the theorem of cor-

responding states, and that the mean potential acting on a molecule in the solution is of the same form as that in the pure component. Average interactions between one molecule and all its neighbors are introduced, and these are taken to be composition-dependent and of the form of the Lennard-Jones 6-12 potential. The cell partition functions of the molecules in the solution are assumed to be identical with those in the pure components but for other well-defined values of reduced variables which depend on composition and which are deduced from experimental data on the pure components. The partition function of the solution yields the correct first-order contribution to the excess thermodynamic functions given by the conformal solution theory,[29] and reduces also to the correct form for the pure components.

We will examine the applicability of this model to metallic solutions by using the refined version which considers that differences in atom sizes will give rise to local inhomogeneities of structure. Because of the negligible error, we will omit all terms having binary products of ρ, δ, and θ, except for ρ^2.

Here,

$$\rho = (r_{BB}^* - r_{AA}^*)/r_{AA}^*$$

$$\delta = (\varepsilon_{BB}^*/\varepsilon_{AA}^*) - 1$$

and

$$\theta = (\varepsilon_{AB}^* - \varepsilon_{AA}^*/2 - \varepsilon_{BB}^*/2)/\varepsilon_{AA}^*$$

where r_{ii}^* and ε_{ii}^* are a characteristic length and energy for the pure component i, such that the interaction energy between an $i-i$ pair is given by

$$\varepsilon_{ii}(r) = \varepsilon_{ii}^* \phi(r/r_{ii}^*)$$

ϕ being a universal function. Also, for the case of the $A-B$ pair,

$$\varepsilon_{AB}(r) = \varepsilon_{AB}^* \phi(r/r_{AB}^*)$$

We will assume that $r_{AB}^* = \frac{1}{2}(r_{AA}^* + r_{BB}^*)$, but we will avoid making any simplifying assumption concerning θ (or ε_{AB}^*) by calculating it from the experimental excess free energy ΔG^e. The value of θ so obtained is used to calculate the enthalpy of solution and $T\Delta S^e$.

TABLE IV. Results of Calculations by Average Potential Model[a]

Alloy	ρ	T°K	Exp. ΔG^e	Exp. ΔH	Calc. $\Delta H(\rho=0)$	Calc. ΔH	Exp. $T\Delta S^e$	Calc. $T\Delta S^e$
$Au_{.5}$ $Ag_{.5}(l)$	~0	1344	−670	−1050	−610	−610	−380	60
$Au_{.6}$ $Ag_{.4}(s)$	~0	800	−790	−1090	−750	−750	−300	40
$Cd_{.5}$ $Sn_{.5}(l)$	~0	773	225	435	186	186	210	−39
$Cd_{.5}$ $Mg_{.5}(l)$	.036	543	−1150	−1300	−1010	−1010	−150	140
$Ag_{.5}$ $Zn_{.5}(l)$	.044	1000	−1320	−1340	−1210	−1200	~0	120
$\alpha Ag_{.6}$ $Cd_{.4}(s)$	.070	673	−1410	−1820	−1330	−1340	−410	72
$Au_{.5}$ $Sn_{.5}(l)$	.072	700	−2634	−2270	−2510	−2500	364	134
$Bi_{.5}$ $Cd_{.5}(l)$	.094	773	−85	190	−64	−54	270	31
$Au_{.5}$ $Cu_{.5}(l)$	.115	1258	−1220	−1780	−1120	−1060	−560	160
$Au_{.5}$ $Cu_{.5}(s)$	.115	700	−1157	−1260	−1130	−1070	−103	87
$Zn_{.5}$ $Sn_{.5}(l)$	.118	710	394	784	340	376	390	−18
$Cd_{.5}$ $Pb_{.5}(l)$	.132	773	500	640	410	455	140	−45
$Au_{.5}$ $Ni_{.5}(s)$	.135	1173	1040	2550	960	1030	1510	−10
$Au_{.5}$ $Tl_{.5}(l)$	.190	973	−475	40	−445	−322	515	153
$Ag_{.5}$ $Pb_{.5}(l)$	.210	1250	550	1550	490	675	1000	125
$Pb_{.8}$ $Zn_{.2}(l)$	.21	926	765	950	675	760	185	−5
$Au_{.5}$ $Pb_{.5}(l)$	.214	873	−570	−90	−566	−400	480	170

[a] Table taken from reference 50. Most of the experimental quantities are taken from Reference 25. The ΔH of column 7 was calculated from Eqs. 10.7.4 and 10.7.5 of Reference 53 and ($T\Delta S^e$) of column 9 was calculated from columns 4 and 7. In these equations, terms in δ^2, $\theta\delta$, $\rho\delta$, and θ^2 were nelgected. ΔH of column 6 was calculated from Eqs. 10.7.4 and 10.7.5 with $\rho = 0$. In column 1, the first-named metal of the alloy was taken as the reference substance. This table corrects some errors in the calculated values in Table 3 of reference 45.

The results of these calculations are compared with experimental information in Table IV. It will be noticed that the extent of agreement between experiment and calculation is little affected by taking the atom-size disparity into account. This degree of agreement is rather poor, considering that one is simply asking of the model how the excess free energy is partitioned into the enthalpy and entropy contributions. The extent of agreement also seems independent of the state of aggregation of the solution, of the magnitude of the atom-size disparity, and of whether the experimental excess thermodynamic quantities for any one solution are all of

one sign, in agreement with the requirement of the conformal solution theory. This latter means that the degree of success of the average-potential model is not related to the necessity for second-order terms, beyond the conformal solution theory.

It is difficult to point to the basic reason why the average-potential model is not better applicable to metallic solutions. Shimoji[60] believes that a Lennard-Jones 6-12 potential is not adequate for metals and that a Morse potential would give better results when incorporated in the same kind of model. On the other hand, it is possible that the main trouble is that metal solutions do not obey a theorem of corresponding states. More specifically, the interaction $\varepsilon_{AB}(r)$ may not be expressible by the same function ϕ as for the pure components because the solute is so strongly modified by the solvent. This point of view is supported by considerations of the electronic models of metal solutions.[45] The idea that the solvent strongly modifies the solute metal is reached also through a consideration of the quasi-chemical theory applied to dilute solutions. This is the topic that we consider next.

C. The Quasi-Chemical Theory Applied to Dilute Solutions

We have already considered the relationship of the quasi-chemical model to the phenomena in metal solid solutions exhibiting superlattices, and, therefore, in solutions of high concentrations. Because at low concentrations complications due to solute-solute interactions are decreased, a very close scrutiny can be given the theory in that domain. We consequently again consider this model in this connection. Kleppa[24] has made a start in this direction by tabulating experimental values of the partial molar heat of solution for a goodly number of solutes in moderately concentrated solution in many liquid metals, as well as experimental values for the variation with concentration of the partial molar heat. Since the quasi-chemical theory, at any degree of approximation, rigidly relates the concentration dependence of $\overline{\Delta H_2}$ to the value of $\overline{\Delta H_2}^0$ (which is $\overline{\Delta H_2}$ extrapolated to zero concentration), one may calculate the theoretical slope from the experimental $\overline{\Delta H_2}^0$. The calculations often disagree with Kleppa's experimental slopes at these concentrations.

It is more interesting to examine the behavior of theory with respect to solutions of moderate dilutions. The partial molar heats of solution of copper, silver, and gold in liquid tin have been measured[51] at solute concentrations from 0.0005 to 0.02. A schematic

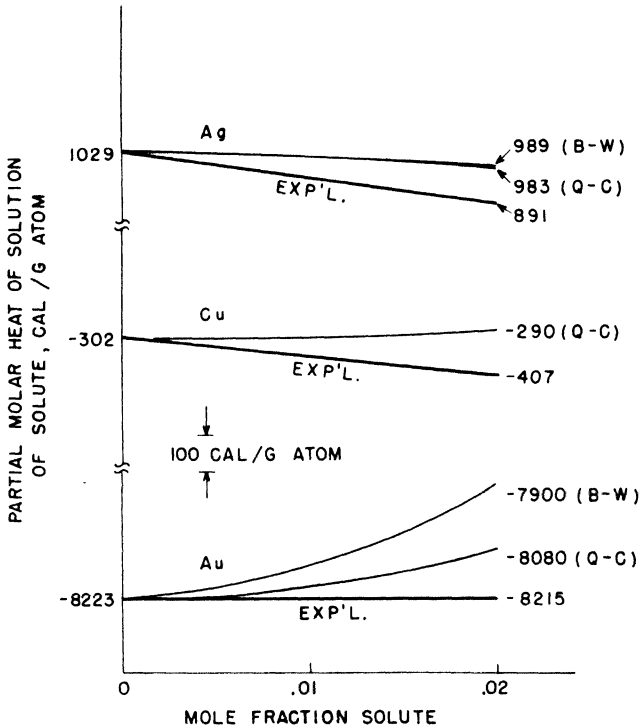

Fig. 3. Schematic diagram for the variation with concentration of the partial molar heat of solution of the liquid noble metals into liquid tin, taken from reference 51. The numbers are the experimental and calculated $\overline{\Delta H}_2$ for the solutes, in cal/g atom, at the two concentrations of 0 and 0.02 mole fraction. Q-C labels the curves calculated by the quasi-chemical theory in first order; B-W labels the curves calculated by the Bragg-Williams, or zeroth-order approximation, which assumes a random solution.

representation of the experimental data, corrected for the heats of fusion of the pure solutes, is given in Fig. 3, along with curves calculated from the experimental $\overline{\Delta H}_2^0$ and the Bragg-Williams (or

zeroth-order) and the first-order quasi-chemical theory. The disparity between calculation by the first-order theory and experiment is much beyond experimental error, and the amount of improvement achieved by the first-order over the zeroth-order theory is small enough so that going to higher approximations cannot bridge the gap. Furthermore, the magnitude of the disparity between theory and experiment is not related to the magnitude or sign of $\overline{\Delta H_2}^0$, and hence with the kind and extent of short-range order that may be presumed to exist in the solution.

Because even at the largest concentrations studied, only about 25 per cent of the solvent atoms are first-neighbors of solute atoms, it is reasonable to believe that the observed disparity is not due to a variation of w, the relevant linear combination of the interaction energies ε_{ij}. Furthermore, it may also be expected that in the short concentration range involved, the nonconfigurational changes accompanying the solution process will be independent of concentration and will make a contribution to the effective w even at the limiting zero concentration.

These considerations have led to the suggestion[51] that the most unlikely assumption in the quasi-chemical theory is that ε_{ii} is the same in the solution as in the pure component i. The removal of this restrictive assumption implies that the partial molar enthalpy of the solute has a term expressing the change in interaction energy, $\Delta\varepsilon_{22}$, in going from the pure solute state to the solution state, and another term which is a function of w. However, w is now to be interpreted only as the linear combination of the bond energies ε_{ij} only as these exist in the solution. Since w determines the variation of $\overline{\Delta H_2}$ with concentration, and since there is no necessary connection between w and $\Delta\varepsilon_{22}$, there also need be no relation between $\overline{\Delta H_2}^0$ and the concentration dependence, or between the sign of $\overline{\Delta H_2}^0$ and the kind of short-range order exhibited by the solution.

We see that the shortcomings of the quasi-chemical theory for dilute solutions also lead to the idea that the interaction between two atoms in solution may be very different from the interaction between the same atoms in the pure state. This is a point of view that can be reached from a consideration of the screening[11] by localized or by conduction-band electrons that must occur about

any solute species. The point of view is strengthened also by the change in atomic magnetic moment that is often observed[61] upon alloying. It is clear that there is a pressing need for the understanding of the interactions between solvent and solute and between solutes in metallic solutions. This is a problem beyond the province of thermodynamics, and furthermore, very little is known about the electronic aspects of alloying.[45] However, there exists in the literature one interaction model about which something can be said from the thermodynamic standpoint, and it is to this model that we turn our attention.

V. THE ELASTIC MODEL OF A SOLID SOLUTION

The elastic model of a solid metallic solution is important because of the frequency of its occurrence in the metallurgical literature. It arose as an attempt to give a quantitative accounting of the often-observed importance of the disparity in atom sizes for the stability of intermetallic compounds and of solid solutions. The essence of the elastic model of a solid solution[43] is that it costs energy to place a large atom into a lattice of small atoms, or a small atom into a lattice of large ones, everything else being equal, and furthermore, that this energy may be calculated from classical elasticity theory. One considers that, in order to make the foreign atom fit into the hole left by removal of a solvent atom from the lattice, the solute atom is hydrostatically compressed or expanded and this is balanced by a distributed shear stress in the rest of the lattice. This model can lead only to a positive excess free energy of solution, and thence to a positive energy of solution. Since many heats of solution are negative quantities, one must say that the elasticity calculation represents only a portion of the whole heat of solution.

The writer[45, 50] has criticized the elasticity theory model on the basis that this partial character renders the theory unverifiable by experiment, unless this model is correlated with another model that may be postulated to represent the negative portion of the ΔH, a correlation which has never been achieved. Another criticism has been the inconsistency of the model when it is applied to the case of solute atom smaller than the solvent atom, as opposed to

the converse case; this is related to the significance of the elastic model with respect to the ion-core repulsions only. However, in this review we shall restrict the discussion of this model to two aspects about which something can be said from the point of view of thermodynamics.

Aslthough the elastic model is unverifiable in its energetic aspect, the ituation is less ambiguous with respect to the excess entropy, ΔS^e. This quantity, when calculated by the elastic model, is proportional to the temperature coefficient of the bulk modulus, and is a positive number. The disparity between a measured negative ΔS^e and the calculated positive value cannot be rationalized in terms of "other contributions," as can a similar disparity in ΔH, since the only conceivable negative contributions to ΔS^e, from the Fermi electrons and from the existing short-range order, are either negligible or can be calculated. (We are referring to alloys and pure components which do not have ferromagnetism.) Therefore, a large gain in verifiability of a deduction from the elastic model results if the excess entropy is calculated, instead of the energy or the excess free energy.

However, a broader criticism can be made against the basic concept of the elastic model of a solid solution, leaving aside all questions of verifiability or of the difficulties associated with specification of the exact procedure for applying the concept. The elasticity theory model purports to explain the effect upon the thermodynamic properties of disparity in atom sizes by a mechanism that would be inoperable in the corresponding liquid solution, since a liquid cannot support static shear. However, liquid solutions also exhibit an atom-size effect. Liquid alkali-metal binaries exhibit a correlation[45] between atom-size disparity and extent of solubility, as do also many other liquid alloys.[3] Atom-size disparity is a factor explicitly considered in the refined versions of the cell model and of the average-potential model for liquid solutions by Prigogine and collaborators.[53] If the atom-size effect in liquid metal solutions is thought to be describable by a model different from that thought to hold for solid metal solutions, one might expect not to find a correlation between the energy of solution, ΔH^s, in the solid phase, and ΔH^L, the energy of solution in the liquid phase, at the same

TABLE V. Energetics of Solid and Liquid Primary Solutions[e]

Alloy	ΔH^S cal/g at.	ΔH^L cal/g at.
$Au_{.5}$ $Cu_{.5}$	−1260 [a]	−1780 [b]
$Au_{.6}$ $Ag_{.4}$	−1090 [c]	−1000,[b] −1200 [d]
$Ag_{.95}$ $Cu_{.05}$	305 [c]	300 [d]
$Cd_{.5}$ $Mg_{.5}$	−1340 [f]	−1740,[f] −1670 [g]
$Ni_{.4}$ $Au_{.6}$	2550 [f]	550 [d]
$Cu_{.8}$ $Zn_{.2}$	−1400 [g]	−1200 [g]
$Tl_{.4}$ $Pb_{.6}$	−320 [f]	−240 [f]
$Cu_{.9}$ $Al_{.1}$	−1700 [f]	−1600 [f]
$Pb_{.9}$ $Sn_{.1}$	310 [h]	130 [i]

[a] Ref. 49.
[b] Ref. 43.
[c] Ref. 47.
[d] Ref. 46.
[e] Adapted from reference 50.
[f] Ref. 25.
[g] Ref. 71.
[h] Ref. 33.
[i] Ref. 22.

concentration. The opposite appears to be the case, however, as shown by Table V. One may conclude that the energetics are similar, though not identical, in both phases, and it is natural to think that in whatever manner the atom-size difference operates in one phase, it operates in essentially the same manner in the other. Consequently, if an atom-size disparity is taken as a fundamental correlative in the energetics of alloys, then a model should be adopted which is in principle applicable to both solid and liquid phases. The elastic model is physically unreasonable in giving the rigidity of a lattice the central role in determining the solution energy in the solid phase. Evidently, the electronic rearrangement in the immediate neighborhood of a solute atom is most important, and this is essentially the same in both phases.

In general, it is expected that ΔH^S will differ from ΔH^L, since the difference in volume between the liquid and solid alloy and the existence of a lattice periodicity will produce slight changes in the distribution of charge between the components, a small change in

the coordination number, and possibly a small change in the short-range order. The difference, $(\Delta H^S - \Delta H^L)$, can be thought of as a misfit energy[43] arising from the imposition of lattice periodicity upon a liquid solution. It appears to be a small quantity, except in the cases of Au—Ni and Pb—Sn (see Table V), and it is not deducible from elasticity theory. In Au—Ni, ΔH^S contains a contribution from magnetic disordering which is not present in ΔH^L; $(\Delta H^S - \Delta H^L)$ for Pb—Sn may be large because of a contribution from the enthalpy difference between tetragonal tin, to which ΔH^S refers, and hypothetical face-centered cubic tin, to correspond to the structure of the solid solution

VI. SUMMARY AND CONCLUSIONS

Whereas the quasi-chemical theory has been eminently successful in describing the broad outlines, and even some of the details, of the order-disorder phenomenon in metallic solid solutions, several of its assumptions have been shown to be invalid. The manner of its failure, as well as the failure of the average-potential model to describe metallic solutions, indicates that metal atom interactions change radically in going from the pure state to the solution state. It is clear that little further progress may be expected in the formulation of statistical models for metallic solutions until the electronic interactions between solute and solvent species are better understood. In the area of solvent-solute interactions, the elastic model is unfruitful. Better understanding also is needed of the vibrational characteristics of metallic solutions, with respect to the changes in harmonic force constants and those in the anharmonicity of the vibrations.

On the experimental side, one may expect most progress from thermodynamic measurements designed to elucidate the nonconfigurational aspects of solution. The determination of the change in heat capacity and the change in thermal expansion coefficient, both as a function of temperature, will aid in the distinction between changes in the harmonic and the anharmonic characteristics of the vibrations. Measurement of the variation of heat capacity and of compressibility with pressure of both pure metals and their solutions should give some information on the

variation of interaction with interatomic distance. But of greater importance for the understanding of metal solutions is the determination of the nature of the electronic environment about a dissolved species as it differs from that about the same atom in the pure state. This is a very difficult nonthermodynamic problem which is seriously hindered by lack of adequate theory.

Notes added in proof:

Preliminary work by solution calorimetry (Oriani and Murphy, to be published) shows clearly that the enthalpy of formation of solid Co-Pt alloys is a negative quantity, so that the statement made on p. 125 is not correct.

The kind of short-range order that exists in solid Au-Ni solutions has been called into question by A. Munster and K. Sagel (National Physical Laboratory Symposium, Teddington, to be published). These authors find negative short-range order, in direct opposition to ref. 10 (see p. 126). At present writing, the situation is not clarified.

Recent work by solution calorimetry (Oriani and Murphy, to be published) has yielded more accurate figures for the enthalpy of formation of solid Au-Ni solutions than those of refs. 58 or 25. The estimated ΔH at $Au_{.6}Ni_{.4}$ is 1400 cal/g atom (see Table V) and at $Au_{.5}Ni_{.5}$ it is 1500 cal/g atom (see Table IV). This changes the experimental ΔS^e to about 0.4 cal/deg g atom (see Table III), if one assumes the ΔG^e at 1173°K of ref. 58 to be correct, and leads to $T\Delta S^e$ of 460 cal/g atom (see Table IV).

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RECENT ADVANCES IN POLYMER CHEMISTRY

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I. INTRODUCTION

I was asked to survey our work on anionic polymerization and to discuss chemistry of "living" polymers. However, in course of writing I decided to enlarge the scope to survey those topics investigated currently by polymer chemists which seem to be the most interesting and most promising for future research. The choice of subjects is highly subjective and strongly biased by my own interest and by the type of research carried out in our laboratories. Moreover, I have not hesitated to discuss problems which are still under investigation as well as ideas which have not even been tested. Hence, this is not an orthodox review, based on well established facts, but is an attempt to survey also some unpublished ideas.

Some phenomena, completely new in the field of polymer chemistry, have been discovered in the last few years. Although their exploration is vigorously pursued by many workers, only a small fraction of the available data is published. Furthermore, as often happens in the early stages of development of a new field, much of the disclosed experimental material is confusing and tends to obscure rather than to clarify the specific problems arising from these studies. I would like, therefore, to speculate about some phenomena which might be of importance in this field and to draw attention to some principles which might serve as a guide in

the welter of contradictory facts. Whenever possible I will try to illustrate these speculations by experimental data, but often I will have to leave them as suggestions without any proof.

II. ADDITION POLYMERIZATION

Certain species produced from monomers are endowed with the ability to add further monomeric units and thus continue their growth by addition polymerization. This property arises from the presence of some reactive groupings located on one or both ends of the growing polymeric chains. It is customary to classify the polymerization processes as radical polymerizations, ionic polymerizations, or coordination polymerizations, depending on whether these reactive groupings are radicals, positive or negative ions, or coordination complexes. This classification is useful although not fully comprehensive, since cases exist, and many more might be found, where a unique assignment of a polymerization process to one particular class is not possible.

The overall polymerization process is composed of three fundamental steps: initiation, propagation, and termination. Recent developments concerned with each of these three steps will be discussed now in this order.

III. INITIATION OF POLYMERIZATION

Classification of polymerization processes can be applied also to the initiators;* we distinguish between initiators which are radicals, positive or negative ions, or coordination complexes. The initiator may be either an independent species existing as such in solution or a moiety of some molecule transferred to the monomer during the initiation process. A free radical moving independently through a solution or an unassociated ion like HN_2^- or Ph_3C^+ exemplify the first class, while a proton transferred from an acid to a monomer acting as a base is an example of an initiator of the second class. In each case the initiation step can be represented symbolically either

* The term initiator is used here in a somewhat different sense than is customarily used in the literature. It denotes the initiating species and not its generator; e.g. a peroxide generates the radicals which in turn initiate polymerization.

by Eq. 1

$$X(\dot{+})+M \rightarrow X—M(\dot{+}) \quad (1)$$

or by Eq. 2

$$XY+M \rightarrow X—M, Y \text{ or } X—M—Y \quad (2)$$

where X or XY denotes the initiator and M the monomer.*

All of these initiation processes have one feature in common: in each of them a stable X—M bond is formed on one end of a bifunctional monomeric unit, while a reactive center is created on the other end. Hence, as the addition of further monomeric units proceeds a polymeric species growing on *one* end only is produced, the other end being blocked by the stable X—M bond.

A different situation arises in the initiation reaction resulting from an electron transfer to a monomer. Such an initiation has been discussed recently[42, 43] and leads to a species containing one extra electron which behaves like a radical ion. It has been pointed out that the extra electron may be conveniently ascribed to the lowest unoccupied π orbital of the monomeric molecule (see Figure 1), a

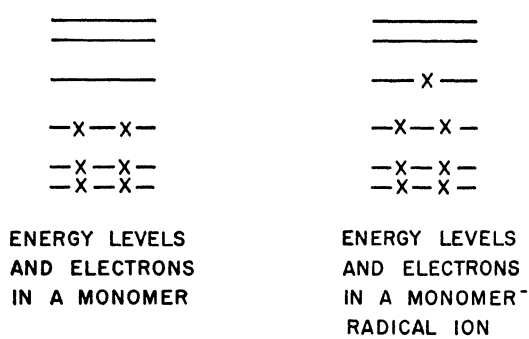


Fig. 1.

description that is preferred to the notation $\cdot CH_2—CHX:$ or $:CH_2—CHX\cdot$, since no actual separation of electrons takes place in the M^- ion formed. On the other hand, addition of one monomeric unit to either end of the M^- ion yields a dimer in which the electrons are truly separated. This is shown in Eq. 3

* X—M, Y might be a pair of ions.

$$CH_2{=}CHX^- + CH_2{=}CHX \rightarrow :CHX{-}CH_2{-}CH_2{-}CHX\cdot \quad (3)$$

The dimer behaves simultaneously as a radical and as a carbanion, and thus the radical end might grow by a radical mechanism, anionic polymerization proceeding from the carbanion end. This behavior is particularly interesting when two monomers are present in the system, one polymerizable by a radical but not by an anionic mechanism, the other behaving in the opposite sense. In such a hypothetical case the resulting product would be a block polymer, ·A—A . . . A—B—B . . . B·.

There are some indications that the situation described above has been realized, at least partially, in the system styrene-methyl methacrylate polymerized by metallic lithium.[29a, 29b] It is known[51] that in a 50-50 mixture of styrene and methyl methacrylate radical polymerization yields a product of approximately the same composition as the feed. On the other hand, a product containing only a few per cent of styrene is formed in a polymerization proceeding by an anionic mechanism. Since the polymer obtained in the 50-50 mixture of styrene and methyl methacrylate polymerized with metallic lithium had apparently an intermediate composition, it has been suggested that this is a block polymer obtained in a reaction discussed above. Further evidence favoring this mechanism is provided by the fact that under identical conditions only pure poly-methyl methacrylate is formed if the polymerization is initiated by butyl lithium and not by lithium dispersion. This proves that incorporation of styrene is due to a different initiation and not propagation.

Let us discuss now the conditions required for the electron transfer process. This reaction requires, of course, a suitable electron donor (a species characterized by a low ionization potential) and a proper electron acceptor, e.g., a monomer characterized by a high electron affinity. Furthermore, the nature of the solvent is often critical for such a reaction. The solvation energy of ions contributes substantially to the heat of reaction, hence the reaction might occur in a strong solvating solvent, but its course may be reversed in a poorly solvating medium. A good example of this behavior is provided by the reaction Na + naphthalene $\rightarrow$ Na^+ + naphthalene$^-$. This reaction proceeds rapidly in tetrahydrofuran or in dimethoxy

ethane; however, if the ether solvent is replaced by a hydrocarbon solvent the reaction is reversed and metallic sodium dust and naphthalene are formed from the green solution of sodium naphthalene.[39]

Alkali metals are obvious examples of electron donors, and indeed polymerization of butadiene or styrene initiated by metallic sodium results from an electron transfer initiation process. This reaction has been, and is still, being studied by many investigators, notably by Ziegler[55] and by Russian workers.[1] In Ziegler's notation the initiation is represented by the equation

$$M + 2Na \rightarrow Na—M—Na \qquad (2)$$

and formation of reactive C—Na bonds is postulated. It is well known that the carbon-sodium bond is highly polar and hence it may be more properly represented by the notation C^-, Na^+.* The environment of this bond determines the extent of its dissociation into ion pairs or free ions. In a medium of high dielectric constant and strong solvating power at least a partial dissociation is expected, while less dissociation occurs in hydrocarbon solvents. Obviously, the C—Na bond is more likely to dissociate than the C—Li bond.

Electron transfer to a suitable monomer leads to the formation of an ion pair like M^-, Na^+. The negative monomer$^-$ ion may react again with sodium forming a Na—M—Na unit. The latter arises, therefore, as a product of two consecutive reactions, e.g.,

$$Na + M \rightarrow Na^+, M^-$$

$$Na + Na^+ M^- \rightarrow Na^+M^{--} Na^+$$

Whether the second step does take place depends on a number of factors. The electron affinity of the M^- ion must be sufficiently great, and this point can be appreciated by considering a few examples. Electron transfer to stilbene or tetraphenyl ethylene leads to the formation of negative ions which in turn rapidly ac-

* I presume that Ziegler's notation C—Na was only symbolical, since when it was proposed the homopolar and heteropolar nature of chemical bonds was not as clearly understood as it is today.

quire a second electron and yield well-stabilized diions:

$$:HC(Ph)—CH(Ph): \quad \text{and} \quad Ph_2\ddot{C}—\ddot{C}Ph_2$$

In fact, the stabilization of the diion formed from tetraphenyl ethylene is so great that the monoion cannot be isolated. On the other hand, the stabilization of the diion of stilbene is less pronounced, and hence both the monoionic and the diionic species are observed. In contrast to these cases, the addition of a second electron to the styrene$^-$ ion or to the 1,1 diphenyl ethylene$^-$ ion would yield a diion possessing one unstabilized end charge, i.e.,

$$:HC(Ph)—CH_2: \quad \text{and} \quad Ph_2\ddot{C}—CH_2:$$

and therefore formation of such diions should not be expected.*

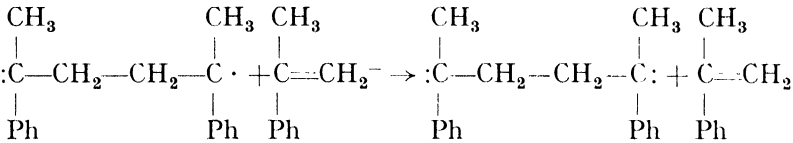
Conversion of monomer$^-$ ions into diions represents one of the possible reactions of these species. Their dimerization, or the addition to them, of a monomeric unit are the other important reactions which we have to discuss. Dimerization of monomer$^-$ ions yields those dimeric diions which have the most stable carbanions, e.g. $2Ph_2C{=}CH_2^- \rightarrow Ph_2\ddot{C}—CH_2—CH_2—\ddot{C}Ph_2$ and not $:CH_2—C(Ph_2)—C(Ph_2)—CH_2:$. This reaction is probably somewhat hindered by the Coulombic repulsion between the two closely located negative centers.

In the same way, the addition of monomer yields the radical ions which possess the most stable carbanion ends and the most stable radical ends, e.g.,

$$\cdot CH_2{-}C(CH_3)(Ph){=}CH_2^- + CH_2{=}C(CH_3)(Ph) \rightarrow :CH_2{-}C(CH_3)(Ph){-}CH_2{-}C(CH_3)(Ph)\cdot$$

* I am referring to ions or diions for the sake of briefness. Actually one always is concerned with ion pairs. Notation like Na—CH·Ph—CH·Ph—Na is also permissible, although not desirable, since the C—Na bonds are highly polar and frequently completely ionized.

The electron affinity of radicals is considerably greater than the electron affinity of monomers, hence in the presence of monomer$^-$ ions, or in the presence of an excess of the primary electron donors, the dimeric radical ions are rapidly converted into dimeric diions, e.g.,



The product is identical with that produced by the direct dimerization of monomer$^-$ ions.

Let us consider the conditions which favor the formation and survival of the dimeric and polymeric radical ions. This might be achieved by keeping the concentration of monomer high, the concentration of monomer$^-$ ions low and by removing the radical ions as rapidly as possible from the zone containing the primary electron donors. Moreover, since the radical ions dimerize, their average life time increases as their concentration decreases. The following experiment should probably produce the best results.

A stream of monomer (or mixture of monomers) is made to flow rapidly over the surface of an alkali metal. If the reaction with the metal is sufficiently slow, a low concentration of monomer$^-$ ions will result. In view of the high concentration of the monomer, the monomeric$^-$ ions would add further monomer to form the dimeric and polymeric radical ions. Of course, the final product is not a radical, but it would result from a polymerization which took place to some extent on the radical ends. The mixture of monomers may be recirculated many times to increase the conversion and a solvent may be added to the system when necessary.

Electron transfer reactions involving alkali metals are heterogeneous, and for many purposes it is desirable to deal with a homogeneous electron transfer system. It was noticed by Scott[39] that sodium and other alkali metals react rapidly with aromatic hydrocarbons like diphenyl, naphthalene, anthracene, etc., giving intensely colored complexes of a 1 to 1 ratio of sodium to hydro-

carbon. For reasons outlined above this reaction occurs only in specific solvents like dimethoxy ethane, tetrahydrofuran and a few others.

Recently, Weissman and his colleagues[52] showed that the product is paramagnetic indicating that it results from an electron transfer process giving one unpaired electron to the hydrocarbon ion. Furthermore, they demonstrated[30] that electron transfer reactions easily proceed in systems containing aromatic$^-$ ions and neutral aromatic hydrocarbon molecules, e.g.,
naphthalene$^-$ + phenathrene → naphthalene + phenanthrene$^-$.

Polymerization of some vinyl monomers initiated by those colored aromatic complexes was described by Scott[38] over twenty years ago, and recently the mechanism of this reaction has been elucidated in our laboratory[43] where we demonstrated that polymerization initiation is due to an electron transfer to monomer, namely $A^- + M \rightarrow A + M^-$. This system is useful, therefore, in studying the homogeneous initiation of polymerization caused by an electron transfer process.

Addition of styrene to a green solution of naphthalene$^-$ Na^+ in tetrahydrofuran leads to an instantaneous change of color from green to red. Styrene polymerizes rapidly and quantitatively within a few seconds, and when the reaction is completed, addition of water converts the red solution of polystyryl carbanions into colorless solution of polystyrene. After precipitation of the polymer it was shown spectroscopically[25] that the residual solution contains an amount of naphthalene equal to that used in the preparation of the initiating catalyst. This observation confirms the proposed mechanism of initiation of the polymerization.

The red solution of polystyryl carbanions can be kept for days without change in color or viscosity. No changes are observed on addition of further amounts of naphthalene to the red solution. These observations raise some questions. An electron transfer, say for example, between naphthalene$^-$ and phenathrene, is a reversible process and it leads eventually to an equilibrium between naphthalene$^-$, naphthalene, phenathrene$^-$, and phenanthrene. Is the reaction involving styrene irreversible? Now, the initial process of electron transfer from naphthalene$^-$ to styrene that produces

styrene$^-$ + naphthalene is reversible. This reaction is followed by an addition of styrene to the styrene$^-$ ion, and then by the dimerization of the dimeric or polymeric radical ions, finally producing polystyryl^{--} diions. The electron affinity of radicals, like the polystyryl radical, is so much greater than the electron affinity of naphthalene that at this stage the electron transfer process is essentially irreversible and no formation of naphthalene$^-$ ions and polystyryl radicals should be expected from naphthalene and polystyryl$^-$ ions. This would still be the case even if the initial equilibrium, naphthalene$^-$ + styrene $\rightarrow$ naphthalene + styrene$^-$, were greatly in favor of naphthalene$^-$ ions.*

Solution of alkali metals in liquid ammonia, containing the so-called solvating electrons, may be used as an alternative homogeneous system to initiate polymerization by an electron transfer process. This system suffers, however, from complications resulting from proton transfer from ammonia leading to the formation of NH_2^- ions, which in turn initiate further polymerization.[4]

Finally, let us consider the monomers whose polymerization can be initiated by an electron transfer process. Such monomers should have an empty orbital of low energy to accommodate the extra electron. This condition is fulfilled in monomers like styrene, butadiene, and many other conjugated vinyl derivatives. The energy of the first empty orbital in monomers like ethylene or propene is, however, much too high; consequently their polymerization cannot be initiated by electron transfer process from common electron donors. Monomers having conjugated, electron withdrawing groups are easily polymerized by electron transfer, as e.g., methyl methacrylate, acrylonitrile, methacrylonitrile, and vinylidene dicyanide. Some monomeric$^-$ ions may decompose easily into radicals and even more stable anions. Tetrafluoroethylene probably belongs to this group—electron transfer to this monomer seems to be followed by the reaction $C_2F_4^- \rightarrow C_2F_3\cdot + F^-$.

Ethylene oxide and cyclic silicones represent an interesting group of monomers that might be polymerizable by an electron transfer process. The initiation would lead to the formation of

* Actually information about the position of this equilibrium is obtained from polarographic studies, e.g., see ref. 22a.

negative $\cdot RO^-$ radical-ions which add further units of ethylene oxide or cyclic silicone respectively.*

An entirely new class of initiators has been discovered recently by a number of independent research workers, notably by Ziegler.[56] The characteristic feature of these initiators is their ability to form coordination complexes with monomers leading to labile organometallic compounds which can again form complexes with new monomeric units. These systems are extremely interesting and are of enormous industrial importance. Since much of the pertinent work is still unpublished, while the published work has been reviewed recently by Natta,[29] by Eirich and Mark,[13] by Tobolsky,[46] by Stille,[40] and by Schildknecht,[37] a detailed discussion of this problem will be omitted here with the exception of one case. This is Bawn's study[3] of the polymerization of diazomethane by BF_3 which provides a good illustration of the general principles governing this type of reactions.

It is highly probable that the monomer is first coordinated onto a vacant position of the complex and then pushed between a boron-carbon bond of the catalyst. The following mechanism, proposed by Bawn, can be considered as a prototype of coordinated complex polymerization:

$$BF_3 + CH_2N_2 \rightarrow F_3B{-}CH_2N_2$$
$$F_3B{-}CH_2N_2 \rightarrow F_2B{-}CH_2F + N_2$$

followed by

$$F_2B{-}CH_2F + CH_2N_2 \rightarrow F_2B(CH_2F)(CH_2N_2) \rightarrow F_2B{-}(CH_2)_2F + N_2,$$

etc. A similar mechanism concerned with Ziegler type of polymerization was discussed recently by Patat.[30a]

Another mode of initiation of polymerization being vigorously studied in numerous laboratories involves the use of ionizing radiation. In the primary process a molecule (not necessarily the monomer) is ionized and thus a positive ion and an electron are formed. The latter is eventually captured by another molecule yielding a negative ion. On recombination of these ions, enough

* Polymerization of ethylene oxide might be initiated by electron transfer process if metallic Na or Li is used as an initiator. On the other hand, initiation by sodium naphthalene involves not electron transfer but addition to naphthalene$^-$ ion.

energy is liberated to dissociate some molecules into radicals and the latter initiate polymerization. Consequently, a polymerization initiated by ionizing radiation is radical in character as has been demonstrated by various workers studying this field.[47] We know, however, that ionic polymerization is feasible, so why is it that the ionic species formed during the irradiation do not initiate polymerization? I believe that the problem really concerns the question of termination of the polymerization, a subject to be discussed thoroughly in a later part of this paper. Ions recombine, and their recombination is one of the possible modes of termination of an ionic polymerization. Hence ionic polymerization can only be observed if relatively *stable* ions are formed, and this is probably not the case in most of the systems involving irradiation that have been investigated. Relatively stable ions would be formed in solvents of sufficiently high solvating power, and one would expect the occurrence of some ionic polymerization in such solvents. Alternatively, irradiation of a solid or very rigid media might lead to the formation of ions which cannot diffuse easily and whose recombination would thus be hindered. However, the propagation step also would be slowed down under these conditions, hence special systems have to be found where the relative rates of diffusion of the respective species could be properly adjusted. The subject of ionic polymerization initiated by ionizing radiation is apparently under investigation in several laboratories, and there are some indications that such a phenomenon has been recently observed.[32]

Addition of metallic oxides to isobutene polymerized by high energy radiation leads to a spectacular increase in the yield.[31a] It seems that some ions are stabilized by complexing with the surface of the oxide and such an interaction prevents their recombination with the gegen-ions. These observations confirm therefore the suggested cause of inefficient ionic polymerization in systems exposed to ionizing radiation.

Some interesting observations have been reported recently by Japanese workers[21] who found that boron trialkyls initiate polymerization. These investigators suggest that the polymerization is anionic in character; however, work carried out by Fordham *et al.*[17]

indicates that this reaction has a radical character. It is not known yet how initiation actually occurs in this system.*

Very powerful initiators of carbonium-ion polymerization were recently reported by Plesch.[32b] They belong to the salt-like class of organic compounds and dissociate readily into ClO_4^- ions and carboxonium positive ions. The latter are sufficiently reactive to initiate carbonium-ion polymerization of styrene.

IV. PROPAGATION OF POLYMERIZATION

The propagation step of polymerization involves an addition of monomeric units to the growing centers followed by regeneration of these centers. A series of consecutive propagation steps yields eventually a long polymeric molecule.

Discussion of the propagation step should embrace the following points: the rate problem, the problem of relative reactivities of various monomers in a mixture (the copolymerization problem) and the problem of probabilites of the various possible modes of addition, namely head-to-head and head-to-tail addition, formation of *d*-configuration and *l*-configuration, 1—2 and 1—4 addition, and formation of *cis* and *trans* configurations. It is desirable to clarify, at the very beginning of this discussion, which factors do and which do not influence the course of the propagation step. In chemical reactions the effect of a force acting at long distance is rarely observed; hence in the propagation reaction one would not expect the inactive end to affect in any way the course of the addition. Thus the rate, the selectivity and the mode of propagation in a radical polymerization must be independent of the nature of the initiating radical, since this species remains attached to the inactive and remote end of the growing chain. The same applies to ionic polymerizations where the nature of the positive ions initiating a carbonium ion polymerization or the negative ions used in an anionic polymerization should not affect the course of the propagation. These ions also form moieties attached to those ends of the polymer that are remote from the reaction

* Apparently oxygen is required in this initiation, hence it is probable that some boron peroxides are the initiators.

centers,* and thus are unable to influence its course. On the other hand, any species which are in the vicinity of the growing center have some effect on the course of the propagation, although the extent of their influence might vary widely from one case to another.

A radical polymerization involves free radical ends which of course do not associate** and which interact only weakly with solvents. Consequently, the early investigators assumed that the course of propagation of radical polymerization is independent of the environment (see, for example, the recent monograph by Walling[50]). Actually, more recent studies, notably by Russell,[36] showed that the nature of the solvent sometimes might considerably affect even the course of radical reactions. Therefore, unusual behavior of the propagation step might be expected in certain solvents.

In ionic polymerizations the growing carbonium ion or carbanion must always be associated with the respective gegen ion. The extent of the association depends on the nature of the gegen ion as well as on the solvent and temperature. Furthermore, the ion pairs frequently form clusters or aggregates, and then the environment of each ion pair is affected by the extent of the aggregation. Hence the rate of an ionic propagation might depend on higher powers of the concentration of the growing centers, moreover different solvents or variation of temperature would affect the reaction in two ways: by changing the structure of the ion pairs, e.g. modifying the structure of the solvation shell, and by affecting their degree of aggregation.

The nature of the gegen ion is probably of the greatest importance in determining the rate of propagation in ionic polymerization. However, it is not clear whether the presence of the gegen ion enhances or inhibits the propagation. One may argue that the

* There are some reports that the nature of the group R in R—Li or R—Na initiators affects the course of the propagation. This problem will be considered later and it will be shown that it may be reconciled with the present statement.

** In this case the association is equivalent to termination; hence, as long as the radical grows it must remain separate from other radicals.

electrostatic field of the growing ion polarizes the approaching monomeric molecule, and this process is responsible for the addition. According to this point of view the presence of gegen ions would inhibit the reaction since they weaken the strength of the polarizing field. On the other hand, the polarization of the monomeric molecule might result from a concerted action of the negative and positive ions interacting with its opposite ends. In this case the presence of a gegen ion should enhance the propagation, since the ions reinforce each other's action. It would be desirable, therefore, to study an ionic polymerization occurring in the absence of gegen ions. Such a study is not impossible, although technically extraordinarily difficult. The results, however, would be most enlightening and could help in clarifying the role of gegen ions in ionic polymerizations.

Ions and ion pairs interact strongly with the solvent, and hence an ionic polymerization is greatly influenced by the environment. Solvation tends to separate the ions and thus the system approaches a state which would be expected in a hypothetical solution deprived of gegen ions. At the same time formation of a solvation shell around the growing center probably slows down the addition. This effect is particularly notable in the termination step and will be discussed further in the next section of this paper.

In a solution containing two solvents greatly different in their solvation power, a local separation of the components is expected. In an extreme case the ions or ion pairs might be surrounded entirely by the molecules of the good solvent, and hence the polymerization would proceed as if this were the only component present in the system. A most interesting example of such a behavior is provided by Korotkov's work.[24] This investigator noticed that the propagation of butadiene polymerization initiated by organolithium compounds was much slower than that of styrene. When both monomers were present, say in a 50-50 mixture, the reaction proceeded slowly, and only butadiene polymerized. However, as soon as the butadiene was consumed the rate of reaction increased markedly and styrene began to polymerize. Apparently, butadiene solvates the ions better than styrene, although the latter reacts more vigorously. Consequently, in a 50–50 mixture the growing ions

are in an environment of butadiene and they consume this monomer only, the slow rate of reaction being characteristic for butadiene polymerization. When this monomer has been consumed it is replaced by styrene which now forms the solvation shell and the reaction continues with the characteristic rate of styrene polymerization.*

In view of these effects one can easily understand that the rate of propagation in an ionic polymerization may depend on some power of the monomer that is higher than unity. The monomer may participate in the solvation process and the change in the composition of the solvation shell influences the reactivity of the growing center. Indeed, studies of the kinetics of many ionic polymerizations show that the rate depends on unexpected and sometimes variable powers of the monomer concentration. Similarly an organometallic compound used in an anionic polymerization or an acid initiating a carbonium ion polymerization may form a part of the solvation shell. Numerous examples of such a behavior are reported in the literature, and the respective kinetic expressions are frequently very complex. In the special case of anionic polymerization initiated by R—Li, the nature of R might influence the rate of the propagation if R—Li participates in the solvation process.**

The rate of a coordination polymerization is obviously determined by the nature of the complex used in the process, and such a system might be greatly influenced by the solvent. Moreover, in a coordination polymerization, propagation might involve two steps: coordination of the monomer with the complex—this step might be reversible—followed by actual polymerization in which the monomer is shifted into the chain. If the first step is rate determining, the kinetics of the polymerization would be first order in monomer; if the second step is much slower than the first, the rate of polymerization would be independent of monomer concentration if it is sufficiently high. In the intermediate case the kinetics should resemble the kinetics of a heterogeneous catalysis or an enzyme reaction. Many of the coordination catalysts are hetero-

* Ability to solvate and ability to polymerize are unrelated properties of a molecule. For example, water solvates well but does not polymerize.

** See the footnote on p. 159.

geneous, and consequently the usual complications characteristic of heterogeneous reactions are encountered.

Some coordination catalysts are probably in equilibrium with the components from which the complex is formed. For instance, this might be the case for an ordinary Ziegler type catalyst obtained from $TiCl_4$ and AlR_3. The precipitate is catalytically active, but if it is filtered from the original solution in which it was precipitated, and then washed thoroughly with pure hexane, it has no catalytic activity when in the form of a hexane suspension. The original filtrate is also catalytically inactive, but addition of this filtrate to the inactive precipitate yields an active catalyst.* These equilibria further complicate the kinetics of such polymerizations, particularly when more than one complex can be formed and each of them might exhibit its own characteristic catalytic activity.

The distinction between coordination polymerization and ionic polymerization is not sharp. Let us consider for example a C—X bond, X being a halogen or a metal. Winstein[54] and Evans[14] have demonstrated that in a compound containing this type of bond an equilibrium may be established in a suitable solvent between

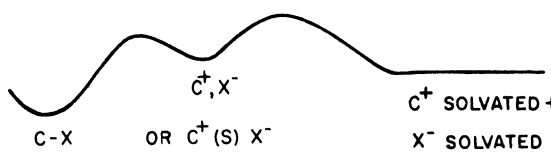


Fig. 2.

C—X, C^+, X^- and $C^+ + X^-$ (see Fig. 2), the solvation energy increasing the driving force of these dissociations. It is possible that a coordination catalyst is not active in the C—X state but only in one or other of the ionized states. Such behavior blurs the distinction between ionic and coordination polymerization.

In most polymerization reactions the monomer is not arrayed prior to the reaction. It might form a part of a solvation shell or be coordinated to the catalytic complex, but there is no long-range order among monomeric units. The possibility of arraying monomeric units prior to polymerization was considered by the author,[41]

* I am indebted to Prof. Mark for this information.

and such a reaction was referred to as replica polymerization. The specific example discussed in his paper seems to be incorrect;[28] nevertheless the idea should not be discarded.* Actually Friedlander[19] visualizes a heterogeneous polymerization resulting from a regularly ordered adsorption of monomeric units on the catalytic surface. The pattern of monomeric units formed in the adsorbed layers is supposedly advantageous for the propagation of the polymerization.

A most interesting observation of Letort,[26] who investigated the spontaneous polymerization of solid acetaldehyde, seems to be explicable in the same terms. Liquid acetaldehyde does not polymerize even if the liquid is supercooled; crystals of acetaldehyde do not polymerize either if they are kept below the melting temperature. However, when the temperature of the crystals is raised to the melting point they polymerize spontaneously. Apparently the polymerization requires orderly arrayed molecules, and this is achieved in the crystal. Below the melting point these molecules are held too rigidly in the lattice and there is not enough freedom of motion to start the reaction. At the melting temperature, however, the required order is still preserved and at the same time there is enough freedom of motion to permit the reaction to occur.

Another example of such a behavior is provided by the interesting polymerization of butadiene molecules imprisoned in tubes of clathrates of urea.[9] Of course, the configuration of the resulting polymer is strongly influenced by the order introduced in the assembly of monomers and thus all trans polybutadiene is formed.

Finally, many biological polymerizations most probably involve templates. These array the monomeric units and the order obtained is reflected in the polymer produced.

A special situation is created in a polymerization of isolated dienes or similar compounds like diisocyanates. Addition of such a monomer to a growing polymeric chain leaves its second reactive unit in the vicinity of the active center. Consequently, the addition of this unit is favored to the addition of any other unit, and in fact it is governed by a unimolecular and not bimolecular kinetic law. Its addition leads to the formation of a ring, and if ring closure is

* We were unable to verify Melville and Watson's results. See ref. 51a.

advantageous the polymerization leads to poly-ring polymers. How many CH_2 units (or other units) should separate the reactive double bonds is determined by their nature. Examples of such polymerizations are provided by work of Marvel and of other investigators.[30b]

We shall consider now the various degrees of order which characterize polymeric molecules. The addition of a monomeric unit to a growing chain may take place in more than one way. In the case of a vinyl or vinylidine monomer, i.e., $CH_2{=}CHA$ or $CH_2{=}CAB$, head-to-head or head-to-tail addition may occur. In most cases the head-to-tail addition has a vastly greater probability than the head-to-head or tail-to-tail addition, and thus the latter is responsible only for small imperfections in the chain structure.* Studies of head-to-tail and head-to-head additions were vigorously pursued in the '30's and '40's, and a good account of this work is available, for example, in Flory's recent monograph.[15]

Even if the addition does take place in a regular head-to-tail manner, the reaction is still not uniquely specified. On examination of a linear polymer stretched into a planar zigzag one finds that the groups A and H (or A and B) are above and below, respectively, the plane determined by the carbon skeleton. Assuming that group A in some unit is above the plane, group A in the following unit may be then either similarly located, i.e., also above the plane, or its location may be reversed to be below the plane. The first sequence of configurations is referred to as an isotactic sequence while the second forms a syndiotactic sequence.

Inspection of models show that the interaction between the nonbonded atoms is different in an isotactic and a syndiotactic sequence. A somewhat naive calculation based on van der Waals' repulsions between the nonbonded atoms, suggests that for nonpolar vinyl monomers the syndiotactic sequence may be favored by a few tenths of a kcal/mole, and this difference might increase to

* Our investigation of the addition of methyl radicals to various monomers suggests that the addition of methyl radicals to the β carbon of styrene is approximately 500 times more probable than their addition to the α carbon.

about one kcal/mole for polar monomers where the repulsion between the polar groups reinforces the van der Waals' repulsion. In the case of vinylidene monomers the situation is even more complex, but on the whole the syndiotactic sequence is apparently favored whenever groups A and B differ considerably in their size.

In a radical polymerization the last unit of the growing polymeric chain has no orientation, since the carbon atom of the radical is either planar or it oscillates rapidly through the plane of its three ligands. However, its orientation becomes definite when the next monomeric unit is added to the chain. It is probable that in such a process the difference between the activation energies of the two possible placements is proportional to the difference in the heats of formation of the two sequences, and if this is true the syndiotactic placement would be favored. The ratio of the probabilities of these two placements should be independent of the nature of the initiating radical for chains grown to the size of about a tenmer or more (see the calculation by Frisch, Schuerch, and Szwarc[20]). On the other hand, this ratio obviously must increase with decreasing temperature, and therefore it is conceivable that an appreciable regularity might be found in polymers produced by a radical initiation at a sufficiently low temperature. Indeed, two independent groups of workers[16, 18] reported recently synthesis of stereo regular polymers by a radical initiation performed at low temperatures.

In an ionic polymerization the strong electrostatic field of the ion pairs should have a pronounced effect on the ratio of the probabilities of the two placements. Furthermore, solvation of an ion pair is much stronger than of a neutral radical, hence the influence of a solvent on stereospecificity of addition is expected to be much more pronounced in an ionic polymerization than in a radical polymerization. The nature of the gegen ion represents still another factor which is of extreme importance in determining the stereospecificity of the polymerization.

While a planar configuration characterizes the last monomeric unit of a polymeric chain growing by a radical or carbonium ion mechanism, a tetrahedral configuration should be attributed to the end of a growing polymeric carbanion.* Hence an isotactic or a

* The tetrahedral configuration is further stabilized if the gegen ion is close to the carbanion.

syndiotactic placement determines the configuration of the last monomeric unit linked to the chain and not, as in a radical or a carbonium ion polymerization, the configuration of the last unit but one of the growing chain. Consequently, a different placement may be favored in a polymerization of the same monomer depending whether the reaction proceeds by an anionic or by a radical mechanism. This seems to be the case in a low temperature polymerization of methyl methacrylate. A syndiotactic placement is apparently favored in a radical polymerization and in an anionic polymerization occurring in solvents of a high solvating power, while the isotactic placement is preferred in an anionic polymerization performed in a poor solvating solvent.[18]

A very high specificity is achieved in polymerization involving coordination complexes associated with the growing ends. In such a reaction a definite configuration characterizes not only the last unit of the growing polymeric chain but probably also the approaching monomeric unit if its association with the complex requires a specific geometrical interrelation of the components prior to the actual reaction. The extent of control gained on the stereospecificity of polymerization is illustrated by the outstanding work of Natta and his colleagues[29] who were able to produce from the same monomer all isotactic or all syndiotactic polymers by using different coordination complexes as catalysts and by proper adjustment of the conditions of the reaction. Whether heterogeneity of the catalyst is required for its high stereospecificity is debatable.

It is probable that most of the complexing agents used as polymerization catalysts do not exhibit optical asymmetry. Hence, the preference for a particular configuration is determined by the configuration of the last ordered unit of the growing polymer.* To realize the significance of this effect let us consider a stereospecific catalyst which greatly favors isotactic placement, and let us denote by *d* the configuration of the last ordered unit of a growing chain. In such a system the probability of the next ordered unit to emerge in a *d* configuration is greater than for it to emerge in an *l*

* The effect of the penultimate groups or even more distant groups is probably of no great importance. A special case when such interactions should be considered will be discussed later.

configuration. However, if an l unit is eventually formed, the same catalyst will continue to favor the formation of further l units. The structure of the polymer produced by such a highly stereospecific catalyst depends on the ratio of two probabilities, the probability p for isotactic placement and the probability q for termination. For $q \gg (1-p)$* the polymers formed would be composed of an approximately equimolar mixture of all d and all l polymers. However, if $q \ll (1-p)$ then block polymers would be formed, i.e., polymeric chains containing blocks of d followed by blocks of l and so on. No block polymers would be formed with a catalyst of a high syndiotactic specificity.

A different situation arises when one considers a stereospecific catalyst which is endowed with optical activity and which favors therefore a specific configuration. Such a catalyst, if highly stereospecific, should form polymers, for example of all d configuration with an occasional inclusion here and there of l units. Of course if a racemic mixture of such a catalyst is used, then formation of a racemic mixture of polymers is expected, each polymeric molecule having an all d configuration incrusted with l units or an all l configuration incrusted with d units.

In the polymerization involving nonoptically active monomers we deal with three species: growing chains terminated by a d unit, growing chains terminated by an l unit, and the monomer. The probability of an isotactic placement is given by k_{iso}/k_p and of a syndiotactic placement by k_{syn}/k_p, where k_{iso} and k_{syn} denote the rate constants of the respective placements while k_p is the usual rate constant for the propagation. Of course, $k_p = k_{iso} + k_{syn}$.

On the other hand if the monomer contains an optically asymmetric center, then four independent species participate in the polymerization although the reaction is still determined by only two rate constants. The relevant reactions are:

$$\sim\sim d + d \longrightarrow \sim\sim dd, \quad k_{iso}$$
$$\sim\sim d + l \longrightarrow \sim\sim dl, \quad k_{syn}$$
$$\sim\sim l + d \longrightarrow \sim\sim ld, \quad k_{syn}$$
$$\sim\sim l + l \longrightarrow \sim\sim ll, \quad k_{iso}$$

* Of course, $q \ll 1$ if a high molecular weight polymer is produced.

This situation resembles the well-known scheme of copolymerization, simplified by the obvious equalities $k_{11} = k_{22}$ and $k_{12} = k_{21}$. If $k_{iso} \gg k_{syn}$, then two essentially independent reactions occur—monomer *d* homopolymerizes and behaves as if no monomer *l* was present in the system, the same applying to monomer *l*. The resulting polymer forms a racemic mixture of all *d* and all *l* polymers if the rate of termination is considerably greater than the rate of a *d-l* or *l-d* addition. If the reverse is true, then a block polymer is produced consisting of blocks of *d* and blocks of *l* units. Apparently such a situation is realized in polymerization of propylene oxide, a monomer containing an asymmetric carbon atom. According to Price[33] who studied this reaction there are two types of catalyst. The reaction catalyzed by sodium hydroxide leads to a random polymer, i.e., in such system $k_{iso} \sim k_{syn}$, while a heterogeneous catalyst described in Dow's patent[12] leads to a racemic mixture of all *d* and all *l* polymers. Of course, both catalysts produce an all *d* polymer, if a pure *d* monomer is used in the reaction, and an optically active polymer is then formed.

Another example of an asymmetric synthesis in addition polymerization has been provided recently by the work of Beredjick and Schuerch.[5] Starting with methacrylic acid esterified with an optically active alcohol they introduced a bias in the polymerization, and consequently one configuration of the newly formed asymmetric carbon has been slightly more favored than the other. It should be realized, however, that in a homopolymer the pertinent carbon atoms are not asymmetric but rather pseudoasymmetric, and hence, even if one particular configuration were maintained throughout the polymeric chain, the resulting product would still remain optically inactive (see Frisch, Schuerch, and Szwarc[20]). To introduce optical activity in the polymer, Beredjick and Schuerch resorted to the following strategem. An alternative polymer of their optically active monomer and maleic anhydride was synthesized, and thus a product containing truly asymmetric carbon atoms located along the chain was formed. Splitting off the optically active alcohol left them eventually with a polymer exhibiting

a minute but still detectable optical activity.* This proved that a preference for one configuration was introduced by the influence of an optically active substituent present in the monomer.

Polymerization of butadiene and of isoprene confronts us with still another configurational problem. The addition may take place in either the 1,2 or 1,4 positions (with an additional possibility of 3,4 addition in the case of isoprene), and, moreover, in the 1,4 addition the new unit may acquire a *cis* or a *trans* configuration. It is known that by proper choice of a catalyst and by judicious adjustment of polymerization conditions processes can be developed which yield polymers of high stereospecificity, namely all 1,4 *cis*, all 1,4 *trans*, all 1,2 isotactic, or all 1,2 syndiotactic polymers.

It was pointed out in previous paragraphs that in ionic or coordination polymerization one might deal with several types of growing ends in equilibrium with each other. The reactivity and the selectivity of each type of end might be different, and since the equilibrium is of a dynamic character, the growing end of type A may be changed into type B and thus continue its growth before termination. Such a phenomenon probably occurs in the anionic polymerization of methyl methacrylate carried out in a mixture of two solvents, a hydrocarbon and an ether. It was mentioned earlier that the reaction carried out in an ether favors syndiotactic placement, while isotactic placement is favored in the hydrocarbon solvent.[18] If the reaction is carried out in a mixture of these two solvents neither of these two types of polymer exclusively nor a mixture of them is obtained.[18] The explanation of the behavior exhibited in the mixed solvent might be that two growing centers are present. One of these, which will be called center A, is well solvated by ether and therefore favors syndiotactic placement, while the other one, center B, is poorly solvated by a hydrocarbon and therefore favors isotactic placement. Since A and B are in dynamic equilibrium a syndiotactic polymerization initiated by A will continue as an isotactic polymerization when A is transformed into B. Conse-

* Fortunately, the optical activity of the polymer freed from the optically active substituent was of the opposite direction than that of the original polymer. Hence, the observed effect cannot be due to a trace of alcohol which was not removed in the hydrolysis.

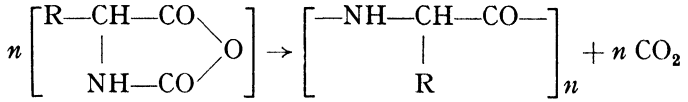
quently, the polymer obtained is a block polymer consisting of syndiotactic and isotactic blocks, the latter being composed of all *d* or of all *l* units.

A stereospecific center is rarely completely specific, enzymes being one of the few examples where complete specificity is approached. Since different modes of addition probably have different activation energies, the specificity would be expected to increase with decreasing temperature. This is usually confirmed by experiment, although sometimes the reverse is observed. For example, stereospecific catalysts which yield all *cis* polybutadiene produce a product of a higher *cis* content at lower temperatures, but the catalyst which yields all *trans* polybutadiene is more specific the higher the temperature within a certain temperature range.[31] It is possible that the following mechanism explains this behavior. There are two growing centers present in this system which are in equilibrium with each other, e.g., a center containing associated ion pair which dissociates into isolated ions, the degree of dissociation increasing at higher temperatures. If the former has a low specificity and the latter is highly specific favoring all *trans* polymerization, then increase in temperature would lead to increase in *trans* content of the product.

All of these examples explain why such a variety of phenomena are observed in ionic or coordination polymerization. What we need to understand is the cause which gives to a particular center this or other properties, e.g., why dissociation into isolated ions leads to one and not another change in the reactivity and the specificity, how changes in solvation shell change the behavior of the growing center. This whole field is still uncharted, and calls for a thorough academic research.

Polymerization of amino acid *N*-carboxyanhydrides to polypeptides exemplifies another interesting reaction which exhibits a number of unusual features. This reaction has been, and is still being, vigorously investigated by several independent groups of workers, and some recent results are particularly intriguing and deserve a detailed discussion.

The polymerization of amino acid *N*-carboxyanhydrides is described by the following overall equation,



The reaction may be initiated by basic reagents like primary, secondary, and tertiary amines, and strong bases such as sodium hydroxide and sodium ethoxide, which produce a high molecular weight material with a degree of polymerization exceeding 1000 under favorable conditions. Furthermore, the polypeptide produced takes the configuration of an α helix when sufficiently high molecular weight is attained. The kinetics of the polymerization initiated by a strong base was studied thoroughly by Blout and his colleagues.[23] Apparently, in this reaction the rate of propagation is very different for an oligomer than for a high-molecular weight polymer.

We are used, on the whole, to the idea that the rate constant of propagation is independent of the degree of polymerization. This certainly is the case when the degree of polymerization is high, since the environment of an active end is then unaffected by any increase in the chain length. On the other hand, if one deals with a dimer growing to a trimer, or with a trimer growing to a tetramer, one might expect a perceptible difference in the rate constant of these additions if compared with the k_p of a polymer of appreciable length. I believe, however, that even in this case the change in k_p is minute since there is negligible interaction between the growing end and centers separated from it by 3 or more carbon atoms. The validity of the simple copolymerization scheme presents the most obvious proof for this assumption.

The situation might be very different if a polymer takes a helical configuration during the process of its growth. Under these conditions, the nth unit (n being the number of monomeric units per turn of the helix) is actually one of the nearest neighbors of the growing end, and if they interact strongly the nature of the nth unit may profoundly influence the rate of the polymerization. Of course, the helix cannot be formed if the degree of polymerization is less than n, and probably at least $2n$ units are required to form a stable helix. Hence, the growing molecule has to attain some

minimum size before its active end acquires the permanent characteristics which are then maintained in the long chain polymer. It appears that in Blout's experiments such an end grows much faster than the end characterizing the low molecular weight polypeptide, and his kinetic results may be explained on this basis.

The interactions leading to a helix formation may give rise to several phenomena. For example, by using suitable solvents and working at appropriate temperatures one can destroy the helix and form a random coil. Such a change might affect profoundly the rate of polymerization, and if it takes place abruptly in a narrow temperature range (or in a narrow range of solvent composition) the rate of the reaction would then be a discontinuous function of temperature (or of solvent composition). A system might be also found in which an equilibrium between the random coil and the helix is established for a wider temperature range. If the rate of propagation of the former is slower than that of the latter, and if the increasing temperature favors the formation of the random coil, then the propagation reaction might exhibit an apparently negative activation energy.

The structure of the chain, i.e., whether it is a helix or a random coil, might influence not only the rate but also the stereospecificity of the growing polymer. For example, it is plausible to expect that in normal vinyl polymerization helix formation might favor specific placement, say isotactic, while either placement would be approximately equally probable in a growing random coil. Formation of a helix requires interaction between polymer segments, and this intramolecular interaction is enhanced by bad solvents particularly those which precipitate the polymer.

These ideas might be used to explain the interesting results obtained recently by Williams *et al.*[53] These workers observed formation of crystalline polystyrene when the reaction was initiated by triphenyl methyl potassium (or some other potassium metallo-organic compounds) in a hexane solution, but an amorphous polymer was formed in benzene. They point out that the catalyst is soluble in benzene but insoluble in hexane, and suggest that the heterogeneity of the catalyst is responsible for the results. Although this might be the case, an alternative explanation could be advanced.[42a]

The polymer precipitates in hexane and consequently a helix might be formed if an isotactic (or a syndiotactic) placement occurred a few times in succession. Such a helix would favor continuation of the same type of placement which obviously should be energetically most favorable, and consequently the process would lead to the formation of a crystalline polymer. Of course, the nature of the gegen ion and of the solvent is still important in determining the stereospecificity of the growing center. For example, in Williams' experiments triphenyl methyl sodium did not produce the crystallinity which was observed when the polymerization was initiated by triphenyl methyl potassium.* This might indicate that in this particular case increase in the cationic size favors greater specificity. Since the effective size of an ion is increased by solvation, one might also expect that replacing hexane by a better ion solvating agent like benzene should increase the specificity. Experimental findings, however, contradict this expectation and suggest that the effect of benzene is not due to its ability to solvate the cations but rather to its power to dissolve the polymer and destroy the helical structure.

Although the explanation advanced might not apply to the specific case investigated by Williams, it brings to light an interesting question, namely whether the precipitation of a polymer during its growth affects the stereospecificity of the reaction. This problem needs further experimentation and a careful examination of polymers formed under these conditions.

V. TERMINATION

The termination step of a polymerization involves a reaction which destroys the activity of the growing end and thus leads to cessation of its growth. The resulting polymeric molecule is frequently referred to as a dead polymer. If the activity of a growing chain is transferred to another molecule, the process is referred to as chain transfer; if it is lost entirely, a normal termination step is involved.

In radical polymerization the normal termination occurs by

* Triphenyl methyl sodium did not even produce crystallinity in hexane in which triphenyl sodium is also insoluble.

interaction between two growing radicals. This destroys the radicals either by combination or by disproportionation. Many investigations were carried out to determine the relative extents of combination and disproportionation in the termination step. Most of these studies suffered from a common difficulty; namely, the conclusion was arrived at by comparing the experimentally determined molecular weight of the polymer with the number of fragments derived from an initiator or from a chain transfer agent. Hence the greatest spread expected in the experimental results would be a factor of 2, and in view of the experimental difficulties in determining number average molecular weight of a high polymer this is hardly sufficient for making a reliable distinction between recombination and disproportionation.

An interesting solution for this problem was found by Bamford *et al.*[2] An initiator containing carboxylic groups was used in polymerization. The polymer produced was expected to be monofunctional, i.e., to contain only one carboxylic group per chain, if the termination occurred by disproportionation. It would be, however, bifunctional, i.e., it would possess two carboxylic groups per chain, if recombination took place, The product obtained with this initiator was reacted then with a bifunctional reagent which linked together two carboxylic groups. As a result of this reaction, the molecular weight of a monofunctional polymer could increase by a factor not greater than 2, while an enormous increase in molecular weight might be expected in a bifunctional polymer. Hence, one may clearly distinguish between polymers formed by disproportionation or recombination.

The termination of radical polymerization cannot be prevented under normal conditions. This would be possible only in a polymerization initiated in rigid media, assuming that no chain transfer occurs, or if the radicals are trapped, for instance, by precipitation of the polymer during the process of its formation. Both methods have been used, and indeed the termination was considerably slowed down or even prevented permanently. However, such systems are of little value for synthesizing polymers according to a preconceived pattern.

Termination of carbonium ion polymerization may result from

any of the following three reactions. Whenever the gegen ion can form a stable bond with the carbonium ion, the recombination of these two ions leads to a termination of the polymerization. For example, let us consider polymerization initiated by HCl. The recombination of Cl^- ion and carbonium ion is feasible and leads to formation of a stable C—Cl bond, and, as a matter of fact, this process might be so fast that no polymer would be formed in the reaction. Hence, one must choose a system in which the recombination of ions is hindered if a high molecular weight polymer is to be formed. Solvation of ions offers a means for hindering their recombination, and indeed a polymer may be formed by HCl initiation if the reaction is carried out in a good solvating solvent like nitrobenzene.

A clear illustration of this principle is found in the polymerization of styrene initiated by trifluoroacetic acid and investigated in our laboratories.[44] A dropwise addition of styrene to trifluoroacetic acid leads to instantaneous formation of a polymer (mol. wt. $\sim$20,000–30,000). On the other hand, a very slow addition of trifluoroacetic acid to styrene yields no polymer. At first these results seem to be paradoxical. In the first experiment a small amount of monomer is introduced into a great excess of initiator and usually these conditions favor the formation of a low molecular weight material while actually a high molecular weight polymer was formed. On the other hand, a high molecular material could be anticipated in the second experiment when small amount of initiator is dispersed in a great excess of monomer. Here, however, no polymer was formed! Consideration of the solvation of the gegen ion rationalizes these observations. In the first experiment the trifluoroacetate ion is hydrogen bonded to trifluoroacetic acid and this association makes it less available for termination and thus allows the carbonium ion to grow. In the second experiment the trifluoroacetate ion is poorly solvated by the hydrocarbon, hence its recombination with the carbonium ion is not hampered and thus the termination takes place before a polymer could be formed.

There are gegen ions, e.g. $(BF_3OH)^-$ ion, which cannot form a bond with a carbonium ion. Protogenic acids yielding such gegen ions are on the whole better initiators of carbonium ion polymeri-

zation and give polymers of higher molecular weight than the acids of the previous class. The termination of polymerization for such initiators usually involves a proton transfer from the last but one carbon of the growing chain to the gegen ion with simultaneous regeneration of the acid and formation of the terminal C=C bond. One expects, therefore, that the termination would be slower as the strength of the acid increases, or, in other words, the proton affinity of the gegen ion decreases. This will be reflected, of course, in the molecular weights of the respective polymers.

One might anticipate that this type of termination in carbonium ion polymerization might be minimized or even completely avoided by complexing the gegen ion with a suitable electron-seeking molecule. Experiments designed with this purpose in mind are presently underway in our laboratories. If the termination could be prevented we would be able to synthesize "living" carbonium ion polymers.

The third mode of termination which occurs in some carbonium ion polymerizations involves rearrangement of the active carbonium ion into an inactive one which cannot continue the propagation. These reactions can be avoided to a great extent by working at sufficiently low temperatures, and on the whole, they only contribute significantly to the termination reaction in a few systems.

In anionic polymerization, as in carbonium ion polymerization, termination does not involve bimolecular reaction between two growing chains. Neither can recombination of ions lead to termination, since a carbon-metal bond is highly polar, in the case of alkali metals frequently completely ionized, and in every case very reactive. The termination step leading to the formation of a terminal C=C double bond is not too probable. This reaction involves the formation of a metal hydride, and this does not contribute greatly to the driving force. Consequently, such a termination is observed at higher temperatures only and it is probably more common in coordination polymerization where the metals involved are less electropositive.

The most common mechanism of termination in anionic polymerization involves reactions with solvents or with impurities. For

example, anionic polymerization may be carried out in liquid ammonia as a solvent, and then proton transfer from an ammonia molecule to the growing anion terminates its growth, although it need not terminate the reaction[22] (NH_2^- ion might start growth of another chain). Similarly, reaction with water or with any other proton donating substance leads to termination. However, if the reaction is carried out in a solvent which does not react with carbanions, and if impurities are rigorously excluded, no termination takes place and polymers are formed with permanently active ends which are always potentially capable of continuing their growth. It has been proposed to refer to such polymers as "living" polymers[42, 43] in contradistinction to dead polymers formed in termination processes.

The lack of termination does not lead to infinite molecular weight. In any polymerizable system, there is a finite amount of monomer, and if some growing centers are formed which do not lose their activity then the number average degree of polymerization is given by the ratio (amount of monomer)/(number of growing ends) assuming each polymeric molecule possesses one growing end. Of course, if polymeric molecules possess two growing ends per chain then the degree of polymerization is given by 2(amount of monomer)/(number of growing ends), and this formula is generalized for polymers possessing still greater numbers of growing ends per chain.

This relation was verified experimentally[7, 49] and it was shown that the degree of polymerization in a system containing "living" polymers is independent of concentrations of initiator or monomer and of temperature. Furthermore, if all the growing centers were formed in a time much shorter than the time of polymerization, a Poisson molecular weight distribution would be obtained. Indeed, by using this technique samples of polystyrene were obtained for which $\bar{M}_w/\bar{M}_n = 1.04$.

It is appropriate to mention here an alternative method for synthesizing monodispersed polymers which was developed by Zimm.[57] Emulsion polymerization is initiated by flash photolysis. The second flash terminates the polymers initiated by the first one, starting on a new chain to be terminated by the third flash, and

so on. The polymeric molecules grow in the interval between the two flashes. The method is particularly useful in obtaining very high molecular weight material, although it is contaminated by a small amount of very low molecular weight polymer.

Lack of termination opens up a great number of interesting possibilities. For example, although no termination takes place in the reaction, the "living" polymers can be "killed" eventually by introducing a suitable killing agent. There are, of course, a number of killing reagents which can be used in this reaction, and thus polymers with desired end groups can be formed. For example, addition of water or of any other proton donor places a hydrogen atom on the end of the polymer, addition of carbon dioxide introduces a terminal carboxylic group, addition of ethylene oxide yields a hydroxylic terminal group, and addition of carbon disulphide gives a thiocarboxylic group.

These reactions are particularly useful if a polymer with two (or more) "living" ends is formed, since the bifunctional (or polyfunctional) polymer formed may be then used to synthesize block polymers via condensation reactions. Interesting examples of such materials were obtained; and the usefulness of this technique is amplified by the fact that each block can be made uniform in size.

Another problem which may be now investigated with great ease is the effect of the end groups on polymer properties, particularly on the thermodynamic, hydrodynamic, and mechanical properties. A batch of "living" polymers can be divided into several portions, and each of them "killed" by a different reagent. Thus, polymers are obtained which are identical in their composition, molecular weight, molecular weight distribution, and differ only in the character of their end groups. Comparison of such polymers permits therefore assessment of the effect of the end group on their properties. Using this technique we have found that polymers possessing $-COO^-Na^+$ end groups are considerably more associated than those with $Ph-\underset{|}{CH}^-$, Na^+ end groups, and a still greater degree of association characterizes polymers having $-CH_2O^-Na^+$ groups.[8] Similarly, we were able to detect both the intra- and the intermolecular association of polymers containing two carboxylic groups per chain.[48]

Still another advantage of "living" polymers lies in the possibility of synthesizing block polymers according to a preconceived pattern. The following example clearly illustrates this idea. We found that "living" polystyrene continues to grow by adding

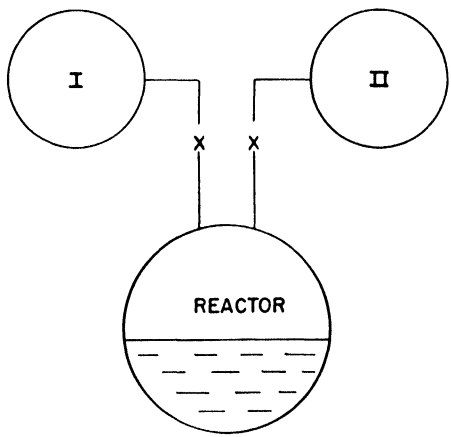


Fig. 3.

butadiene if this monomer is introduced into the system, and conversely "living" polybutadiene adds styrene monomer. Polymerization of these two monomers may be carried out in a system such as that depicted in Fig. 3, and this reaction may be performed in several ways. Equimolecular amounts of styrene and butadiene are held in containers I and II respectively, and the initiator is present in the reactor *R*. Styrene is then introduced and after polymerization is complete the butadiene is added. The resulting polymer molecules consist of two equal blocks, one of styrene and one of butadiene, i.e.,

$$S \ldots SB \ldots B$$

The experiment can be repeated with the modification that half of the styrene is added, followed by half of the butadiene, then the remaining styrene followed by the remaining butadiene. The product obtained in this experiment has the same composition and the same molecular weight as the previous product, but the distribution of monomers would be different; namely,

$$S \ldots SB \ldots BS \ldots SB \ldots B$$

The experiment in which one quarter of styrene is added followed by one quarter of butadiene, etc. yields

$$S \ldots SB \ldots BS \ldots SB \ldots BS \ldots SB \ldots BS \ldots SB \ldots B$$

and so forth. Hence, one can produce a whole spectrum of products all identical in respect to their composition and molecular weights but differing in distribution of monomers along the chain. Their properties as a function of monomer distribution may then be investigated.

Formation of block polymers is not limited to hydrocarbon monomers only. For example, "living" polystyrene initiates polymerization of methyl methacrylate and a block polymer of polystyrene and of polymethyl methacrylate results.[34] However, methyl methacrylate represents a class of monomers which may be named a "suicide" monomer. Its polymerization can be initiated by carbanions or by an electron transfer process, the propagation reaction is rapid but eventually termination takes place. Presumably, the reactive carbanion interacts with the methyl group of the ester according to the following reaction

$$\sim\!\sim\!\sim CH_2\!-\!\underset{\displaystyle COO-CH_3}{\overset{\displaystyle |}{C}}\!-\!(C^-H_3) \longrightarrow \sim\!\sim\!\sim CH_2\!-\!\underset{\displaystyle COO^-}{\overset{\displaystyle |}{C}}(CH_3)_2$$

and a stable ion is formed which is unable to continue the propagation. Since the propagation is very rapid indeed, a complete conversion of methyl methacrylate to a polymer can be easily attained by anionic polymerization, but the product loses its reactivity within a few seconds after completion of the reaction and addition of more monomer does not lead to further polymerization.

Ethylene oxide and its analogues or cyclic silicons like

$$\left[\begin{array}{c} CH_3 \\ -SiO- \\ CH_3 \end{array}\right]_4$$

represent another interesting class of monomers, polymerization of which may be carried out without termination. These are, indeed, the classical examples of polymerization without termination which were known a long time ago.

Polymerization of these monomers can be initiated either by an

electron transfer process or by any strong base. Hence, their addition to "living" polystyrene or polybutadiene yields corresponding block polymers, as was indeed demonstrated in our work.[35] These block polymers contain, e.g., polystyrene followed by polyethylene oxide and not *vice versa*, since the CH_2O^- ion is not sufficiently reactive to initiate polymerization of styrene, while the polystyryl$^-$ ion does initiate polymerization of ethylene oxide. Nevertheless, a polyblock polymer can be obtained by initiating, e.g., polymerization of ethylene oxide by a "living" polystyrene possessing two active ends, and then by condensing the resultant terblock polymer by means of diisocyanate or another suitable reagent.

Acrylamides represent still another interesting class of monomers.[6] Their anionic polymerization may be initiated by strong bases, like, e.g., amides. The growing chain contains the unit $—CH_2—CH^-—CO—NH_2$ and intramolecular proton transfer competes efficiently with its carbanionic growth. Since the rearrangement

$$\sim\sim\sim CH_2—CH^-—CO—NH_2 \longrightarrow \sim\sim\sim CH_2—CH_2—CO—HN^-$$

takes place very rapidly, the addition occurs at the NH^- ion and not at the carbanion. The resulting polymer is therefore a polyamide of a nylon type.

Finally, an interesting example of anionic polymerization has been observed in our laboratories. Anionic polymerization of styrene in tetrahydrofuran solution is a very rapid reaction, the polymerization being complete in a few seconds. Polymerization initiated by triphenyl methyl sodium seems to occur just as rapidly, in spite of the fact that triphenyl methyl sodium is a slow initiator. This slow initiation produces a higher molecular weight product than that expected from the ratio monomer: catalyst since only a fraction of the initiator actually reacts. The rapid reaction, however, is followed by a slow process during which the viscosity of the solution gradually increases until finally a solid mass is formed. This process takes from half an hour to an hour, the red color of the solution of "living" polymer remaining unchanged. The molecular weight of the final product is of the order of 10^6–10^7.

These experimental results indicate that styrene originally present in the solution polymerizes completely in a few seconds, but

that the polymer formed slowly polymerizes further, thus increasing the molecular weight and the viscosity. The following explanation might account for this phenomenon. The original "living" polystyrene is composed of chains having a triphenyl methyl group on one end and a benzyl carbanion on the other, and therefore the following reaction might be possible

$$\begin{array}{l}\overline{C}H\sim\sim C(Ph_3)\\ |\\ Ph\end{array} + \begin{array}{l}\overline{C}H\sim\sim C(Ph_3)\\ |\\ Ph\end{array} \longrightarrow \begin{array}{l}CH^-\sim\sim CH\sim\sim C(Ph_3)\\ |\qquad\quad |\\ Ph\qquad Ph\end{array} + CPh_3^-$$

i.e., a benzyl$^-$ ion replaces the triphenyl methyl moiety and a triphenyl methyl$^-$ ion is formed. The greater stability of the latter ion as compared with the former provides the driving force for the reaction which polymerizes polymeric molecules into greater and greater units.

Lack of termination in a polymerization process has another important consequence. Propagation is represented by the reaction $P_n+M \rightarrow P_{n+1}$ and the principle of microscopic reversibility demands that the reverse reaction should also proceed, i.e., $P_{n+1} \rightarrow P_n+M$. Since there is no termination, the system must eventually attain an equilibrium state in which the equilibrium concentration of the monomer is given by the equation $P_n+M \rightleftharpoons P_{n+1}$. Hence the equilibrium constant, and all other thermodynamic functions characterizing the system monomer-polymer, are determined by simple measurements of the equilibrium concentration of monomer at various temperatures.

This method was first applied by McCormick[27] and by Bywater and Worsfold[11] to the system α-methylstyrene/poly-α-methylstyrene, and the free energy, entropy and heat of polymerization as well as the ceiling temperature were determined. Similar studies concerned with the system styrene/polystyrene are being carried out in our laboratories.

The equilibrium between monomer and "living" polymer is dynamic and therefore the molecular weight distribution of the polymer will change with time until the equilibrium distribution is reached. This is a peculiar process in which the amount of polymer present in the system, as well as its number average molecular weight is constant. This means also that, the number of polymeric

molecules present in solution remains constant, although the weight average molecular weight varies with time. It was shown by Brown and Szwarc[10] that the equilibrium molecular weight distribution in such a system is the "most probable" molecular weight distribution, and the kinetics of the approach to the equilibrium distribution was fully discussed.

The formation of "living" polymers enables uniformity to be obtained in many systems where usually a random distribution prevails. Polymerization usually yields a product with a certain molecular weight distribution, but the "living" polymer technique permits one to produce practically monodispersed systems. (As mentioned previously, samples of polystyrene were obtained with $\bar{M}_w/\bar{M}_n = 1.04$.) Conventional techniques leading to the formation of polyblock polymers yield a mixture of molecules, possessing variable numbers of blocks of variable sizes, often mixed with the respective homopolymers. Using "living" polymers one is able to obtain monodispersed material where each molecule has the same number of blocks, each of the required size, arrayed according to a preconceived pattern. Moreover, complete exclusion of homopolymers is achieved. Conventional techniques can be used to obtain star-shaped polymers—molecules possessing several branches radiating from a common center. Such material is polydispersed, the branches have variable sizes and a mixture of molecules possessing variable numbers of branches is formed. The use of "living" polymers would allow the formation of star-shaped polymers in which all the molecules have the same number of branches, each branch being the same size. The idea is explained by the following two examples which need not be the most practical and which illustrate only some of many variants potentially useful for such a synthesis. $C(P_6H_4Li)_4$ could be prepared and used for initiating the polymerization, the monomer being introduced very slowly into the reaction flask to ensure equally rapid growth of each chain. In this way a polymer is obtained consisting of four branches of equal length radiating from one common center. Alternatively, monodispersed "living" polymers possessing only one active end per molecule could be made to react with a stoichiometric amount of $C(CHO)_4$ and a similar type of star-shaped polymer would be obtained.

Potentialities of these methods are illustrated further by the following proposed experiments.

"Living" polymers of monomer A possessing one active end per molecule are reacted with

$$CH_2{=}CH{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}\underset{\displaystyle Br}{\underset{|}{CH}}{-}CH{=}CH_2$$

This would lead to a polymer*

$$CH_2{=}CH{-}\underset{\displaystyle A}{\underset{|}{CH}}{-}\underset{\displaystyle A}{\underset{|}{CH}}{-}CH{=}CH_2$$
$$\begin{matrix} A & A \\ | & | \\ A & A \end{matrix} \qquad +2NaBr$$

The polymer is converted into tetrabromide and the latter reacted with another "living" polymer of monomer B. In this way a star-shaped polymer is formed possessing 2 arms composed of A units and 4 arms composed of B units, each A arm and each B arm respectively having a uniform size predetermined by the experimenter.

If monodispersed "living" polymers possessing 2 active ends per chain are reacted with equimolar amount of $CH_2Br{-}CH{=}CH{-}CH_2Br$ a long polymer is formed

$$A\ldots A{-}CH_2{-}CH{=}CH{-}CH_2{-}A\ldots A{-}CH_2{-}CH{=}CH{-}CH_2A\ldots$$

in which the CH=CH groups are spaced at regular distances along the chain. These groups can be reacted with HBr or with Br_2 thus forming reactive centers which could react with another monodispersed "living" polymer made out of monomer B and possessing only one active end per chain. In this way a graft polymer could be synthesized with branches spaced at uniform distances along the main chain and each branch having a uniform length.

Summarizing these speculations one may conclude that the technique of "living" polymers permits to introduce a uniformity and regularity of sizes and spacings in building up polymers of desirable shapes while the conventional techniques lead to randomness of sizes and spacings. It has to be seen what the advantage of these regularities would be.

* Isolated double bonds do not react with "living" polymers.

This work was supported by the National Science Foundation through a Grant (NSF-G2761). This help is gratefully acknowledged.

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NUCLEAR QUADRUPOLE RESONANCE IN IRRADIATED CRYSTALS*

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I. INTRODUCTION

The aim of this report is to discuss in some detail the whole problem of the effect of the action of high energy radiation on solids as studied by quadrupole resonance. This new method of approach has been developed by our group recently, and it now seems desirable to give a full account of this work. Though work has been undertaken on ionic crystals, greater attention has been devoted to molecular crystals, for, in spite of the importance of these, especially as regards their inspiring value in the field of biological systems, they would seem to have been studied less than other

* The research reported in this document has been sponsored in part by the Air Office of Scientific Research of the Air Research and Development Command, United States Air Force, under contract AF 61(514)—1212, through the European Office, ARDC.

solids. The method, which is based on the estimation of the intensity of the quadrupole lines has the advantage of being simple, though it cannot be claimed to be very sensitive. Indeed radiation doses of about 10^6 roentgens are required in order to produce observable changes in intensity. This results from the fact that the imperfections induced are not directly recorded. Their magnitude is deduced from a small intensity difference between the lines corresponding to the unperturbed molecules in the nonirradiated and irradiated compounds. Finally, not all radiations may be studied through this method, and in fact only when they have a small absorption coefficient are observable phenomena produced. This is why only gamma-rays and fast neutrons will be considered here. The characteristic of the method is that it integrates the whole of the imperfections thus produced, and in this lies its main advantage over other methods, though the nature of the new species formed cannot be identified. It seemed to us that careful and systematic observations especially on organic halogen crystals in homologous series might help in the discovery of the laws of radiation resistance. Before going into the details, we would like to describe briefly the principles of quadrupole spectroscopy as regards method and technique. In the course of this report attention will be drawn to unsolved problems and to the direction to be followed for further work.

II. NUCLEAR QUADRUPOLE RESONANCE

The pure quadrupole resonance spectroscopy of solids yields information on the coupling of nuclei to the electrons.[9,16,32] The quantity measured is the nuclear quadrupole coupling constant which is the product of the quadrupole moment (eQ) of the nucleus and the electric field gradient ($q \equiv \delta^2V/\delta z^2$) at the nucleus along the direction z. The applications of the method are restricted to a rather limited class of isotopes, because nuclei with zero or half-unit spins have no quadrupole moment. The energies which correspond to the allowed orientations of the nucleus in the molecular electrostatic field at the nucleus give rise to levels characterized by spacings lying in the radiofrequency region. The actual coupling of the nuclear moment to the field is quantized and the number of

levels depends on the magnitude of the nuclear spin. For instance, the frequency for Cl isotopes for which $I = \frac{3}{2}$ is given by $\nu = \frac{1}{2}eQq/h$. Though the position of the energy levels is determined by electrical forces, the transitions between these levels in the radiofrequency region are dipolar and magnetic. Thus, the sample of the appropriate molecules is placed in the coil of a tuned circuit of a radiofrequency oscillator where it is submitted to the alternating magnetic field. The oscillator is frequency modulated at, say, 100 cycles/sec. When the frequency of the field is equal to the quadrupole resonance, magnetic dipole transitions occur. Each time the resonance line is crossed, energy is absorbed from the oscillator coil, and the amplified signal is observed on an oscillograph and, if useful, recorded after phase detection.

A. Valency Questions

If the field gradient has no axial symmetry, then a more complicated expression is found, involving an asymmetry parameter which is often moderate. In particular, the study of this parameter has been useful for the determination of resonance structures and for the understanding of the bonding in solid iodine. The contribution of each of the molecular electrons to q is given by a relation of the form

$$q = -e \int |\psi_i|^2 [(3 \cos^2 \theta_i - 1)/r_i^3] d\tau$$

where θ, φ, r, are the polar coordinates of the electron considered relative to axes whose origin is at the nucleus and in which the direction $\theta = 0$ lies along the axis of symmetry. From this it may be seen that when the electron cloud surrounding the nucleus is spherically symmetrical, then there is no contribution to q. Since the inner-core electrons are, to a first approximation, of that symmetry, only the valency electrons which have a high probability of being found near the nucleus contribute essentially to the magnitude of q. Among them, the electrons in s orbitals, which are spherically symmetrical too, can make no contribution to q.

However, a p orbital which represents a charge density concentrated along one axis, gives rise to a coupling. Because of the slight penetration of d and f orbits into regions close to the nucleus, it

was found that the contribution to q by d and f electrons may be neglected. It is because the value of q at the nucleus essentially depends upon the p orbitals that the method is valuable for studying the nature of chemical bonds in molecules.* Quantities of the order of magnitude of a few grams are generally required for the spectrum to be observed, so that the method is unfortunately not appropriate for substances which may only be obtained in minute quantities.

B. Resonance Intensity in Mixed Crystals

In addition to the above method, interest has recently been concentrated on measurements of intensity, and has opened up a new way to study defects produced in matter either directly by isomorphous impurities (solid solutions) or indirectly by imperfections induced by high-energy radiation. In the former case, it was first shown by Duchesne and Monfils[17] that the pure quadrupole resonance absorption is decreased in the case of solid solutions in which one of the components acts as an impurity. For instance, minute quantities of p-dibromobenzene ($\sim 10^{-1}$ mole per cent) in mixed crystals with p-dichlorobenzene at room temperature have a measurable decreasing effect on the height of the resonance line corresponding to ^{35}Cl. The effectiveness of an impurity in reducing the quadrupole signal was shown by Monfils and Grosjean[27] to depend on both the difference in volume and the difference in electric dipole moment of the resonant and impurity molecules. The assertion of Michel and Spence[26] who found no evidence for dependence on dipole moment does not seem definitely established because they fail to consider the most noteworthy cases such as that concerned with p-chloraniline which gives in p-dichlorobenzene a much bigger ν_r than any other halogeno-benzenes in spite of the fact that the volumes of NH_2 and Cl are little different. It was shown furthermore[17] that, at least within the range of small concentrations, no appreciable broadening of the lines occurred. In

* Of course there are other contributors to the value of q besides the valence electrons. Additional effects are due to molecular interactions,[22] induced quadrupole moments (Sternheimer, R. M., *Phys. Rev.* **105**, 158, (1957), etc.)

particular Monfils and Grosjean[14,27] derived the formula

$$I/I_0 = e^{-v_r C} \tag{1}$$

for representing the fact. In this equation I_0 and I are respectively the line intensities corresponding to the pure compound and the solid solution. C is the molar concentration, and v_r, which is associated with each impurity molecule, represents the volume (using the volume of the main constituent as unity) in which q characterizing the main molecule is sufficiently perturbed by that impurity molecule to displace the corresponding part of the resonance line beyond the wings of the absorption line. It is clear that such a definition adopted for v_r assumes an unexpected form for the expression of Δq in terms of the distance to the perturbed point: an abrupt fall at the boundary of the v_r volume. It is therefore not surprising if the relation suggested is only valid, as observed, within the range of low concentrations. It is interesting to notice here that the work of Woessner and Gutowsky[33] on the special case of mixed crystals has demonstrated that the relaxation times T_1 and T_2 are practically unaffected by the impurities in the range of 0.5 to 20 mole per cent. It is therefore to be concluded that we are here confronted with a pure case in which the whole line intensity changes are due to the stress field provoked in the crystal lattice by impurity molecules and by their electrical properties. Of course several species of impurity may be involved, and then each of them ought to be characterized by its own v_r. However, no multicomponents case has been studied until now. It is worth-while noticing that in some cases an increase of intensity has been observed instead of a decrease. This has been observed in the case of chemically defined compounds such as $CHI_3 \cdot 3S_8$ (CHI_3 does not give any resonance) and in cases of nonisomorphous compounds which nevertheless show a sufficient resemblance as regards crystal lattice like durene and p-$C_6H_4Br_2$,[15] and naphthalene and γ-hexachlorocyclohexane.[13]

III. RESEARCH IN RADIATION CHEMISTRY

It was anticipated from the foregoing results that the method reported might be extended to the study of the damage produced by high-energy radiation (dislocations, induced impurities, etc.) if

the radiation dose was sufficient to produce a quantity of defects, disturbing the crystalline electric field and of the order of magnitude of that observed in mixed crystals. The first experiments which were performed using the radiation of a ^{60}Co source (1.17 and 1.33 Mev) of 200 curies and p-$C_6H_4Cl_2$ as a test compound entirely confirmed this expectation. About 10.3×10^8 roentgens were necessary to decrease by 40 per cent the height of the resonance line of 34.274 Mc/sec at 23°C.[18] In fact, on account of the recording method, the derivative curves of the absorption curves are observed so that the measurements of the height are usually made on these between the points corresponding to the inflection points and to the maximum of the original curve. It is to be noticed that no significant shift in frequency has been observed until now, even for doses which almost annihilate the resonance lines. It would seem that small changes were observed for mixed crystals, but for the rather high concentration of 10 per cent of p-$C_6H_4Br_2$ in p-$C_6H_4Cl_2$.[8]

A. Analysis of the Method

In order to avoid any source of inaccuracy that might arise from the fact that the absolute intensity line cannot be reproduced, on account of the nature of the instruments themselves, the intensity is always measured with respect to that of a standard sample. Let us suppose that I_0/I_s represents the ratio of the line height of the compound which is to be irradiated to that of the standard sample. After irradiation, the new ratio has become I/I_s. On eliminating I_s then we get I/I_0 which represents the intensity change on going from the irradiated to the nonirradiated compound. Suppose now that the concentration of the new chemical species or, in general terms, imperfections induced by irradiation be proportional to the amount of radiation absorbed in the sample. Then the relation which represents the impurity effect may immediately be written as follows:

$$I/I_0 = e^{-v_r kD} \tag{2}$$

where k is a coefficient of proportionality and D the dose involved. In other words, $\log I/I_0$ was expected to vary linearly with the dose, which has been verified in all the cases studied for doses

which leave a residual intensity of about 30 per cent.[10,18] Beyond the threshold value, the intensity influence of the dose is much less pronounced, a fact which will be discussed in Section VIII. We will now examine to what extent the validity of the law proposed may be controlled by independent experiments.

With this in view, cryoscopic measurements have been made on γ-$C_6H_6{}^{35}Cl_6$ irradiated with gamma-rays of ^{60}Co. The choice of this substance has been made only because it furnishes at the same time a good resonance spectrum, a relatively high sensitivity to irradiation, and finally because its cryoscopic constant was known (19 degrees mole^{-1}/1000 g). From this it has been shown that the molar concentration of impurities for a dose of 7.4×10^6 roentgens amounts to 5.7×10^{-3}. From Eq. 1, v_r may be deduced to amount to about 100, which is of the order of magnitude of the values found by Monfils and Grosjean[27] in their study of the impurity effect. On the other hand, p-dichlorobenzene has been submitted to sublimation in vacuum after irradiation with a dose of 5×10^8 roentgens. In this manner, it has been possible to separate an amount of heavy impurities corresponding to a molar concentration of about 10^{-4}. From this $v_r = 1400$ may be deduced. This value seems much too high and therefore indicates that polymers do not predominate among the impurities induced. It is to be noted that most of the lightest impurities have been removed along with the vapor of p-$C_6H_4Cl_2$.

It is now quite clear that the method is well suited for the type of research planned.

B. Scope of Research

We have limited our investigations to the action of gamma-rays and fast neutrons on aromatic, alicyclic, aliphatic, and ionic compounds. The absorption coefficients for these types of radiation have an order of magnitude of 10^{-1}/cm which is particularly adequate. Shallow penetrating radiations would only alter the superficial layers and would obviously not be able to affect the intensity of the quadrupole line substantially. This is for instance the case for ultraviolet light which has been shown to be unable to produce any effect on the resonance line of iodoform ($CHI_3 \cdot 3S_8$)

in spite of its photochemical reactivity in surface.[13] The interest of the study of halogen organic compounds not only lies in the fact that homologous series may be considered; there is also the advantage that their radiation behavior is already known in solution and in the liquid state, so that comparisons will be possible. The aim of the research here developed is an understanding of radiation resistance with its implications such as post effects and oxygen effects.

C. Radiation Resistance to Gamma-Rays

Not only are quantitative data on radiation resistance rare, especially for the solid state, but the origin of the big differences in radiation resistance which characterize the organic molecular crystals is not well understood in spite of the theoretical interest and of the considerable practical importance of the problem. Though the expression "radiation resistance" is of wide usage, its meaning is not without ambiguity because, in general, it does not denote the total damage produced but only the changes in certain physical properties with radiation dosage, or the total yield (G) related to some particular transformations. It is worth-while noticing here that a recent investigation related to the problem of impurities in the case of nuclear magnetic resonance by Bloembergen[3] concluded that the quadrupole effects (this concerns the fine structure) are expected to be more pronounced than the magnetic effects. It is therefore obvious that pure quadrupole spectroscopy is the best method. In cases where no direct transition can be observed the fine structure in nuclear magnetic resonance may be usefully substituted. On the other hand, it appears that it would be advantageous to complete quadrupole spectroscopy by electron paramagnetic resonance in order to be able to detect among the different kind of imperfections those related to the presence of paramagnetic centers.

Now the main point is to define what we call radio resistance. According to Eq. 2 we could conventionally adopt as a measure of it the amount of radiation needed to be absorbed to produce a fixed value for I/I_0 or correspondingly for $v_r C$ or $v_r kD$. To achieve accuracy in the measurements and to assure the validity of the law involved, the value of 0.6 for I/I_0 has been chosen, which cor-

responds to a decrease of the line intensity by 40 per cent. Since v_r represents the intensity of the strain which a type of imperfection is able to produce in the crystal, it seems reasonable to express the damage produced by $v_r C$ and not by C which, on the other hand, cannot yet be estimated with any degree of accuracy.

It is to be anticipated, and this will be in fact confirmed experimentally, that post effects may be followed in the same way.

(*1*) γ-$C_6H_6{}^{35}Cl_6$. The quadrupole spectrum of γ-hexachlorocyclohexane contains six lines. The line located at 36.379 Mc/sec (23°C) has been chosen and the dose needed to decrease its intensity by forty per cent was about 7.4×10^6 roentgens.[20]

When $\log I/I_0$ is plotted against D, a straight line is obtained in a rather large region (4×10^6 to 4×10^7 roentgens) as in all the cases which will be handled here. No post effect was observed. Such a phenomenon has only been detected for $CHI_3\cdot 3S_8$ which will be studied in a next paragraph.

(*2*) p-$C_6H_4{}^{35}Cl_2$. The line located at 34.274 Mc/sec (23°C) was considered and the forty per cent dose was found to be about 13.3×10^8 roentgens.[10,18,19] No post effect was detected.

(*3*) p-$C_6H_4{}^{79}Br_2$. The line located at 267.62 Mc/sec was considered, and the forty per cent dose was about 0.36×10^8 roentgens.[10]

(*4*) p-$C_6H_4{}^{127}I_2$. The forty per cent dose corresponding to the line located at 276.38 Mc/sec was about 1.8×10^8 roentgens.[10]

(*5*) $C_6{}^{35}Cl_4(OH)_2$. The spectrum presents a doublet structure. The resonance line located at 36.744 Mc/sec was considered. The forty per cent dose is about 20.8×10^8 roentgens.[13]

(*6*) o-$C_6H_4{}^{127}I(OH)$. The forty per cent dose amounts to about 3.30×10^7 roentgens[13] (resonance line considered located at 277.670 Mc/sec).

(*7*) p-$C_6H_4{}^{127}I(OH)$. The forty per cent dose is about 3.63×10^7 roentgens[13] (resonance line located at 271.132 Mc/sec).

(*8*) p-$(C_6H_4)_2{}^{79}Br_2$. Four lines corresponding to ^{79}Br were recorded in p-dibromodiphenyl. The components of the fine structure which have been measured at 23°C have frequencies at 264.095, 265.960, 267.096, and 267.816 Mc/sec. Only the line located at 267.816 Mc/sec was considered. The forty per cent dose is about 5×10^8 roentgens.[13]

(*9*) $CH^{127}I_3 \cdot 3S_8$. The forty per cent dose is about 1.9×10^8 roentgens[13] (resonance line located at 303.435 Mc/sec). The intensity of the resonance line does not remain unaffected after irradiation, and this post effect is dependent upon dose and temperature.

(*10*) $Na^{35}ClO_3$. The forty per cent dose is about 0.34×10^8 roentgens[13] (resonance line located at 29.932 Mc/sec).

On the basis of these results, the relative scale of radiation resistance of aliphatic, alicyclic, aromatic, and ionic solid compounds may be immediately deduced. Table I summarizes these data including the G values, which have been obtained on assuming for v_r an average value of 200.

TABLE I. Radiation Resistance to Gamma-Rays

Compounds	Dose in 10^8 r	Rel. rad. resist. to γ-rays[a]	Dose in ev/ molecule[b]	G[c]
γ-$C_6H_6Cl_6$	0.074	1	0.2	1.4
C_6Cl_6	16.7	225	47	0.005
p-$C_6H_4Cl_2$	13.3	180	20	0.01
p-$C_6H_4Br_2$	0.36	5	0.8	0.3
p-$C_6H_4I_2$	1.8	25	5.5	0.05
o-$C_6H_4I(OH)$	0.33	5	0.6	0.43
p-$C_6H_4I(OH)$	0.36	5	0.7	0.39
p-$C_6Cl_4(OH)_2$	20.8	280	52	0.005
p-$(C_6H_4)_2Br_2$	5	65	15.6	0.02
$NaClO_3$	0.34	5	0.3	1.0
$CHI_3.3S_8$	1.9	25	17	0.01

[a] The values given here do not take into account the rather weak changes in the absorption coefficients on going from one compound to the other.

[b] It is known that one million roentgens liberates 0.06×10^{21} ev per gram of water.

[c] Number of molecules transformed per 100 ev.

IV. DISCUSSION OF THE RESULTS

Halogenated derivatives of the same kind are much more radiation resistant for aromatic than for alicyclic compounds. The resulting order is aromatic > ionic > alicyclic. Even when the

number of chlorines is constant as in the molecules $C_6H_6Cl_6$ and C_6Cl_6, no essential change with respect to this rule is observed. On the other hand, the accumulation of chlorine on an aromatic cycle (p-$C_6H_4Cl_2 \rightarrow C_6Cl_6$) does not seriously modify the radiation resistance, a characteristic which was also found in the liquid state.[4] The special resistance of aromatics is already well known for the gaseous and liquid systems.[7] According to estimations made for pure liquid compounds such as cyclohexane and benzene irradiated with 1.5 Mev electrons the 100 ev total yield is approximately ten times greater in the former case than in the latter. It is to be remarked that the action of gamma-rays of ^{60}Co and of 1.5 Mev electrons is expected not to be very different. Indeed the projected primary electrons have in this case an average energy of about 600 Kev[26] which is of the same order of magnitude as for the electrons here considered. In the gas state α particles only give a ratio of about 2 to 1. Consequently the aromatic effect seems more important in the solid state than in any other; it decreases regularly with the dilution of matter. Since very little information is known on the difference of behavior of varied radiations, this remains in need of confirmation. In the particular case of polymers it was already well known that aromatics are particularly resistant[1] to ionizing radiations.

Substitution of bromine or iodine for chlorine reduces radiation resistance in the benzene derivatives. An anomaly, however, appears in the series in the case of p-dibromobenzene which gives rise to a particularly weak radiation resistance. Let us therefore try to discuss this point in detail. What we should indeed expect is that the proportion of imperfections created by the irradiation would be greater in $C_6H_4I_2$ than in $C_6H_4Br_2$. If, therefore, v_r were to decrease substantially on going from $C_6H_4Br_2$ to $C_6H_4I_2$, then C could easily be greater in the latter case than in the former one. Then the problem is to find a process by which v_r might decrease. An interesting suggestion has been recently made by Depireux.[10] It is well known that p-dichloro and p-dibromobenzenes crystallize in the monoclinic system, whereas p-diiodobenzene corresponds to the orthorhombic one. In both groups, the benzene rings are almost coplanar and the molecular axes are parallel. However, whereas

the spacing between the lattice planes is almost the same in the first group (3.75 A), it is much higher in *p*-diiodobenzene and amounts to 6.21 A.[30] Since it is highly probable that the action of radiation consists, among other things, in the rupture of a CX bond (X = halogen),[7] it is reasonable to suppose that the free halogens tend to migrate in the region between the molecular planes. If so, the strain which they may induce in the crystal depends upon the ratio of the covalent radius of the halogens to the lattice spacing. For the chlorinated and brominated compounds 0.26 and 0.30 are found respectively, whereas 0.20 characterizes *p*-$C_6H_4I_2$. This shows that the strain, or v_r, may be substantially smaller in $C_6H_4I_2$ than in the other compounds which can explain the inversion found. Though it is still impossible to evaluate the importance of this, it is seen that factors of purely crystallographic origin may interfere with molecular structural factors to produce radiation resistance in solids. Parallel researches in the gaseous and liquid states would be very desirable. It may be predicted that the nature of the halogen substitution in these phases would alter the radiation resistance much less.

On going from *o*-iodophenol to *p*-iodophenol there appears to be no significant change in the magnitude of this property. This indicates that the internal hydrogen bond which characterizes the former compound and is lacking in the latter is not influential. Both molecules are much more radiosensitive than *p*-$C_6H_4I_2$, which is presumably to be correlated with the presence of the OH group. Such a behavior is not found in the case of *p*-$C_6Cl_4(OH)_2$ which has about the same radiation resistance as C_6Cl_6. Iodoform, on the other hand, is not to be expected as radiation resistant as $C_6H_4I_2$, but in complexion with sulfur ($CHI_3 \cdot 3S_8$) it becomes of the same order of magnitude. This result seems to indicate that sulfur acts as a good protector. It might therefore be suggested that we are confronted with a mechanism such that a part of the energy absorbed in CHI_3 is finally dissipated by internal conversion in the sulfur. If iodine in CHI_3 has an ionization potential larger than that of sulfur—and this is not to be excluded—then the condition[7] is realized in order that positive charge may be transferred with high probability from the former to the latter component. In order that

this mechanism may be realized it is necessary, according to recent general considerations,[6] that sulfur may depopulate excited states of CHI_3 in less time than is necessary for predissociation decomposition to appear. It might be that the particular coupling of these molecules is favorable to this. It should be most interesting to go further with this question by appropriate methods such as electron paramagnetic resonance which might give the possibility of studying the distribution of the magnetic centres, due to the action of the radiations, between CHI_3 and sulfur.

Finally it is remarkable that among the aromatics themselves, the radiation resistance may vary in the ratio of 3 to 1.

V. TENTATIVE INTERPRETATIONS OF RADIATION RESISTANCE

The projected electrons have a limited range in solids and therefore dissipate all their energy in the medium in which they are produced. Though atomic displacements are not excluded, it may be expected that the energy absorbed is mainly used in ionization and in optical excitations. According to results obtained by Magee and Burton[25] for the gaseous state it appears that in the spectrum of secondary electrons, due to primary electrons of energy of 1 Mev, approximately half the electrons have energies less than 5 ev. Fano's opinion[23] that much energy goes into excitation of optical levels is therefore confirmed. It is to be presumed that these results remain valid for molecular crystals in which the intermolecular forces are weak compared with the intramolecular ones. The fact that aromatic compounds have a particularly great radiation resistance obviously suggested that π electrons are especially concerned in the processes. Their predominant role might perhaps arise from their delocalization. On account of the Franck-Condon principle it is to be expected that ionization or electronic excitation leaves the molecule in highly excited vibrational states, but approximately with an equal amount of energy in the different bonds for π transitions.[5] Consequently, the threshold of energy necessary for bond rupture is much less easily reached than when all the energy is localized in only one bond, as would, for example, occur for σ excitation which perturbs mainly one bond and then selects vibra-

tions of this bond more especially. This conclusion is substantiated in the gaseous phase by photochemical studies of benzene which show that this substance photolyses between 2000 and 1850 A with a low quantum yield.[5]

Now that the high radiation resistance may be understood on the basis of this simple picture, it was interesting to examine the origin of the differences obtained in the group of aromatic compounds themselves. We thought that the degree of delocalization of π electrons might be tested to see if it might be used as the classifying factor. The degree of molecular magnetic anisotropy may be considered as a measure of delocalization. In order to represent it, we have adopted the difference between the value of the principal molecular diamagnetic susceptibility corresponding to the axis normal to the plane and the mean value corresponding to the other axes. For the molecules p-$C_6H_4Cl_2$, C_6Cl_6, and p-$(C_6H_4)_2Br_2$ which have radiation resistances in the ratios 1 : 1.2 : 0.35 values of 1 : 1.4 : 0.3 were found respectively.[2,24,29] The agreement appears to be satisfactory. However, for the last compound, the validity of the result implies that a substitution of chlorine for bromine would not change the radiation resistance essentially. As the influence of the nature of the substituted halogen is largely bound to peculiarities in crystal structure in benzene derivatives, it is to be expected that in other cases, especially for molecules with two benzene rings, the role of halogens tends to vanish. This point remains to be confirmed experimentally.

New data have to be obtained in order to verify to what extent the present results remain valid. In particular, olefinic and acetylenic conjugated compounds ought to show a higher specific radiation resistance than the corresponding aliphatic compounds in proportion to the delocalization of the π electrons. The question now arises why σ electrons which are characterized by high values of oscillator strengths do not play a major role in the aromatic systems. In order to explain this, it appears to be necessary to assume that when π electrons are present the energy distribution among the secondary electrons is modified in such a way that the proportion of electrons of somewhat higher energy necessary to excite the σ electrons is considerably decreased.

Finally, it is to be remarked that the molecular symmetry in itself may be sufficient to modify radiation resistance. This is suggested by the well-known fact that a change in symmetry may transform a forbidden transition into an allowed one.[31] This case is realized for π-π transitions in benzene and its less symmetrical halogen derivatives. The phenomenon might occur on condition that the transitions considered play a sufficient relative part in radiation resistance.

VI. POST EFFECTS AND OXYGEN EFFECT

The post effects identified for iodoform ($CHI_3 \cdot 3S_8$) have the advantage of being quite characteristic; they have been examined in detail.[13] At room temperature, the line intensity of the irradiated compound is dependent on the time factor. For a dose of 13×10^8 roentgens, the line intensity decreases by 15 per cent during a first period of three days, and then starts to increase, reaching from the sixth day a more or less constant value which is about 10 per cent greater than the value immediately after irradiation. This expresses the fact that we are not confronted with a true recovery. When the sample is heated after irradiation up to 313°K (the observation is again made at room temperature), the minimum of the curve for the same dose is deeper (about 30 per cent of the initial state instead of 15 per cent at room temperature) and the asymptotic part starts earlier. The effect of the dose on the evolution of the resonance line is also well marked. The depth of the minimum seems to vary more or less proportionally. There is therefore a certain analogy in the intensity behavior with respect to temperature and dose. These phenomena certainly manifest a complex mechanism. It might however be suggested that they are at least partially the result of a random walk of some products of molecular dissociation inside the crystals. These could be iodine atoms expelled from CHI_3 and this would be able to produce a decrease in intensity. As the atoms may recombine to form I_2 molecules, these, in their turn, may distribute themselves through the crystal. The result may be a decrease of the strain and thus a subsequent increase may occur as regards the line intensity. When irradiation is made in an oxygen atmosphere

instead of in vacuum,[13] there is a remarkable result: no post effect can be detected at all (the intensity of the resonance line remains practically constant), and the line intensity just after irradiation is slightly different from that found in vacuum. This shows that the presence of oxygen modifies to some extent the processes during irradiation as well as those appearing afterwards. To interpret the annihilation of the post effects, the assumption might be put forward that the photochemically dissociated oxygen atoms (or even the oxygen molecules) diffused in the crystals thanks to irradiation prevent at least partially the dissociation of the CHI_3 molecules into iodine atoms. Then oxygen in this case would behave as a protector!

VII. NEUTRON-IRRADIATED SODIUM CHLORATE[11]

The tests were run at 95°C in the Belgian BR-1 reactor at flux levels of 2×10^{12} neutrons/cm^2/sec for times which gave integrated doses of 2×10^{14}, 10^{15}, and 2×10^{15} fast neutrons/cm^2. The observations performed on $Na^{35}ClO_3$ at 23°C showed that the height of the line corresponding to chlorine-35 was correspondingly decreased by about 25, 36, and 52 per cent. The gamma flux level was negligible (2×10^2 roentgens/sec) as compared with the neutron one, and in fact the integrated dose much too low to have any appreciable effect on the line intensity. A plot of $\log I - \log I_0$ (irradiated sample minus nonirradiated sample) against the neutron flux gave a straight line, showing that in this case too an exponential law describes the intensity behavior. Within the range of doses used, no significant shift in frequency was found to occur. The forty per cent dose is about 3×10^{15} neutrons/cm^2. A slight post effect has been detected, but it is so slow that long periods of time are necessary to study it, and it is still premature to discuss the preliminary results obtained. On comparing the ability of both gamma-rays and neutrons to decrease by forty per cent the resonance line intensity, it may be deduced that the latter are about 10 times more efficient in producing imperfections than the former. This ratio may become still more favorable for lower corresponding doses.

VIII. STUDY OF THE BROADENING EFFECT OF RESONANCE LINES[12]

Fused samples of $Na^{35}ClO_3$, irradiated by gamma-rays of ^{60}Co, have been chosen on account of the sharpness of the resonance line. The derivative curves obtained, for several doses, have been mechanically integrated with a view to determining the properties of the absorption lines as regards height, width, and area. It is found that for weak doses the area under the absorption curve decreases as its height so that the width remains practically constant. This confirms the conjecture already obtained in the other compounds handled here and clearly shows that the imperfections first induced in the crystals disturb considerably the field gradients which, on the whole, are displaced beyond the wings of the lines. When irradiation reaches a threshold of about 8×10^7 roentgens, then a line broadening develops at the same time as a decrease in height, but the line area is still decreasing. This indicates that the proportion of the gradients which are only slightly deviated from the central part of the line is rather small, but is able to show its influence at relatively high doses.* This nonhomogeneous distribution of gradients which manifests itself here cannot be accounted for in the

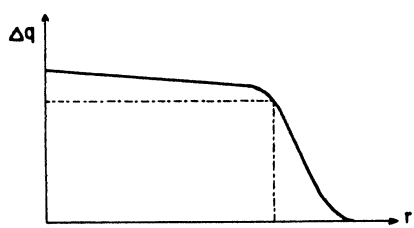

Fig. 1. The solid and dotted lines represent, respectively, the law now suggested and the law implied in the definition of v_r.

hypothesis concerning the v_r volumes according to which the Δq's suddenly vanish on the surface. On the contrary, if a law such as that represented in Figure 1 (in which Δq is plotted against r) is accepted, it is clear that a small proportion of the perturbed mole-

* Induced paramagnetic impurities might play some part. It seems however, that the concentration which they can reach at room temperature is so low that their effect is insignificant.

cules may now produce small Δq's. Consequently, the broadening effect may only be expected to occur for large doses. Furthermore, the shape of the distribution found implies that mechanical distortions of the internal electrical field are more important than the electrical charge effect which is described by an r^{-3} law. It is to be noted that our results are different from those reported by Woessner and Gutowsky[33] in the case of mixed crystals where the integrated intensities should remain constant in the range of 0 to 4 mole per cent.

The exponential law does not hold beyond a threshold value ($\sim 1.3 \times 10^{6} r$) where we are confronted by a kind of saturation showing that the photons become much less efficient in creating new imperfections. This effect is presumably the result of an energy-transfer mechanism of the same kind as that which we assumed in the case of $CHI_3 \cdot 3S_8$ and analogous to that occurring in scintillation phenomena, achieved here through the induced impurities in proper concentrations. In order for this mechanism to be realized, the excitation potential of the impurities must be lower than that of the substratum. The energy of the photons is therefore dissipated by fluorescence or converted into heat. In order to be able to study in detail the laws governing what may be called a self-protection phenomenon, which may be of wide application, further experiments have to be performed.

IX. GENERAL CONCLUSIONS

There is much potentially valuable information which can be derived from the analysis of quadrupole spectra, even in the limited area considered here. Independently of problems of direct theoretical interest, such as those connected with the distribution of field gradients and with the mechanisms of radio resistance and radio protection, practical information can be obtained in the analysis of impurities and in the study of radiation damage. Resonance is already known for nuclei such as ^{10}B, ^{11}B, ^{14}N, ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br ^{127}I, ^{33}S, ^{63}Cu, ^{65}Cu, ^{69}Ga, ^{71}Ga, ^{75}As, ^{115}In, ^{121}Sb, ^{123}Sb, ^{201}Hg, ^{209}Bi, and it is to be hoped that it will soon be detected in several other cases. This simple enumeration shows the development which from now on may already be given to the new method as far as the

solid state is concerned. In the liquid state, the molecular rotations prevent the resonance phenomenon from being observed, but Seiden[28] has recently given arguments for believing that quadrupole resonance might be detected in viscous liquids. However, this prediction has not yet been confirmed experimentally.

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CORRELATION PROBLEM IN MANY-ELECTRON QUANTUM MECHANICS*

I. REVIEW OF DIFFERENT APPROACHES AND DISCUSSION OF SOME CURRENT IDEAS

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* The research in this paper has been sponsored in part by King Gustaf VI Adolf's 70-Years Fund for Swedish Culture, Knut and Alice Wallenberg's Foundation, the Swedish Natural Science Research Council, the Texas-Swedish Cultural Foundation, and in part by the Aeronautical Research Laboratory, Wright Air Development Center of the Air Research and Development Command, United States Air Force, through its European Office under a contract with Uppsala University.

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I. INTRODUCTION

According to modern science, all various kinds of matter consist essentially of a few types of elementary particles combined together in different ways. Since these particles do not obey the laws of classical physics but the laws of modern wave mechanics, the problem of the constitution of matter is a quantum-mechanical many-particle problem of a much higher degree of complexity than even the famous classical three-body problem.

In many cases classical mechanics provides a first approximation to quantum theory, but, in the treatment of many-particle systems, there are certain new features which are entirely without classical correspondence, namely the symmetry laws and the exchange phenomena. Because of Heisenberg's uncertainty relation, an elementary particle cannot simultaneously have a fixed position and a fixed momentum, and the idea of the existence of the classical orbit must therefore be abandoned. This implies also that, if we consider a system of similar particles having the same charge and the same mass, it is in principle impossible to distinguish the different particles individually from each other, since an observer cannot follow them in any orbits. In the quantum-mechanical system, two particles may therefore exchange their places without any possibility of the observer discovering this phenomenon experimentally. Mathematically this "identity principle" implies that, if a physically or chemically measurable quantity depends on the coordinates of the particles, the outcome of the measurement must be independent of any attempt to label the particles of the system, i.e., the measurable quantity must be a symmetric function of the coordinates. This basic symmetry law is further supplemented by Pauli's exclusion principle which leads to the antisymmetry requirement of the wave function. The exchange phenomena introduced in this way give rise to a new form of energy, the "exchange energy" which is characteristic for modern quantum mechanics and which seems to be of basic importance for our understanding of the nature of the electronic clouds within the atoms, the homopolar chemical bond, ferromagnetism, the saturation of the nuclear forces, and many other phenomena.

So far, most of the quantum-mechanical many-particle problems

have been treated only approximately, but very successfully, by means of a simple model called the "one-particle scheme." This model meets us in atomic and molecular theory under the name of the Hartree-Fock approximation, in solid-state physics in the form of the band theory, and in nuclear physics as the shell model. The basic idea of this model is simply that each particle moves independently of all other particles in a certain spin orbital $\psi_i(\boldsymbol{x}_i)$, the form of which depends only on the "average" motion of the other particles. The total wave function is then assumed to be a simple product (Hartree product):

$$\Psi = \psi_1(x_1)\psi_2(x_2) \ldots \psi_N(x_N) \tag{I.1}$$

and we note that in such a wave function we have entirely neglected the "collisions" of the particles of the system. In order to fulfill the Pauli exclusion principle automatically, we may select the antisymmetric component of this product, which (except for a constant factor) transforms the wave function into a Slater determinant:

$$\Psi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(x_1)\,\psi_2(x_1) & \ldots & \psi_N(x_1) \\ \psi_1(x_2)\,\psi_2(x_2) & \ldots & \psi_N(x_2) \\ \cdots\cdots\cdots & & \\ \psi_1(x_N)\psi_2(x_N) & \ldots & \psi_N(x_N) \end{vmatrix} \tag{I.2}$$

We note that such a wave function also fulfills the basic symmetry law derived from the identity principle.

The quantum-mechanical exchange phenomena were discovered and investigated initially by means of this independent-particle model. It was applied to atoms, molecules, crystals, and nuclei, and the success was so great that it was tempting to believe that one had found a comparatively simple tool for treating quantum-mechanical many-particle systems. Calculations of higher accuracy have later shown, however, that a wave function approximated by a single Slater determinant is usually a rather poor solution to the Schrödinger equation, and furthermore that such a wave function in many cases is not even reliable as a basis for drawing qualitative conclusions. It has instead turned out that phenomena depending on the individual motions of the different particles, are of almost the same importance as the exchange phenomena and that a better

theory of many-particle systems can be obtained only if this *correlation* between the individual motions is in some way taken into proper account. The correlation problem is today therefore of crucial importance not only in atomic, molecular, and solid-state theory, but also in nuclear physics.

The purpose of this review is to try to throw some light on the historical development of the treatment of the correlation problem and also to describe the present situation and current ideas. Special attention is paid to a careful *definition of the basic concepts* as, e.g., the correlation energy, since a great deal of confusion seems to exist on this point. According to Pines,[29] "correlation energy is the difference between the energy in the Hartree-Fock approximation and that calculated using any better approximation," and, since other authors use other definitions, one can easily understand the background for Slater's[38] complaint: "the term correlation energy has meant so many things to different people that [Slater] feels it perhaps better not to use the word at all." It is clear that, under such circumstances, it is many times more difficult to compare the results of the various theories, and, for the future, it would be highly desirable to try to reach some international agreement on the terminology and nomenclature in this important field.

Mainly for considerations of space, it has seemed desirable to limit the framework of the present review to the standard methods for treating correlation effects, namely the method of superposition of configurations, the method with correlated wave functions containing r_{ij}, and the method using different orbitals for different spins. Historically these methods were developed together as different branches of the same tree, and, as useful tools for actual applications, they can all be traced back to the pioneering work of Hylleraas carried out in 1928–30 in connection with his study of the ground state of the helium atom.

Comparatively little space will therefore be devoted to some rather recent approaches, such as the plasma model of Bohm and Pines, the two-body interaction method developed by Brueckner in connection with nuclear theory, Daudel's loge theory, and the method of variation of the second-order density matrix. This does not mean that these methods would be less powerful or less impor-

tant, but, so far, the more conventional ideas have been tested much more thoroughly. In a series of applications, it has been possible to compare numerically the outcome of various theoretical calculations according to the standard methods with each other and with experiment, and the discussion of the results gives an over-all view of the accuracy of the different approaches. On this basis, one can hence obtain a fairly reliable idea of the general importance of the correlation effects.

II. FORMULATION OF THE CORRELATION PROBLEM

A. Schrödinger Equation for an Electronic System

For the sake of simplicity, we will here confine ourselves to consider a system of N electrons moving in a given nuclear framework. The stationary states of such a system are described by the solutions to the Schrödinger equation

$$H_{\text{op}}\Psi = E\Psi \tag{II.1}$$

where $\Psi = \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \ldots, \boldsymbol{x}_N)$ is a wave function depending on the N electronic coordinates $\boldsymbol{x}_i = (\boldsymbol{r}_i, \zeta_i)$, each consisting of a space coordinate $\boldsymbol{r}_i$ and a spin coordinate ζ_i. In order to get the Pauli principle automatically fulfilled, we require further that the wave function Ψ should be antisymmetric under a permutation P of the coordinates

$$P\Psi = (-1)^p\Psi \tag{II.2}$$

where p is the parity of the permutation.

The Hamiltonian operator for such a system may be written under the form

$$H_{\text{op}} = H_0 + \sum_{i=1}^{N} H_i + \tfrac{1}{2}\sum_{i,j=1}^{N}{}' H_{ij} \tag{II.3}$$

where we have separated the contributions in zero-, one-, and two-electron terms; the prime on the summation sign for a double sum indicates that we omit all terms having the two indices equal. Let Z_g be the atomic number of the nucleus at the given point g. Neglecting relativistic effects including all spin couplings in a first approximation, we can specify the terms in Eq. II.3 as follows: H_0 is

the Coulomb repulsion energy between the nuclei, H_i is the kinetic energy of the electron i plus its potential energy in the field of the nuclei, and H_{ij} is the Coulomb interaction energy between the electrons i and j:

$$H_0 = \frac{e^2}{2} \sum_{gh}{}' \frac{Z_g Z_h}{r_{gh}}$$
$$H_i = \frac{\boldsymbol{p}_i^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{ig}}, \qquad H_{ij} = \frac{e^2}{r_{ij}} \tag{II.4}$$

The eigenvalues $E_0, E_1, E_2, \ldots$ of the Schrödinger equation (Eq. II.1) form the electronic energies of the system under consideration. It is evident that the solution of Eq. II.1 must involve considerable mathematical difficulties, and so far, the strongest tool we know for handling this problem is the variation principle. If the wave function Ψ is properly normalized so that

$$\int |\Psi|^2 (dx) = 1 \tag{II.5}$$

where

$$\int (dx) = \int dx_1 dx_2 \ldots dx_N$$

means integration over all space coordinates and summation over all spin coordinates, the expectation value of the Hamiltonian is defined by

$$\langle H_{\text{op}} \rangle_{\text{Av}} = \int \Psi^* H_{\text{op}} \Psi (dx) \tag{II.6}$$

The variation principle then says that the energy E_0 of the ground state is the lower bound of the quantity Eq. II.6 for arbitrary normalized trial wave functions Ψ and that further all eigenfunctions satisfy the relation

$$\delta \langle H_{\text{op}} \rangle_{\text{Av}} = 0 \tag{II.7}$$

with the supplementary condition that the eigenfunction Ψ_n for an excited state must be orthogonal to all the functions $\Psi_0, \Psi_1, \ldots, \Psi_{n-1}$ having lower energies.* It is therefore of importance to have a simple method for evaluating the expectation value, Eq. II.6.

* The severe restriction of orthogonality towards the exact eigenfunctions of lower energy has recently been removed, see ref. 33.

B. Density Matrices

The expectation value of any physical quantity Ω_{op} expressible in the form

$$\Omega_{\text{op}} = \Omega_0 + \sum_{i=1}^{N} \Omega_i + \frac{1}{2!} \sum_{i,j=1}^{N}{}' \Omega_{ij} + \frac{1}{3!} \sum_{ijk}^{N}{}' \Omega_{ijk} + \dots \qquad \text{(II.8)}$$

is most simply evaluated by introducing the generalized density matrices

$$\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1) = N \int \Psi^*(\boldsymbol{x}'_1 \boldsymbol{x}_2 \dots \boldsymbol{x}_N)\, \Psi(\boldsymbol{x}_1 \boldsymbol{x}_2 \dots \boldsymbol{x}_N)\, d\boldsymbol{x}_2 d\boldsymbol{x}_3 \dots d\boldsymbol{x}_N$$

$$\Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2|\boldsymbol{x}_1 \boldsymbol{x}_2) = \binom{N}{2} \int \Psi^*(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \boldsymbol{x}_3 \dots \boldsymbol{x}_N) \Psi(\boldsymbol{x}_1 \boldsymbol{x}_2 \boldsymbol{x}_3 \dots \boldsymbol{x}_N) d\boldsymbol{x}_3 \dots d\boldsymbol{x}_N$$

$$\Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \dots \boldsymbol{x}'_p|\boldsymbol{x}_1 \boldsymbol{x}_2 \dots \boldsymbol{x}_p)$$
$$= \binom{N}{p} \int \Psi^*(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \dots \boldsymbol{x}'_p \boldsymbol{x}_{p+1} \dots \boldsymbol{x}_N) \Psi(\boldsymbol{x}_1 \boldsymbol{x}_2 \dots \boldsymbol{x}_p \boldsymbol{x}_{p+1} \dots \boldsymbol{x}_N) d\boldsymbol{x}_{p+1} \dots d\boldsymbol{x}_N$$

$$\Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \dots \boldsymbol{x}'_N|\boldsymbol{x}_1 \boldsymbol{x}_2 \dots \boldsymbol{x}_N) = \Psi^*(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \dots \boldsymbol{x}'_N) \Psi(\boldsymbol{x}_1 \boldsymbol{x}_2 \dots \boldsymbol{x}_N) \qquad \text{(II.9)}$$

The definitions are here given under the assumption that the wave function Ψ is either antisymmetric or symmetric; for a trial function without symmetry property, one has to replace the binomial factor ${}^N C_p$ before the integrand by a factor $1/p!$ and sum over the $N(N-1) \dots (N-p+1)$ possible integrals which are obtained by placing the fixed coordinates $\boldsymbol{x}'_1, \boldsymbol{x}'_2, \dots, \boldsymbol{x}'_p$ in various ways in the N places of the first factor Ψ^* and the fixed coordinates $\boldsymbol{x}_1, \boldsymbol{x}_2, \dots, \boldsymbol{x}_p$ similarly in the second factor Ψ. By using Eq. II.8 we then obtain

$$\langle \Omega_{\text{op}} \rangle_{\text{Av}} = \int \Psi^* \Omega_{\text{op}} \Psi(dx)$$
$$= \Omega_0 + \int \Omega_1 \gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1)\, d\boldsymbol{x}_1 + \int \Omega_{12} \Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2|\boldsymbol{x}_1 \boldsymbol{x}_2)\, d\boldsymbol{x}_1 d\boldsymbol{x}_2$$
$$+ \int \Omega_{123} \Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \boldsymbol{x}'_3|\boldsymbol{x}_1 \boldsymbol{x}_2 \boldsymbol{x}_3)\, d\boldsymbol{x}_1 d\boldsymbol{x}_2 d\boldsymbol{x}_3 + \dots \qquad \text{(II.10)}$$

where we have introduced the convention that, in the integrands, the operators $\Omega_1, \Omega_{12}, \Omega_{123}, \dots$ shall work only on the unprimed coordinates $\boldsymbol{x}_1, \boldsymbol{x}_2, \boldsymbol{x}_3, \dots$ and that, after these operations have

been carried out, we have to put $\boldsymbol{x}'_1 = \boldsymbol{x}_1$, $\boldsymbol{x}'_2 = \boldsymbol{x}_2$, etc. before the integrations.

For the expectation value (Eq. II.6) of the Hamiltonian we obtain in particular

$$\langle H_{\text{op}} \rangle_{\text{Av}} = \frac{e^2}{2} \sum_{gh}{}' \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \boldsymbol{p}_1^2 \gamma(\boldsymbol{x}'_1 | \boldsymbol{x}_1)\, d\boldsymbol{x}_1 - e^2 \sum_g Z_g \int \frac{\gamma(\boldsymbol{x}_1|\boldsymbol{x}_1)}{r_{1g}}\, d\boldsymbol{x}_1 + e^2 \int \frac{\Gamma(\boldsymbol{x}_1\boldsymbol{x}_2|\boldsymbol{x}_1\boldsymbol{x}_2)}{r_{12}}\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2 \tag{II.11}$$

This expression is exact within our original approximation, where we have neglected relativistic effects of the electrons and the zero-point motions of the nuclei. The physical interpretation is simple: the first term represents the repulsive Coulomb potential between the nuclei, the second the kinetic energy of the electronic cloud, the third the attractive Coulomb potential between the electrons and the nuclei, and the last term the repulsive Coulomb potential between the electrons.

In order to evaluate the expectation value of the energy for an electronic system it is hence sufficient to know the generalized second-order density matrix $\Gamma(\boldsymbol{x}'_1\boldsymbol{x}'_2|\boldsymbol{x}_1\boldsymbol{x}_2)$, from which the first-order density matrix may be obtained by using the formula

$$\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1) = \frac{2}{N-1} \int \Gamma(\boldsymbol{x}'_1\boldsymbol{x}_2|\boldsymbol{x}_1\boldsymbol{x}_2)\, d\boldsymbol{x}_2 \tag{II.12}$$

We note that the diagonal elements $\gamma(\boldsymbol{x}_1|\boldsymbol{x}_1)$ and $\Gamma(\boldsymbol{x}_1\boldsymbol{x}_2|\boldsymbol{x}_1\boldsymbol{x}_2)$ are sufficient for determining all Coulomb interactions, but that we need the nondiagonal element $\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1)$ in evaluating the kinetic energy of the electrons.

The diagonal elements of the density matrices have a simple physical meaning. The quantity $|\Psi|^2(dv)$ gives the probability for finding the system within the volume $(dv) = dv_1 dv_2 \ldots dv_N$ around the point $\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N$ in the configuration space and, by successive integration, we obtain further:

$\gamma(\boldsymbol{x}_1|\boldsymbol{x}_1)dv_1$ = probability for finding anyone of the electrons within the volume dv_1 around the point $\boldsymbol{r}_1$ having the spin ζ_1, when all the other particles have arbitrary positions and spins.

$\Gamma(\boldsymbol{x}_1\boldsymbol{x}_2|\boldsymbol{x}_1\boldsymbol{x}_2)dv_1dv_2$ = probability for finding anyone of the electrons within the volume dv_1 around the point $\boldsymbol{r}_1$ with the spin ζ_1 and another electron within the volume dv_2 around the point $\boldsymbol{r}_2$ with the spin ζ_2, all others having arbitrary positions and spins, etc. All these diagonal elements are positive definite; they are further symmetric in the coordinates and normalized so that

$$\int \gamma(\boldsymbol{x}_1|\boldsymbol{x}_1)\,dx_1 = N, \qquad \int \Gamma(\boldsymbol{x}_1\boldsymbol{x}_2|\boldsymbol{x}_1\boldsymbol{x}_2)\,dx_1dx_2 = \binom{N}{2} \quad \text{(II.13)}$$

The nondiagonal elements are needed to preserve the complementary character of wave mechanics, e.g., to permit the description of a certain physical situation in ordinary space as well as in momentum space.

C. Coulomb Correlation. General Remarks

(1) *Effect of the Two-Particle Repulsion*

The main difficulty in solving the Schrödinger equation (Eq. II.1) for a many-electron system comes from the two-electron interaction terms

$$H_{ij} = \frac{e^2}{r_{ij}} \quad \text{(II.14)}$$

which represents the *mutual repulsion* between the electrons i and j. This repulsion energy becomes infinite for $r_{ij} = 0$, and this implies that it is energetically highly unfavorable for two electrons to come very close to each other in space. This has then the consequence that the two-electron probability density $\Gamma(\boldsymbol{x}_1\boldsymbol{x}_2|\boldsymbol{x}_1\boldsymbol{x}_2)$ must vanish or be very small when $\boldsymbol{r}_1 = \boldsymbol{r}_2$, i.e., *each one of the electrons is surrounded by a "Coulomb hole" with respect to all the other electrons*. Hence the repulsive potential tries to keep the different electrons apart and, in addition to this rather evident effect, the interaction terms H_{ij} influence also the nondiagonal elements $\Gamma(\boldsymbol{x}'_1\boldsymbol{x}'_2|\boldsymbol{x}_1\boldsymbol{x}_2)$ and $\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1)$ and consequently even the kinetic energy of the electrons. This result follows more directly from the virial theorem which says that, in a stationary state of an electronic system, the kinetic energy T is half the potential energy V with reverse sign:

$$T = -\tfrac{1}{2}V \quad \text{(II.15)}$$

Any changes in the potential energy because of the Coulomb correlation must therefore also influence the kinetic energy. The virial theorem will be further discussed below.

(2) *Pauli Principle and the Fermi Hole*

The fundamental laws which determine the behavior of an electronic system are the Schrödinger equation (Eq. II.1) and the Pauli exclusion principle expressed in the form of the antisymmetry requirement (Eq. II.2). We note that even the latter auxiliary condition introduces a certain correlation between the movements of the electrons.

Let us consider an arbitrary trial function $f(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ without any symmetry properties at all. By means of the antisymmetrization operator

$$A = (N!)^{-\frac{1}{2}} \sum_P (-1)^p P \tag{II.16}$$

where p is the parity of the permutation P and the sum is to be taken over all $N!$ permutations, we can then easily construct a wave function

$$\Psi = Af = (N!)^{-\frac{1}{2}} \sum_P (-1)^p Pf(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \tag{II.17}$$

which has the antisymmetry property (Eq. II.2) desired. The arbitrary function f may be considered as the sum of components of different symmetry types, and by means of the operator Eq. II.16 we have simply selected the antisymmetric component and multiplied it by the factor $(N!)^{\frac{1}{2}}$. This result follows from the fact that the operator $(N!)^{-\frac{1}{2}}A$ is a *projection operator* fulfilling the characteristic relation $O^2 = O$, and by means of such an operator we can always select a component of any symmetry type desired. If the operation is repeated twice, we shall still be left with the same component, hence the relation $O^2 = O$.

The antisymmetrization of the trial function has a definite effect on the generalized density matrices $\Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \ldots \boldsymbol{x}'_p | \boldsymbol{x}_1 \boldsymbol{x}_2 \ldots \boldsymbol{x}_p)$ defined by Eq. II.9 since, except for the first-order matrix, they will now all be antisymmetric in each set of the indices. For $p = 2$, we have in particular:

$$\Gamma(x'_2 x'_1|x_1 x_2) = -\Gamma(x'_1 x'_2|x_1 x_2)$$
$$\Gamma(x'_1 x'_2|x_2 x_1) = -\Gamma(x'_1 x'_2|x_1 x_2) \qquad \text{(II.18)}$$

This implies that

$$\Gamma(x'_1 x'_2|x_1 x_2) = 0 \qquad \text{for } x'_1 = x'_2$$

and

$$\Gamma(x'_1 x'_2|x_1 x_2) = 0 \qquad \text{for } x_1 = x_2$$

In general the diagonal element $\Gamma(x_1 x_2|x_1 x_2)$ will therefore vanish of at least the *second order* for $x_1 = x_2$, i.e., for $r_1 = r_2$ and $\zeta_1 = \zeta_2$:

$$\Gamma(x_1 x_2|x_1 x_2) = 0 \qquad \text{for } x_1 = x_2 \qquad \text{(II.19)}$$

This vanishing of the probability density for $r_1 = r_2$ and $\zeta_1 = \zeta_2$ means that it is unlikely for two electrons having *parallel spins* to be in the same place ($r_1 = r_2$). The phenomenon is called the "Fermi hole" and we note that it is a direct consequence of the Pauli principle for electrons with the same spin.

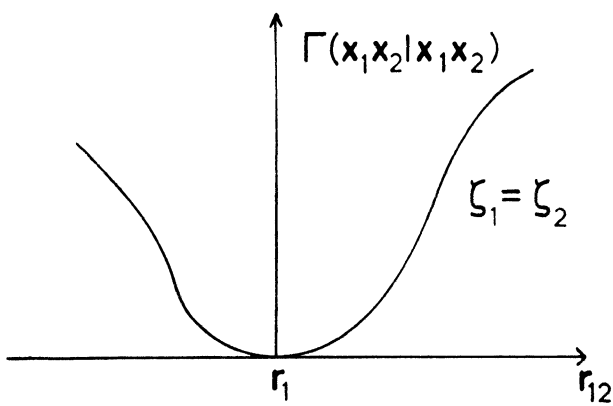


Fig. 1. The "Fermi hole" for electrons with parallel spins.

It is clear that, for electrons with parallel spins, the auxiliary condition (Eq. II.2) gives rise to a correlation effect which very closely resembles the correlation effect coming from the Coulomb repulsion in the Hamiltonian: for $\zeta_1 = \zeta_2$ the "Fermi hole" replaces to a certain degree the "Coulomb hole." This means that, if

one neglects the Coulomb correlation entirely, there will be only a small error connected with the correlation of electrons with parallel spins, whereas the main error will be associated with the lack of correlation between the electrons with antiparallel spins. The problem of the Coulomb correlation is therefore essentially a question of finding a proper treatment of the correlation between electrons with opposite spins.

(3) *Virial Theorem and Scaling*

It has been pointed out above that the correlation between the movements of the electrons influences not only their mutual potential energy but also their kinetic energy. Because of the mutual repulsion, the electrons will try to avoid each other as much as possible, and the more complicated motions arising in this way will evidently be connected with an increase in the kinetic energy. The exact proof is given by the virial theorem (Eq. II.15) showing that a lowering of the potential energy is always associated with an increase in the kinetic energy which is half as large in absolute magnitude.

If a trial function φ_1 leads to a kinetic energy T_1 and a potential energy V_1 which do not fulfill the virial theorem (Eq. II.15), the total energy (T_1+V_1) is usually far from the correct result. Fortunately, there exists a very simple "scaling procedure" by means of which one can construct a new trial function which not only satisfies the virial theorem but also leads to a considerably better total energy. The scaling idea goes back to a classical paper by Hylleraas (1929), but the connection with the virial theorem was first pointed out by Fock.[5] It is remarkable how many times this idea has been rediscovered and published in the modern literature.

Let us here reproduce part of Fock's original derivation. Let us consider n particles (electrons, nuclei, etc.) having the electric charges $e_1, e_2, \ldots, e_n$, the masses $m_1, m_2, \ldots, m_n$, and the coordinates $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n$, respectively. The Hamiltonian H_{op} is then the sum of the operators for the kinetic energy and the potential energy:

$$H_{\text{op}} = T_{\text{op}} + V_{\text{op}}$$

$$T_{\text{op}} = \sum_{k=1}^{n} \frac{\boldsymbol{p}_k^2}{2m_k} = -\frac{h^2}{8\pi^2} \sum_{k=1}^{n} \frac{1}{m_k} \Delta_k$$
$$V_{\text{op}} = \tfrac{1}{2} \sum_{k,l=1}^{n}{}' \frac{e_k e_l}{r_{kl}} \tag{II.20}$$

If $\varphi_1 = \varphi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n)$ is an arbitrary normalized trial function, we will further consider the "scaled function":

$$\varphi_\eta = \eta^{3n/2} \varphi(\eta \boldsymbol{r}_1, \eta \boldsymbol{r}_2, \ldots, \eta \boldsymbol{r}_n) \tag{II.21}$$

which is also normalized. The parameter η is called the scale factor, and the transformation corresponds to a stretching of all vectors $\boldsymbol{r}$ from origin uniformly by a factor η. In evaluating the expectation values of T_{op} and V_{op} with respect to φ_η, we will in the integrals introduce the substitutions $\boldsymbol{r}'_i = \eta \boldsymbol{r}_i$, which leads to the results

$$T(\eta) = \eta^2 T(1), \qquad V(\eta) = \eta V(1) \tag{II.22}$$

and consequently

$$E = \langle H_{\text{op}} \rangle_{\text{Av}} = \eta^2 T(1) + \eta V(1) \tag{II.23}$$

Varying the parameter η and applying the variation principle (Eq. II.7), we obtain

$$\partial E / \partial \eta = 2\eta T(1) + V(1) = 0 \tag{II.24}$$

Let us first assume that φ_1 is the exact solution. This implies that the variation principle must be fulfilled for $\eta = 1$, and substitution of this value into Eq. II.24 leads then to the virial theorem in the form of Eq. II.15.

Let us then consider the case when φ_1 is an arbitrary trial function which does not satisfy the virial relation. From the relation Eq. II.24 follows

$$\eta = -V(1)/2T(1) \tag{II.25}$$

and, according to Eq. II.22, we obtain then for the scaled function φ_η:

$$T(\eta) = V^2(1)/4T(1), \qquad V(\eta) = -V^2(1)/2T(1) \tag{II.26}$$

which relations show that we again have $T(\eta) = -\frac{1}{2} V(\eta)$, i.e., that the virial theorem is fulfilled for φ_η. Instead of varying $\langle H_{\text{op}} \rangle_{\text{Av}}$, it

is many times more convenient to try to minimize the quantity $(T+V)$:

$$T(\eta)+V(\eta) = -V^2(1)/4T(1) \tag{II.27}$$

since one has then separated the scaling problem from all other possible variations and will obtain a final result where the virial relation (Eq. II.15) is automatically fulfilled. Equation (II.27) is due to Hylleraas.[14]

In the derivation above, we have included the kinetic energy of the nuclei in the Hamiltonian and considered a stationary state. In Eq. II.3, this term has been neglected, and we have instead assumed that the nuclei have given fixed positions. It has been pointed out by Slater[34] that, if the nuclei are not situated in the proper equilibrium positions, the virial theorem will appear in a slightly different form. (A variational derivation has been given by Hirschfelder and Kincaid.[11])

For the sake of simplicity, we will consider a diatomic molecule with the internuclear distance R, but the result is directly generalizable to a system with several internuclear distances $R_1, R_2, \ldots$. In addition to the trial function $\varphi_1 = \varphi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N, R)$, we will now also consider the scaled function:

$$\varphi_\eta = \eta^{3N/2}\varphi(\eta\boldsymbol{r}_1, \eta\boldsymbol{r}_2, \ldots, \eta\boldsymbol{r}_N, \rho) \tag{II.28}$$

where

$$\rho = \eta R \tag{II.29}$$

In Eq. II.21 we stretched each one of the position vectors to the nuclei by the factor η; in Eq. II.28 it is sufficient to scale the internuclear distance. Instead of Eq. II.22 we obtain

$$T(\eta, R) = \eta^2 T(1, \rho), \qquad V(\eta, R) = \eta V(1, \rho) \tag{II.30}$$

Let us now keep the parameter R fixed and vary η in the expectation value of the energy

$$E(\eta, R) = \eta^2 T(1, \eta R) + \eta V(1, \eta R) \tag{II.31}$$

Applying the variation principle (Eq. II.7) with respect to η, we obtain

$$\begin{aligned}\partial E(\eta, R)/\partial\eta = {} & 2\eta T(1, \eta R) + V(1, \eta R) \\ & + \eta^2 R T_\rho(1, \eta R) + \eta R V_\rho(1, \eta R)\end{aligned} \tag{II.32}$$

where T_ρ and V_ρ indicate the partial derivatives of $T(1;\rho)$ and $V(1;\rho)$ with respect to ρ.

Let us first assume that φ_1 is the exact solution. Since the variation principle is then fulfilled for $\eta = 1$ and $R = \rho$, Eq. II.32 gives

$$2T+V+RdE/dR = 0 \tag{II.33}$$

which is Slater's form for the virial theorem when the nuclei have given fixed positions. From Eq. II.33 and the relation $E = T+V$, one can then obtain the expressions

$$\begin{aligned} T &= -E-RdE/dR \\ V &= 2E+RdE/dR \end{aligned} \tag{II.34}$$

which permit the calculation of T and V from, e.g., an empirical intermolecular energy curve. Slater pointed out that Eq. II.33 goes over into the ordinary virial theorem (Eq. II.15) when the nuclei are in their equilibrium positions or at infinite separation.

Our derivation of Eq. II.33 based on the use of the variation principle is different from Slater's original treatment, but so far follows Hirschfelder and Kincaid. Here we will now show that it also permits such a scaling of an arbitrary trial function φ_1 that the relation (Eq. II.33) will be automatically fulfilled for the function φ_η. In this connection we have only to observe that we get simultaneously a scaling of the internuclear distance according to Eq. II.29.

If the basic relation (Eq. II.32) is not satisfied for $\eta = 1$, we will make the substitution $\rho = \eta R$, and consider ρ as an auxiliary basic parameter in which everything is expressed. Solving with respect to η, we obtain

$$\eta = -\frac{V(1,\rho)+\rho V_\rho(1,\rho)}{2T(1,\rho)+\rho T_\rho(1,\rho)} \tag{II.35}$$

By multiplying Eq. II.32 by η and by using Eq. II.30 and Eq. II.31, it is then easily checked that the virial theorem (Eq. II.33) is satisfied for the scaled function φ_η and the internuclear distance $R = \eta^{-1}\rho$. The distance R is here a simple function of ρ, and, after establishing the relationship in the form of a graph or a table, we can also solve the reverse problem of finding the properly scaled func-

tion φ_η satisfying the virial relation (Eq. II.33) for a *given* value R of the internuclear distance.

The calculation of the derivatives T_ρ and V_ρ means usually a great deal of additional computations, and it is therefore important to observe that, if we are interested only in determining the energy E_0 and the internuclear distance R_0 for the equilibrium situation, we can use the simpler relations, Eq. II.25 and Eq. II.27. In such a case, E_0 is the minimum of the quantity

$$-[V(1,\rho)]^2/4T(1,\rho) \tag{II.36}$$

and, if this minimum appears for $\rho = \rho_0$, one can determine the scale factor η_0 from Eq. II.25. The actual equilibrium distance R_0 is then given by the relation $R_0 = \eta_0^{-1}\rho_0$.

The considerations in this section show that there is an intimate connection between the potential energy and the kinetic energy of the electrons, and a stationary state is certainly established by a delicate balance between these quantities. This indicates also that, in a discussion of correlation effects, one cannot only treat the Coulomb potential but one must even investigate the influence on the kinetic energy. We observe, however, that for any type of trial function one can always get the basic virial theorem fulfilled by using the simple scaling procedures described above. In this way one can usually obtain a considerable lowering of the energy. Since the scaling procedures can be applied to trial functions in the one-electron scheme as well as in approximations of higher accuracy, they are of basic importance in studying correlation effects. Even a "correlated wave function" which does *not* satisfy the virial relation can always be essentially improved by scaling.

D. Independent-Particle Model and Correlation Error

(1) *The Hartree-Fock Scheme*

If the Hamiltonian would be the sum of one-electron operators only, one could easily separate the variables in the basic Schrödinger equation (Eq. II.1), and the total wave function Φ would then be the product of N one-particle functions $\psi_i(\boldsymbol{x}_i)$, each one being an eigenfunction to the corresponding one-particle operator:

$$\Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2)\ldots\psi_N(\boldsymbol{x}_N) \tag{II.37}$$

In addition to the Schrödinger equation we have the antisymmetry requirement (Eq. II.2) connected with the Pauli principle and, by means of the antisymmetrization operator (Eq. II.16), the Hartree product (Eq. II.37) is then transformed into a Slater determinant:

$$\begin{aligned}\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots \boldsymbol{x}_N) &= A\Phi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \\ &= (N!)^{-\frac{1}{2}} \sum_P (-1)^p P\psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_2) \ldots \psi_N(\boldsymbol{x}_N) \\ &= (N!)^{-\frac{1}{2}} \begin{bmatrix} \psi_1(\boldsymbol{x}_1)\psi_2(\boldsymbol{x}_1) & \ldots \psi_N(\boldsymbol{x}_1) \\ \psi_1(\boldsymbol{x}_2)\psi_2(\boldsymbol{x}_2) & \ldots \psi_N(\boldsymbol{x}_2) \\ \cdots\cdots\cdots\cdots & \\ \psi_1(\boldsymbol{x}_N)\psi_2(\boldsymbol{x}_N) & \ldots \psi_N(\boldsymbol{x}_N) \end{bmatrix} \\ &= (N!)^{-\frac{1}{2}} \det\{\psi_k(\boldsymbol{x}_i)\} \end{aligned} \tag{II.38}$$

Unfortunately the actual Hamiltonian (Eq. II.3) also contains a two-electron part, which prevents the separation of the variables mentioned above. Since the two-electron operator may be written in the form

$$\tfrac{1}{2}\sum_{ij}{}' H_{ij} = \sum_{i=1}^{N} [\tfrac{1}{2}\sum_{j\neq i} H_{ij}] \tag{II.39}$$

it is certainly very tempting to try to replace the last sum in "average" by a one-electron operator:

$$\tfrac{1}{2}\sum_{j\neq i} H_{ij} \rightarrow \bar{H}_i \tag{II.40}$$

The problem of finding the best approximation of this type and the best one-electron set $\psi_1, \psi_2, \ldots, \psi_N$ is handled in the Hartree-Fock scheme. Of course, a total wave function of the same type as Eq. II.38 can never be an exact solution to the Schrödinger equation, and the error depends on the fact that the two-electron operator (Eq. II.39) cannot be exactly replaced by a sum of one-particle operators. Physically we have neglected the effect of the "Coulomb hole" around each electron, but the results in Section II.C(2) show that the main error is connected with the neglect of the Coulomb correlation between electrons with opposite spins.

Before discussing the correlation error, we will make some introductory remarks about the Hartree-Fock approximation based on the use of the Slater determinant (Eq. II.38). We note that, if we

carry out a linear transformation of the basic one-electron set $\psi_1, \psi_2, \ldots, \psi_N$, the total wave function is changed only by a constant factor. We may choose the basic set orthonormal, and the wave function (Eq. II.38) is then normalized according to Eq. II.5. The wave function and the physical situation is apparently unchanged by a unitary transformation of the basic set $\psi_1, \psi_2, \ldots, \psi_N$, and the fundamental invariant of the theory is instead the Fock-Dirac density matrix:

$$\rho(\boldsymbol{x}_1, \boldsymbol{x}_2) = \sum_{k=1}^{N} \psi_k^*(\boldsymbol{x}_1)\psi_k(\boldsymbol{x}_2) \tag{II.41}$$

which fulfills the matrix relations

$$\boldsymbol{\rho}^2 = \boldsymbol{\rho}, \qquad \mathrm{Tr}\,(\boldsymbol{\rho}) = N \tag{II.42}$$

where Tr (= trace) means formation of the diagonal sum. It is easily shown that the density matrix of order p defined by Eq. II.9 is expressible in the form

$$\Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2 \ldots \boldsymbol{x}'_p | \boldsymbol{x}_1 \boldsymbol{x}_2 \ldots \boldsymbol{x}_p) = \frac{1}{p!} \det\{\rho(\boldsymbol{x}'_i, \boldsymbol{x}_j)\} \tag{II.43}$$

and for $p = 1$ and $p = 2$, we have in particular

$$\begin{aligned} \gamma(\boldsymbol{x}'_1 | \boldsymbol{x}_1) &= \rho(\boldsymbol{x}'_1, \boldsymbol{x}_1) \\ \Gamma(\boldsymbol{x}'_1 \boldsymbol{x}'_2 | \boldsymbol{x}_1 \boldsymbol{x}_2) &= \frac{1}{2} \begin{vmatrix} \rho(\boldsymbol{x}'_1, \boldsymbol{x}_1)\rho(\boldsymbol{x}'_1, \boldsymbol{x}_2) \\ \rho(\boldsymbol{x}'_2, \boldsymbol{x}_1)\rho(\boldsymbol{x}'_2, \boldsymbol{x}_2) \end{vmatrix} \end{aligned} \tag{II.44}$$

These relations show that the Fock-Dirac density matrix is identical with the first-order density matrix, and that consequently the first-order density matrix determines all higher-order density matrices and then also the entire physical situation. This theorem is characteristic for the Hartree-Fock approximation.

According to Eqs. II.11 and II.44, the Hartree-Fock energy of our molecular system is now given by the formula

$$\begin{aligned} \langle H_{\mathrm{op}} \rangle_{\mathrm{Av}} = \frac{e^2}{2} \sum_{gh}{}' \frac{Z_g Z_h}{r_{gh}} + \frac{1}{2m} \int \boldsymbol{p}_1^2 \rho(\boldsymbol{x}'_1, \boldsymbol{x}_1) d\boldsymbol{x}_1 - e^2 \sum_g Z_g \int \frac{\rho(\boldsymbol{x}_1, \boldsymbol{x}_1)}{r_{1g}} d\boldsymbol{x}_1 \\ + \frac{e^2}{2} \int \frac{\rho(\boldsymbol{x}_1, \boldsymbol{x}_1)\rho(\boldsymbol{x}_2, \boldsymbol{x}_2) - \rho(\boldsymbol{x}_1, \boldsymbol{x}_2)\rho(\boldsymbol{x}_2, \boldsymbol{x}_1)}{r_{12}} d\boldsymbol{x}_1 d\boldsymbol{x}_2 \end{aligned} \tag{II.45}$$

The best wave function of the approximate form (Eq. II.38) may then be determined by the variational principle (Eq. II.7), either by varying the quantity ρ as an entity, subject to the auxiliary conditions (Eq. II.42), or by varying the basic set $\psi_1, \psi_2, \ldots, \psi_N$ subject to the orthonormality requirement. In both ways we are lead to *Hartree-Fock functions* ψ_k satisfying the eigenvalue problem

$$H_{\text{eff}}(1)\psi_k(\boldsymbol{x}_1) = \varepsilon_k \psi_k(\boldsymbol{x}_1) \tag{II.46}$$

where the "effective Hamiltonian" is given by the expression

$$H_{\text{eff}}(1) = \frac{1}{2m}\boldsymbol{p}_1^2 - e^2 \sum_g \frac{Z_g}{r_{1g}} + e^2 \int \frac{\rho(\boldsymbol{x}_2, \boldsymbol{x}_2) - \rho(\boldsymbol{x}_2, \boldsymbol{x}_1)P_{12}}{r_{12}} d\boldsymbol{x}_2 \tag{II.47}$$

and P_{12} is a permutation operator interchanging $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$. The eigenvalues ε_k are called the "orbital energies," and their physical meaning is given by Koopman's theorem about the first ionization energies. Today it is hardly necessary to emphasize the essential difference between the total energy (Eq. II.45) and the sum of the orbital energies of the occupied spin orbitals, but in the earlier literature there was a great deal of confusion on this point.

The last term in Eq. II.47 gives apparently the "average" one-electron potential we were asking for in Eq. II.40. The Hartree-Fock equations (Eq. II.46) are mathematically complicated non-linear integro-differential equations which are solved by Hartree's iterative self-consistent field (SCF) procedure.

For practical purposes two different approaches have been used. If the nuclear framework has a center with high degree of symmetry, it may be convenient to expand the Hartree-Fock functions $\psi_k(\boldsymbol{r})$ in terms of spherical harmonics $Y_{lm}(\theta, \varphi)$ around this center:

$$\psi_k(\boldsymbol{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} R_{k,lm}(r) Y_{lm}(\theta, \varphi) \tag{II.48}$$

and the radial functions R may then be found by numerical integration. This method was first successfully applied to atoms by Hartree and his father and to solid-state systems by Wigner and Seitz in the "cellular method." For a survey of the SCF results for atoms and solids, respectively, we will refer to Hartree's book[9] and to an article by Löwdin.[17]

Instead of using numerical integration, one can expand the unknown Hartree-Fock functions $\psi_k(\boldsymbol{r})$ in terms of a fixed complete basic set $\phi_\mu(\boldsymbol{r})$:

$$\psi_k(\boldsymbol{r}) = \sum_\mu \phi_\mu(\boldsymbol{r})\, C_{\mu k} \tag{II.49}$$

If the basic set is chosen to consist of atomic orbitals, this relation forms the fundament for the MO-LCAO method in molecular and crystal theory. In its SCF form this approach was first used by Coulson (1938), and later it has been systematized by Roothaan (1951). More details about the SCF results within molecular theory will be given later in a special section.

In conclusion it should be added that, during the last few years, even methods for the direct evaluation of the first-order density matrix $\rho(\boldsymbol{x}_1, \boldsymbol{x}_2)$ have been developed (McWeeny, 1956).

(2) *Construction of Pure Spin States in the* HF *Method*

Since the Hamiltonian defined by Eqs. II.3 and II.4 does not contain the electronic spin explicitly, the wave functions for the stationary states must necessarily be *pure spin states*, being eigenfunctions to the operator S^2 for the total spin. One of the main advantages of the Hartree-Fock scheme is the extraordinary simplicity by which the basic Slater determinant (Eq. II.38) can be brought to correspond to such a pure spin state. The starting point is the classical formulation of Pauli's exclusion principle which permits two electrons with opposite spins to occupy the same orbital in space. If the electrons are paired together in this way as far as possible so that the remaining electrons are all of the same spin, the resulting Slater determinant represents a pure spin state.

Before proving this theorem, we will make some general remarks about the nature of the one-electron functions $\psi_k(\boldsymbol{x})$ or spin orbitals. For the two values of the spin coordinate $\zeta = \pm 1$, such a function $\psi_k(\boldsymbol{r}, \zeta)$ has two space components

$$\psi_+(\boldsymbol{r}) = \psi_+(\boldsymbol{r}, +1), \qquad \psi_-(\boldsymbol{r}) = \psi_-(\boldsymbol{r}, -1) \tag{II.50}$$

which may be combined to a vector. Introducing the basic spin functions

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{II.51}$$

we obtain

$$\psi(\boldsymbol{r}, \zeta) = \begin{bmatrix} \psi_+(\boldsymbol{r}) \\ \psi_-(\boldsymbol{r}) \end{bmatrix} = \psi_+(\boldsymbol{r}) \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_-(\boldsymbol{r}) \begin{pmatrix} 0 \\ 1 \end{pmatrix} \\ = \psi_+(\boldsymbol{r})\alpha(\zeta) + \psi_-(\boldsymbol{r})\beta(\zeta) \tag{II.52}$$

This is the most general form of a spin orbital, but if the Hamiltonian does not contain the spin explicitly, it may be more convenient to try to introduce simplified spin orbitals which contain only one nonvanishing component and hence are of either pure α or β character. Corresponding to the idea of the doubly occupied orbitals, the spin orbitals are often constructed in pairs simply by multiplying the same orbital $\psi(\boldsymbol{r})$ with α and β, respectively.

Let us now consider a system of N electrons, where N_+ electrons occupy spin orbitals of α character or plus spin, and N_- electrons occupy spin orbitals of β character or minus spin. By using the separation of the one-electron functions $\psi_k(\boldsymbol{x})$ into two groups having different spins, we may write the fundamental invariant (Eq. II.41) in the form

$$\rho(\boldsymbol{x}_1, \boldsymbol{x}_2) = \rho_+(\boldsymbol{r}_1, \boldsymbol{r}_2)\alpha(\zeta_1)\alpha(\zeta_2) + \rho_-(\boldsymbol{r}_1, \boldsymbol{r}_2)\beta(\zeta_1)\beta(\zeta_2) \tag{II.53}$$

where

$$\rho_+(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{k=1}^{N_+} f_k^*(\boldsymbol{r}_1) f_k(\boldsymbol{r}_2) \\ \rho_-(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{l=1}^{N_-} g_l^*(\boldsymbol{r}_1) g_l(\boldsymbol{r}_2) \tag{II.54}$$

$\boldsymbol{\rho}_+$ is obtained by summing over the orbitals $f_k(\boldsymbol{r})$ associated with plus spin and $\boldsymbol{\rho}_-$ by summing over the orbitals $g_l(\boldsymbol{r})$ associated with minus spin. The matrices $\boldsymbol{\rho}_+$ and $\boldsymbol{\rho}_-$ are "projection operators" in the ordinary space satisfying the relations

$$\boldsymbol{\rho}_+^2 = \boldsymbol{\rho}_+, \qquad \mathrm{Tr}\,(\boldsymbol{\rho}_+) = N_+, \\ \boldsymbol{\rho}_-^2 = \boldsymbol{\rho}_-, \qquad \mathrm{Tr}\,(\boldsymbol{\rho}_-) = N_-. \tag{II.55}$$

Of special interest also is the matrix

$$\boldsymbol{\omega} = \boldsymbol{\rho}_+\boldsymbol{\rho}_- \tag{II.56}$$

Let us now consider the quantity

$$\mathrm{Tr}\,(\omega) = \int \rho_+(\boldsymbol{r}_1, \boldsymbol{r}_2)\rho_-(\boldsymbol{r}_2, \boldsymbol{r}_1)\, dv_1 dv_2. \qquad \text{(II.57)}$$

In the special case, when the orbitals involved can be simply divided into singly and doubly occupied ones, this integral is equal to the number of doubly occupied orbitals. If we carry out different unitary transformations of the two sets $\{f_k\}$ and $\{g_l\}$, the naive distinction between singly and doubly occupied orbitals vanishes, but the quantity Tr (ω) remains invariant. If we further vary the orbitals $\{f_k\}$ and $\{g_l\}$, so that even the matrices ρ_+ and ρ_- are changed, Tr (ω) is no longer necessarily an integer, and, by considering the overlap matrix between the functions f_k and the functions g_l, it may now be shown that Tr (ω) is a positive number which lies between 0 and the smallest of the numbers N_+ and N_-. The quantity Eq. II.57 may therefore be considered as a generalization of the "number of doubly occupied orbitals."

The total spin $\boldsymbol{S}$ of the system will here be measured in units of $\hbar$. The operators $\boldsymbol{S}^2$ and S_z have the eigenvalues $S(S+1)$ and m, respectively, where $S = \frac{1}{2}N, \frac{1}{2}N-1, \ldots, 0$ or $\frac{1}{2}$ (depending on whether N is even or odd) and $m = S, S-1, \ldots, -S+1, -S$. In our system we have apparently $m = (N_+-N_-)/2$, and for the sake of simplicity we will further assume that $N_+ \geqq N_-$. According to Dirac,[2] the properties of $\boldsymbol{S}^2$ may be found from the formula:

$$\begin{aligned} \boldsymbol{S}^2 &= \sum_{ij} \boldsymbol{S}_i \cdot \boldsymbol{S}_j \\ &= -\tfrac{1}{4}N(N-4) + \tfrac{1}{4}\sum_{ij}{}'(1+\boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j) \\ &= -\tfrac{1}{4}N(N-4) + \tfrac{1}{2}\sum_{ij}{}' P_{ij}{}^{\xi} \end{aligned} \qquad \text{(II.58)}$$

where $P_{ij}{}^{\xi}$ is a permutation operator interchanging the two spin variables ζ_i and ζ_j. The operator $\boldsymbol{S}^2$ contains a constant term and a two-electron part, and, by using Eq. II.10, we obtain for its expectation value

$$\langle \boldsymbol{S}^2 \rangle_{\mathrm{Av}} = -\tfrac{1}{4}N(N-4) + \int \Gamma(\boldsymbol{r}_1\zeta_1, \boldsymbol{r}_2\zeta_2 | \boldsymbol{r}_1\zeta_2, \boldsymbol{r}_2\zeta_1) dx_1 dx_2 \qquad \text{(II.59)}$$

The second-order density matrix is in the Hartree-Fock approximation given by Eqs. II.44 and II.53, and we obtain directly

$$\langle \mathbf{S}^2 \rangle_{\mathrm{Av}} = -\tfrac{1}{4}N(N-4)+\tfrac{1}{2}\int \begin{vmatrix} \rho(\boldsymbol{r}_1\zeta_1, \boldsymbol{r}_1\zeta_2)\, \rho(\boldsymbol{r}_1\zeta_1, \boldsymbol{r}_2\zeta_1) \\ \rho(\boldsymbol{r}_2\zeta_2, \boldsymbol{r}_1\zeta_2)\, \rho(\boldsymbol{r}_2\zeta_2, \boldsymbol{r}_2\zeta_1) \end{vmatrix} dx_1\, dx_2$$

$$= \tfrac{1}{4}(N_+ - N_-)^2 + \tfrac{1}{2}(N_+ + N_-) - \mathrm{Tr}\,(\boldsymbol{\omega})$$

$$= m(m+1) + [N_- - \mathrm{Tr}\,(\boldsymbol{\omega})] \qquad \text{(II.60)}$$

According to the law for the eigenvalues, our determinant could possibly be a mixture of spin states associated with the quantum numbers $S = m, m+1, \ldots, \frac{1}{2}N$. However, in the special case $\mathrm{Tr}\,(\boldsymbol{\omega}) = N_-$, we have $\langle \mathbf{S}^2 \rangle_{\mathrm{Av}} = m(m+1)$, and this is possible only if the wave function is an eigenfunction associated with the eigenvalue $S = m$. There holds further the general theorem:

A single Slater determinant with $N_+ \geqq N_-$ represents a pure spin state if, and only if, the number of doubly filled orbitals defined by Eq. II.57 *equals N_-.*

This case is, of course, realized if N_- orbitals are doubly occupied and the remaining $(N_+ - N_-)$ orbitals are all occupied by electrons having plus spin. By using Eq. II.58, we can very easily check that a Slater determinant constructed in this way is actually an eigenfunction to $\mathbf{S}^2$ associated with the quantum number $S = \frac{1}{2}(N_+ - N_-)$.

The second part of the theorem is proved by considering the width $\Delta\mathbf{S}^2$, defined by

$$(\Delta \mathbf{S}^2)^2 = \langle (\mathbf{S}^2 - \langle \mathbf{S}^2 \rangle_{\mathrm{Av}})^2 \rangle_{\mathrm{Av}} = \langle \mathbf{S}^4 \rangle_{\mathrm{Av}} - \langle \mathbf{S}^2 \rangle_{\mathrm{Av}}^2$$

This quantity vanishes if, and only if, the wave function under consideration is a pure eigenfunction to S^2. Using Eq. II.58, we obtain for a single determinant that

$$(\Delta S^2)^2 = [N_- - \mathrm{Tr}\,(\boldsymbol{\omega})][N_+ - \mathrm{Tr}\,(\boldsymbol{\omega})] + 2\mathrm{Tr}\,(\boldsymbol{\omega} - \boldsymbol{\omega}^2)$$

where none of the terms of the right-hand member can be negative. From the properties of the overlap matrix between the functions f_k and g_l follows further that

$$\mathrm{Tr}\,(\boldsymbol{\omega}^2) \leqq \mathrm{Tr}\,(\boldsymbol{\omega}) \leqq N_-$$

and that the first equality sign is a consequence of the second. The relation $\mathrm{Tr}\,(\boldsymbol{\omega}) = N_-$ is hence a necessary and sufficient condition for the vanishing of the quantity $(\Delta \mathbf{S}^2)^2$, i.e., for the occurrence of an eigenfunction to $\mathbf{S}^2$.

More abstractly the condition Tr $(\rho_+\rho_-) = N_-$ implies that the part of the Hilbert space defined by the projection operator ρ_- should be fully contained in the part defined by the projection operator ρ_+. If we now vary ρ_- slightly so that this condition is no longer fulfilled, Eq. II.60 shows that the pure spin state previously described by the Slater determinant becomes mixed up with states of higher quantum numbers $S = m+1, \ldots$. The idea of the electron pairing in doubly occupied orbitals is therefore essential in the Hartree-Fock scheme in order to secure that the Slater determinant really represents a pure spin state. This means, however, that, in the calculation of the best spin orbitals $\psi_k(\boldsymbol{x})$, there is a new auxiliary condition of the form

$$\text{Tr } (\rho_+\rho_-) = N_- \tag{II.61}$$

which should be considered in the variation procedure leading to the Hartree-Fock equations (Eq. II.46). This condition implies that, in addition to the orbital energies ε_k, there will also be nondiagonal elements ε_{kl} which cannot be transformed away. This fact was observed by Hartree and Hartree* in an investigation of the first excited states ^3P and ^1P of beryllium, where they were forced to keep a nondiagonal element $\varepsilon(1s, 2s) \neq 0$, since they assumed the $1s$ orbital to be doubly filled. They suggested also that it would be both physically and analytically significant to introduce different $1s$ orbitals for the two spins involved, but we observe that the basic determinant would then no longer represent a pure state. This "unrestricted" Hartree-Fock method has recently been further developed by Pratt,[30] and it will be discussed in greater detail in a later section.

(3) *The Correlation Error*

In Section II.C we gave a general discussion of the Coulomb correlation, and we will now define the correlation error in the independent-particle model in greater detail. It is convenient to study the first- and second-order density matrices and, according to the definitions (Eq. II.9) applied to the symmetryless case, we obtain

* See reference 10, particularly p. 594. Compare also Fock and Petrashen.[6]

easily for the Hartree product Φ given by Eq. II.37

$$\gamma(x'_1|x_1) = \sum_i \psi_i^*(x'_1)\,\psi_i(x_1)$$
$$\Gamma(x'_1 x'_2|x_1 x_2) = \tfrac{1}{2}\sum_{ij}{}' \psi_i^*(x'_1)\,\psi_j^*(x'_2)\,\psi_i(x_1)\,\psi_j(x_2) \qquad \text{(II.62)}$$

From Eq. II.62 follows that the two-electron probability density does not show any "Coulomb hole" for pairs of either parallel or antiparallel spins, and this implies that the Hartree scheme is certainly affected by a large correlation error.

If we take the Pauli principle into account and instead start from the Slater determinant (Eq. II.38), we obtain

$$\gamma(x'_1|x_1) = \sum_i \psi_i^*(x'_1)\,\psi_i(x_1)$$
$$\begin{aligned}\Gamma(x'_1 x'_2|x_1 x_2) &= \tfrac{1}{2}\{\gamma(x'_1|x_1)\,\gamma(x'_2|x_2) - \gamma(x'_1|x_2)\,\gamma(x'_2|x_1)\} \\ &= \tfrac{1}{2}\sum_{ij}{}' \psi_i^*(x'_1)\,\psi_j^*(x'_2)\,\psi_i(x_1)\,\psi_j(x_2) \\ &\quad -\tfrac{1}{2}\sum_{ij}{}' \psi_i^*(x'_1)\,\psi_j^*(x'_2)\,\psi_i(x_2)\,\psi_j(x_1)\end{aligned} \qquad \text{(II.63)}$$

where, in the last two sums, the terms for $i = j$ are omitted since they cancel each other. The first-order density matrices in Eq. II.62 and Eq. II.63 are apparently the same, but the second-order density matrix in the latter case is antisymmetric in each set of its indices, and this gives rise to the "Fermi hole" for electron pairs with parallel spins in accordance with Eq. II.19. For a more detailed discussion of this phenomenon, we will refer to Slater (1951) and to Maslen (1956).

The correlation error can, of course, be defined with reference to the Hartree scheme but, in modern literature on electronic systems, one usually starts out from the Hartree-Fock approximation. This means that the main error is due to the neglect of the Coulomb correlation between electrons with opposite spins and, unfortunetely, we can expect this correlation error to be fairly large, since we force pairs of electrons with antiparallel spins together in the same orbital in space. The background for this pairing of the electrons is partly the classical formulation of the Pauli principle, partly the mathematical fact that a single determinant in such a case can

be brought to correspond to a pure spin state, as pointed out in the preceding section.

In order to get at least a formal definition of the problem, we will write the exact solution to the Schrödinger equation (Eq. II.1) in the form

$$\Psi = \Psi_{\mathrm{HF}} + \Psi_{\mathrm{corr}} \tag{II.64}$$

where Ψ_{HF} (HF = Hartree-Fock) means the single determinant of Eq. II.38 and Ψ_{corr} represents the "correlation error" in the wave function itself. The density matrices $\boldsymbol{\Gamma}$ may be evaluated by using Eq. II.9, and we note that each matrix consists of a HF term in the form of a determinant of the matrix $\rho(\boldsymbol{x}_1, \boldsymbol{x}_2)$ and a correlation term:

$$\boldsymbol{\Gamma} = \boldsymbol{\Gamma}_{\mathrm{HF}} + \boldsymbol{\Gamma}_{\mathrm{corr}} \tag{II.65}$$

where the last term contains the contributions obtained by integrating the products $\Psi_{\mathrm{corr}} \cdot \Psi^*_{\mathrm{HF}}$ and $\Psi^*_{\mathrm{corr}} \cdot \Psi_{\mathrm{corr}}$. The normalization in Eq. II.64 is chosen so that Ψ_{HF} satisfies Eq. II.5, and this implies that the trace of each one of the terms $\boldsymbol{\Gamma}_{\mathrm{corr}}$ must vanish:

$$\mathrm{Tr}\,(\boldsymbol{\Gamma}_{\mathrm{corr}}) = 0 \tag{II.66}$$

The "exact" expression (Eq. II.11) for the total energy may now be written in the form

$$\langle H_{\mathrm{op}} \rangle_{\mathrm{Av}} = E_{\mathrm{HF}} + E_{\mathrm{corr}} \tag{II.67}$$

where E_{HF} is the Hartree-Fock energy (Eq. II.45) and E_{corr} is the *correlation energy* coming from the correlation terms in the density matrices. Since the highest interaction in the Hamiltonian is of order $p = 2$, we can apparently express the correlation energy directly in the correlation term of the second-order density matrix $\Gamma_{\mathrm{corr}}(\boldsymbol{x}'_1 \boldsymbol{x}'_2 | \boldsymbol{x}_1 \boldsymbol{x}_2)$, from which we get

$$\gamma_{\mathrm{corr}}(\boldsymbol{x}'_1 | \boldsymbol{x}_1) = \frac{2}{N-1} \int \Gamma_{\mathrm{corr}}(\boldsymbol{x}'_1 \boldsymbol{x}_2 | \boldsymbol{x}_1 \boldsymbol{x}_2)\, d\boldsymbol{x}_2 \tag{II.68}$$

By using Eq. II.11, we then obtain

$$E_{\mathrm{corr}} = \int \left\{ \frac{2}{N-1} \left(\frac{\boldsymbol{p}_1^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{1g}} \right) + \frac{e^2}{r_{12}} \right\} \Gamma_{\mathrm{corr}}(\boldsymbol{x}'_1 \boldsymbol{x}_2 | \boldsymbol{x}_1 \boldsymbol{x}_2)\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2 \tag{II.69}$$

which is the expression desired. We note that the correlation energy evidently consists of a kinetic energy term, a nuclear attraction energy term, and a Coulomb repulsion term. The relation between these contributions is regulated by the virial theorem discussed in Section II.C(3).

We note that the virial theorem is automatically fulfilled in the Hartree-Fock approximation. This result follows from the fact that the single Slater determinant (Eq. II.38) built up from the Hartree-Fock functions $\psi_k(\boldsymbol{x})$ satisfying Eq. II.46 is the optimum wave function of this particular form, and, since this wave function cannot be further improved by scaling, the virial theorem must be fulfilled from the very beginning. If we consider a stationary state with the nuclei in their equilibrium positions, we have particularly $T_{\mathrm{HF}} = -\frac{1}{2}V_{\mathrm{HF}}$, and for the correlation terms follows consequently that

$$T_{\mathrm{corr}} = -\tfrac{1}{2}V_{\mathrm{corr}} \tag{II.70}$$

The variation principle tells us that E_{HF} is always larger than the exact energy, and this implies that the *total correlation energy is always a negative quantity.* From Eq. II.70 it follows then that T_{corr} is always positive, whereas V_{corr} is negative according to the formulas:

$$T_{\mathrm{corr}} = -E_{\mathrm{corr}}\,, \qquad V_{\mathrm{corr}} = +2E_{\mathrm{corr}} \tag{II.71}$$

The kinetic energy in the Hartree-Fock scheme is evidently too low, owing to the fact that we have assumed the existence of a simplified uncorrelated motion, whereas the particles in reality have much more complicated movements because of their tendency to avoid each other. The potential energy, on the other hand, comes out much too high in the HF scheme essentially due to the fact that we have compelled a pair of electrons with opposite spins together in the same orbital in space.

According to Eq. II.67, the correlation energy is simply defined as the difference between the exact energy and the energy of the Hartree-Fock approximation. Let us repeat this definition in a more precise form:

The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree-Fock approximation for the state under consideration.

The correlation energy is therefore essentially a mathematical quantity telling us the error in the energy of the independent-particle model. We note that the correlation energy is *not* the difference between the experimental energy and the HF energy of the Hamiltonian (Eq. II.4), since the experimental energy also contains contributions from the relativistic terms and the zero-point vibrations of the nuclei, which are neglected in Eq. II.4. To each electronic system in nature, there exists a series of Hamiltonians of different degree of accuracy, and each one of these Hamilton operators has then a definite correlation energy for the state under consideration. One can therefore speak of unrelativistic correlation effects, relativistic correlation effects, and correlation effects associated with the nuclear motion, depending on the accuracy of the Hamiltonian which is chosen as a basis for the description. Among these terms, the unrelativistic correlation effects are definitely of main importance, but, in more accurate calculations in the future, one has probably also to consider the higher effects.

In conclusion, we observe that many writers in the modern literature seem to agree about the convenience of the definition (Eq. II.67), but that there has also been a great deal of confusion. For comparison we would like to refer to Slater,* and Arai (1957). Almost the only exception seems to be Green *et al.* (1953, 1954), where the exact wave function is expanded as a superposition of orthogonal contributions with the HF determinant as its first term:

$$\Psi = c_1 \Psi_{\mathrm{HF}} + \overline{\Psi}_{\mathrm{corr}}$$

Because of the orthogonality requirement

$$\int \overline{\Psi}^*_{\mathrm{corr}} \cdot \Psi_{\mathrm{HF}}(dx) = 0$$

* See reference 38, particularly p. 208.

the correlation term gives now a contribution to the normalization integral, which implies $|c_1| < 1$. Green *et al.* define then their "correlation energy" by the relation

$$E_{\text{exact}} - |c_1|^2 E_{\text{HF}}$$

but the use of this quantity is complicated by the fact that the coefficient c_1 is usually not known. In the following we will therefore simply let the quantity $E_{\text{exact}} - E_{\text{HF}}$ be the correlation energy.

(4) *Magnitude of the Correlation Energy*

Let us now try to get an idea of the order of magnitude of the unrelativistic correlation energy for some actual systems. In considering the difference

$$E_{\text{exact}} - E_{\text{HF}} \tag{II.72}$$

we observe that the first quantity is known exactly (or with sufficiently high accuracy) only in very few cases, and one can therefore instead try to determine E_{exact} semiempirically by starting from a reliable experimental value for the energy and adding theoretical corrections for the relativistic effects and the movements of the nuclei. In a first rough approximation, the relativistic terms may be considered as a small perturbation in the actual Hamiltonian, and one can try to estimate their influence by calculating their expectation value with respect to the unrelativistic Hartree-Fock wave function. Unfortunately, one actually needs their expectation value with respect to the correlated wave function, but so far the difference between the two expectation values has not been investigated, and one can only hope that it is small. Except for the very lightest atoms, the relativistic corrections are of an appreciable order of magnitude in comparison to the unrelativistic correlation energy, so this problem must be handled with extreme care.

In considering the Hartree-Fock energy E_{HF} given by Eq. II.45, we observe that, even for atoms, there are actually only a few such energies published in the literature and that, even in simple cases, there may be discrepancies between the results of different authors. The point is that the atomic Hartree-Fock functions are usually tabulated with only three decimal figures, and this numerical accuracy is often not sufficient for obtaining the accuracy desired

in using Eq. II.45 which contains several large terms with different signs giving rise to a certain cancellation of significant figures. The situation would be enormously helped if, in the future, the atomic SCF functions would be determined and published with at least five or six decimals.

One could try to replace the present tables of atomic SCF functions by analytic approximations[20, 21, 24] which then may be the starting point for the energy calculations. It turns out, however, that different analytic fits are possible which correspond to slightly different energies, but there is at least a unique connection between the start and the end in this case.

It is perhaps more tempting to try to introduce the orbital energies ε_k given by Eq. II.46 and the relation

$$\int H_{\text{eff}}(1)\,\rho(x'_1, x_1)dx_1 = \sum_{k=1}^{N} \varepsilon_k \tag{II.73}$$

into the energy expression Eq. II.45, which then may be written in the two following ways:

$$E_{\text{HF}} = \frac{e^2}{2}\sum_{gh}{}' \frac{Z_g Z_h}{r_{gh}} + \sum_{k=1}^{N} \varepsilon_k - \frac{e^2}{2}\int \frac{\rho(\boldsymbol{x}_1, \boldsymbol{x}_1)\,\rho(\boldsymbol{x}_2, \boldsymbol{x}_2) - \rho(\boldsymbol{x}_1, \boldsymbol{x}_2)\,\rho(\boldsymbol{x}_2, \boldsymbol{x}_1)}{r_{12}}\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2 \tag{II.74}$$

$$E_{\text{HF}} = \frac{e^2}{2}\sum_{gh}{}' \frac{Z_g Z_h}{r_{gh}} + \tfrac{1}{2}\sum_{k=1}^{N} \varepsilon_k - \frac{e^2}{2}\sum_{g} Z_g \int \frac{\rho(\boldsymbol{x}_1, \boldsymbol{x}_1)}{r_{1g}}\, d\boldsymbol{x}_1 \tag{II.75}$$

Here the last expression was found by taking the arithmetic mean between the two forms, Eq. II.45 and Eq. II.74. Formulas of this type have actually been used in the "cellular method" for treating crystals, but our own experience from work on atoms is that the orbital energies ε_k seem to be the quantities in the HF scheme which are most easily influenced by numerical uncertainties and errors. Even if Eqs. II.74 and II.75 are practically simpler to handle than Eq. II.45, they are probably less numerically reliable. Further investigations on this point are desired.

With the present three-decimal tables for the atomic SCF functions, it seems very hard to circumvent the difficulties connected

with the calculation of the total energy. Another approach would be to rely on the virial theorem (Eq. II.15), which is actually fulfilled by the Hartree-Fock functions, and try to evaluate the energy by the formula

$$E_{\mathrm{HF}} = -T_{\mathrm{HF}} = -\frac{1}{2m}\int \boldsymbol{p}_1^2 \rho(\boldsymbol{x}'_1, \boldsymbol{x}_1) d\boldsymbol{x}_1$$
$$= \frac{h^2}{8\pi^2 m}\sum_{k=1}^{N}\int \psi_k^*(\boldsymbol{x}_1) \Delta_1 \psi_k(\boldsymbol{x}_1) d\boldsymbol{x}_1 \qquad \text{(II.76)}$$

i.e., by summing the kinetic energy of all the electrons with reverse sign. In the atomic case, the SCF functions $\psi_k(\boldsymbol{x})$ with $k = (nlms)$ are of the form

$$\psi_k(\boldsymbol{r}, \zeta) = \frac{f_{nl}(r)}{r} Y_{lm}(\theta, \varphi) \begin{cases} \alpha(\zeta) \\ \beta(\zeta) \end{cases} \qquad \text{(II.77)}$$

and, in order to evaluate the kinetic energy, the following transformation formula by Freeman and Löwdin[7] may be useful:

$$\int \psi_k^*(\boldsymbol{x}_1) \Delta_1 \psi_k(\boldsymbol{x}_1) d\boldsymbol{x}_1 = -\int_0^\infty \left\{\frac{dF_{nl}(r)}{dr}\right\}^2 r^{2l+2} dr \qquad \text{(II.78)}$$

$$F_{nl}(r) = f_{nl}(r)/r^{l+1} \qquad \text{(II.79)}$$

The function $f_{nl}(r)$ given in the standard tables is usually rapidly varying and is therefore difficult to differentiate numerically. The function $F_{nl}(r)$ is varying much more slowly, and Eq. II.78 is hence more convenient as the starting point for the numerical work. The accuracy of this method for evaluating the HF energy is now being tested for the atomic case.

In molecular applications the calculation of the HF energy is a still more difficult problem. It should be observed that, in the SCF-MO-LCAO now commonly in use, one does not determine the exact HF functions but only the best approximation to these functions obtainable within the framework given by the ordinarily occupied AO's. Since the set of these atomic orbitals is usually very far from being complete, the approximation may come out rather poor, and the correlation energy estimated from such a calculation may then turn out to be much too large in absolute order of magnitude. The best calculation so far is perhaps Coulson's treatment of

the H_2 molecule (Coulson 1937), which will be further discussed below.

Even if the semiempirical method for determining the order of magnitude of the correlation energy from the difference (Eq. II.72) at first sight seems very simple, there are apparently considerable difficulties both in evaluating the relativistic and "thermal" corrections, which distinguish the observed energy from the eigenvalue to the approximate Hamiltonian under consideration, and in calculating the Hartree-Fock energy. The problem seems important, however, and work along the abovementioned lines is in progress in Uppsala.

(a) *Correlation Energy of the* He*-like Ions.* Let us now study some figures. The simplest systems showing any Coulomb correlation are the two-electron systems represented by the He-like ions in their ground state $(1s)^2$. Here the correlation energies may be evaluated purely theoretically, since E_{exact} has been determined very accurately by Hylleraas (1930, 1956):

$$E_{\text{exact}} = -2Z^2+\tfrac{5}{4}Z-0.315311+0.01707Z^{-1}-0.00068Z^{-2} \\ -0.00164Z^{-3}-0.00489Z^{-4}\ldots \quad \text{(II.80)}$$

It should be observed that the subscript "exact" here refers to the lowest eigenvalue of the unrelativistic Hamiltonian; the energy is here expressed in the unit $hcR_\infty(1+m/M_Z)^{-1}$ and Z is the atomic number. If the HF energies are taken from Green *et al.*,[8] we get the correlation energies listed in the first column of Table I expressed in electron volts. The slow variation of this quantity is noticeable and may only partly be understood by means of perturbation theory.

It is interesting to compare the theoretical values with the results of a semiempirical calculation recently carried out by Fröman (1958), using the formula

$$E_{\text{corr}} = E_{\text{exp}}-E_{\text{rel}}-E_{\text{HF}} \quad \text{(II.81)}$$

where he obtained the relativistic correction E_{rel} by using the results of Bethe and Salpeter (1955) and the Dirac theory. Fröman's values for the correlation energy are remarkably constant, particularly for $Z \geqq 4$, and it would be valuable to find an ex-

planation for this phenomenon. We note also the slight discrepancies between the theoretical and semiempirical values for E_{corr}, which are within the experimental errors, but which may otherwise indicate the existence of a small effect which is not yet fully understood.

TABLE I. Correlation energies of the He-like Ions in ev

Element	Theoretical calculation E_{corr}	Semiempirical calculation		
		$E_{exp} - E_{HF}$	E_{rel}	E_{corr}
H^-	−1.08			
He	−1.14	-1.145_2	-0.003_6	−1.142
Li^+	−1.18	−1.197	−0.015	−1.182
Be^{+2}	−1.20	−1.250	−0.056	−1.194
B^{+3}	−1.22	−1.345	−0.149	−1.196
C^{+4}	−1.23	−1.521	−0.324	−1.197

(b) *Correlation Energy of* Be, F^-, *and* Al^{3+}. Fröman (1958) has also calculated the correlation energies according to Eq. II.81 for some heavier atoms and ions for which experimental data are available from spectroscopy. The value for E_{exp} is obtained by summing the successive experimental ionization potentials taken from Moore,[26] except for the last one which is actually evaluated by Dirac's formula for hydrogen-like systems. The value of E_{rel} is estimated by considering the relativistic terms in a generalization of Bethe-Salpeter's Hamiltonian operator and taking their expectation value with respect to the unrelativistic Hartree-Fock functions. The results for Be, F^-, and Al^{3+} are summarized in Table II.

TABLE II. Correlation Energies for Be, F^-, and Al^{3+} in ev

Element	Z	N	$E_{exp} - E_{HF}$	E_{rel}	E_{corr}	Eq. II.82
Be	4	4	− 2.43	− 0.06	− 2.37	− 2.35
F^-	9	10	−13.24	− 2.55	−10.69	
Al^{+3}	13	10	−22.11	−11.11	−11.00	−12.3

It is perhaps somewhat surprising that, for Al^{3+}, the relativistic corrections are of the same order of magnitude as the correlation

energy. Fröman points out that, for the four-electron system in Be, the correlation energy is about twice as large as in the He-like ions, whereas the addition of the $(2p)^6$ shell to form a Ne-like structure causes a further increase of about -8.4 ev in the correlation energy. This implies that the correlation energy per doubly filled $2p$ orbital would be -2.8 ev in comparison to the value -1.2 ev per doubly filled $1s$ or $2s$ orbital, but the entire interpretation of these data is uncertain, of course.

In order to get an estimate of the order of magnitude of the correlation energy, Fröman makes it plausible that the correlation energy should be roughly proportional to the total Coulomb repulsion energy of all the electrons within the system, and he suggests the formula

$$E_{\text{corr}} \approx C(Z) \left\langle \frac{e^2}{r_{12}} \right\rangle_{\text{Av, HF}} \tag{II.82}$$

where the coefficient $C(Z)$ depends only on the atomic number Z and $\langle e^2/r_{12} \rangle$ is the expectation value of the Coulomb repulsion evaluated in the Hartree-Fock approximation. Calculating $C(Z)$ from the results for the He-like ions, Fröman applied the formula to other electronic systems, and the results for Be and Al^{3+} obtained in this way are listed in the last column of Table II; the value for Be is excellent, whereas the result for Al^{3+} is at least of the correct order of magnitude. It is clear that Eq. II.82 will give good results only if the constant $C(Z)$ is evaluated by means of a system, which is not too different from the system under consideration.

(c) *Correlation Energy of the Covalent Bond; the* H_2 *Molecule.* For theoretical chemists, it is of essential interest to get an idea of the order of magnitude of the correlation energy in the covalent bond, and, for the H_2 molecule, there are some data available which may be considered typical. The correlation energy for the ground state of H_2 may be estimated by using either the semi-empirical approach or James and Coolidge's (1933) energy eigenvalue. If the value for E_{HF} is taken from Coulson (1938), one obtains in both cases

$$E_{\text{corr}} = -1.06 \text{ ev} \tag{II.83}$$

for the equilibrium value of the internuclear distance, i.e., a value of the same magnitude as those found in the He-like ions. From Eq. II.71 follows further

$$T_{\text{corr}} = +1.06 \text{ ev}, \qquad V_{\text{corr}} = -2.12 \text{ ev} \tag{II.84}$$

showing that the error in the Coulomb potential is actually twice as large but partly compensated by a corresponding error in the kinetic energy.

Let us now discuss the situation in valence theory and recall that 1 ev = 23.07 kcal/mol. Since the covalent bond is associated with an electron pair having opposite spins, one can expect that, in the HF-scheme, there will probably be a correlation error of the order -23 kcal/mol, consisting of an error of -46 kcal/mol in the potential energy and an error of $+23$ kcal/mol in the kinetic energy. Since these figures are many times comparable with the bond energies themselves, we can ask ourselves whether one can really draw any definite qualitative and quantitative conclusions concerning the chemical bonds from the Hartree-Fock approximation. Let us be optimistic and hope that this is the case, but let us also treat the situation with a great deal of care.

Let us finally study the variation of the correlation energy with the internuclear distance R. The problem of the variation of the total energy of a molecule or crystal for different internuclear distances is of essential importance in many connections and has been investigated in great detail by Slater starting with a fundamental paper in 1930. It has been shown that if the total wave function of a molecule or crystal is approximated by a single determinant constructed from molecular spin orbitals or the appropriate Hartree-Fock functions, then the cohesive energy shows a wrong asymptotic behavior for separated atoms, since such a wave function permits electrons of different spins to accumulate on the same atom[41] and give rise to negative and positive ions with higher energy than the ordinary dissociation products; see Figure 2. This is a typical "correlation error" in the independent-particle model since, in nature, the strong Coulomb repulsion between the electrons prevents the formation of negative ions with too many electrons. Following Slater (1930, 1953, 1956), we will again con-

sider the H_2 molecule as a typical example and supplement his qualitative arguments with some numerical data.

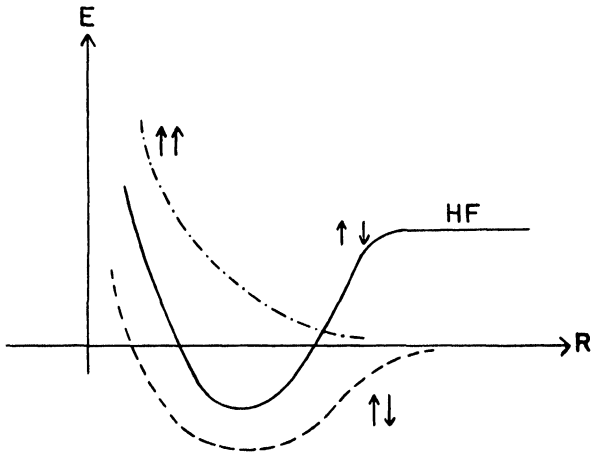


Fig. 2. Energy as a function of internuclear distance: the full line refers to a single determinant, the lower curve (— — —) represents the true behavior, the upper curve (— · — ·) gives the energy of a state with parallel spins.

If $\psi(\boldsymbol{r})$ is the basic Hartree-Fock function or molecular orbital for H_2, the total wave function may be approximated by a single determinant:

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = 2^{-\frac{1}{2}} \det \{\psi\alpha, \psi\beta\} = \psi(\boldsymbol{r}_1)\psi(\boldsymbol{r}_2)(\alpha_1\beta_2 - \alpha_2\beta_1)/\sqrt{2} \quad \text{(II.85)}$$

Because of the symmetry of the molecule, we may express ψ in the form

$$\psi = (u_a + u_b)/\sqrt{[2(1+S_{ab})]} \quad \text{(II.86)}$$

where u_a and u_b are associated with the nuclei a and b, respectively, and

$$S_{ab} = \int u_a u_b \, dv$$

In the conventional MO-LCAO theory, the function u is approximated by a 1s orbital, but better approximations may be obtained by including higher orbitals. The total wave function is such that, for separated atoms, there is a fifty per cent chance that the mole-

cule will dissociate into H^- and H^+ and a fifty per cent chance that it will dissociate into two H atoms, and the total energy is given by the expression

$$E_{HF,\infty} = \tfrac{1}{2}(H^+ + H_{u^2}{}^-) + \tfrac{1}{2}(H_u + H_u) \qquad \text{(II.87)}$$

where $H_{u^2}{}^-$ is the expectation value of the H^- Hamiltonian with respect to the wave function $u(1)u(2)$, H_u is the expectation value of the H Hamiltonian with respect to u, and the electronic energy of H^+ is zero. It is clear that the minimization of Eq. II.87 with respect to the orbital u is not a trivial problem; if both terms are minimized separately, one gets the value -0.743913 at.u.$_H$ which is definitely far below the true minimum obtainable for an orbital u which refers to a weighted compromise between H and H^-. The result of the evaluation of Eq. II.87 for some trial functions are listed in Table III. In order to get the virial theorem fulfilled, all trial functions have also been properly scaled according to Eq. II.25. The optimum orbital u should actually be determined by

TABLE III. Energy of the Combined System $\frac{1}{2}(H^- + 2H)$ in at.u.$_H$

Trial function	Scale factor	Energy
SCF-function for H^-	1.0	−0.685 88
1s	1.0	−0.687 57
SCF-function for H^-	1.202 992	−0.705 98
1s	0.843 783	−0.711 97
Sum of two exponentials	—	−0.715 418

means of a self-consistent-field procedure corresponding to the minimization of Eq. II.87. Previous experience[20,8] has shown, however, that the HF-functions for the atomic two-electron systems may be accurately approximated by the sum of two exponentials:

$$u(r) = (A_1 e^{-a_1 r} + A_2 e^{-a_2 r}) \qquad \text{(II.88)}$$

where, in addition to the normalization constant and a scale factor, we have two variable parameters. Varying Eq. II.87 with respect to these parameters,* we have obtained the minimum energy:

* The author is greatly indebted to Fil. kand. Klaus Appel for carrying out the numerical work by means of an electronic computer of type Alwac III-E.

$$E_{\mathrm{HF},\infty} = -0.715\,418 \text{ at.u.}_{\mathrm{H}} \tag{II.89}$$

The corresponding values of the parameters are:

$$A_1 = 1.046\,214 \qquad a_1 = -0.726\,955$$
$$A_2 = 0.633\,901 \qquad a_2 = -1.455\,655$$

giving the "compromise" HF function for the combined system $\frac{1}{2}(H^- + 2H)$. We note that the energy value obtainable by a single 1s orbital is not too far off, provided that the function is properly scaled.

The exact unrelativistic energy for two separated H atoms is -1 at.u.$_{\mathrm{H}}$ and, according to the definition (Eq. II.72), we thus get for the correlation energy of the H_2 system in the limit $R = \infty$:

$$\begin{aligned} E_{\mathrm{corr},\infty} &= -0.284\,582 \text{ at.u.}_{\mathrm{H}} \\ &= -7.73693 \text{ ev}, \end{aligned} \tag{II.90}$$

showing an enormous correlation energy for $R = \infty$. The figure indicates clearly a very low accuracy of the *molecular* Hartree-Fock scheme for separated atoms. This is in agreement with the results of previous investigations[1] which have shown that the molecular-orbital theory gives fairly good results for R values within a certain region around the equilibrium point R_0, but also that the entire approach breaks down as soon as R increases over a

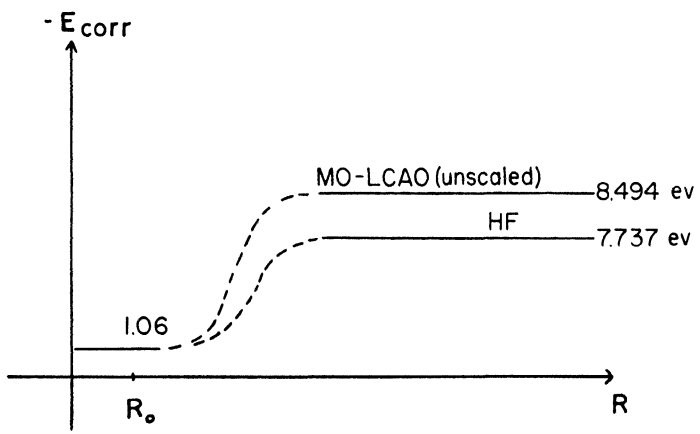


Fig. 3. Correlation energy of H_2 as a function of the internuclear distance R.

certain critical value. In Figure 3, we have tried to sketch the behavior of the correlation energy as a function of R; it would definitely be of interest to get a few more points on this curve to localize the critical region where the system apparently changes from molecular to atomic character. The correlation curve will be discussed in greater detail below.

(d) *Cancellation of Correlation Effects.* One should definitely not underestimate the accuracy of the Hartree-Fock approximation. In comparison to the total energy E_{HF}, the correlation energy E_{corr} is a fairly small quantity, and the relative accuracy is often very high. The unfortunate thing is that neither physicists nor chemists are interested in total energies but in *energy differences*, which are usually small quantities. In forming the difference between two large quantities, the absolute accuracy of each term will be of essential importance, and this implies that, because of the actual demands of the physicists and chemists, the correlation energy is a key quantity which cannot be neglected at all.

The fact that we are mainly interested in energy differences is not only disadvantageous, however. The figures given in Tables I, II, and III suggest that *two isoelectronic systems have approximately the same correlation energy per doubly filled orbital* or at least the order of magnitude of these energies is the same. This implies that, if we form the energy difference in the HF approximation between two states having the same number of doubly filled orbitals, the correlation errors will cancel to a large extent, and the final result may be quite good. Such a cancellation of errors may be the main reason for the excellent results one actually finds in evaluating the cohesive energy of, e.g., an ionic crystal in the one-particle scheme. On the other hand, if the two states under consideration have different numbers of doubly filled orbitals, one cannot expect such a cancellation of the correlation errors, and this fact disturbes apparently all HF calculations of the cohesive energy of molecules and metals. These questions are also of essential importance in investigating excitation energies and molecular spectra.

The occurrence of such cancellation of errors implies that, in the investigation of an *energy difference*, one cannot consider a good agreement between a theoretical value and experiment as an

absolute test for the validity of the theory, since the agreement may often be entirely fortuitous. It may be true that a very simple theory can sometimes give a remarkably good agreement with experience for a whole series of similar systems, but, in such a case, there is very likely a cancellation of errors which is fortuitous but at the same time systematic in the sense that it repeats itself, e.g., in a sequence of similar molecules. In considering binding and excitation energies of electronic systems, such a simplified theory may often be quite useful for interpolating or extrapolating data, but one must not be tempted to believe that it really gives a deeper insight into the electronic structure of the system. A criterion for the accuracy of a theory can actually be found only by separately investigating each state involved. Because of the existence of such cancellation of errors under certain circumstances, a theoretical investigator must many times face the discouraging fact that an essential refinement of the theory may not lead to a corresponding improvement in the agreement with experience, but that instead everything may become worse. In treating magnetic properties by comparing the total energies of different types of spin alignments, this phenomenon becomes particularly clear in going over from the Hartree scheme to the Hartree-Fock approximation by introducing the antisymmetry requirement. According to Section II.C(2), the occurrence of the "Fermi hole" diminishes the correlation energy for electrons with parallel spins, whereas this error remains unchanged for electrons with antiparallel spins.

Scheme	↑↑	↑↓	Remark
Hartree	bad	bad	balance
Hartree-Fock	good	bad	out of balance

Our little table of accuracy shows that, in the Hartree scheme, there is a certain balance between the correlation errors for the two spin types which, in some cases, may lead to a cancellation of these errors with good theoretical results as a consequence. After the introduction of "exchange," this balance is gone and, if the correlation between electrons with opposite spins is not taken into proper account, the final results may be influenced by this large

error and be way off. According to Slater (1953), Pines (1955), and others, a theory of ferromagnetism and general magnetic properties based on the simple band theory or Hartree scheme leads often to more sensible results than the more elaborate band theory containing exchange.

The failure of the Hartree-Fock scheme in treating magnetic properties has also been clearly demonstrated by Slater (1951, 1953, 1956) by discussing the asymptotic behavior of the energy curves for separated atoms. Let us consider the curves in Figure 2: the curve for parallel spins ($\uparrow\uparrow$) has the correct asymptotic form, since the correlation error is vanishing for $R = \infty$, whereas the curve for antiparallel spins ($\uparrow\downarrow$) does not approach the line $E = 0$ but another line which, according to Eq. II.90, lies high above the R axis. This means that the two energy curves ($\uparrow\uparrow$) and ($\uparrow\downarrow$) will always show an artificial crossing point, which has nothing to do with the actual spin alignment in the system under consideration. In order to get a reliable theory for the spin states and the associated magnetic properties, it is hence necessary to remove the correlation error connected with electrons having antiparallel spins.

It is clear that, in the long run, we cannot rely on a more or less fortuitous cancellation of errors, the nature of which we do not know about in detail. The theory may be in a dilemma, but the only way out is probably to overcome our desire to get "quick results" and to start investigating the correlation effects in full detail.

III. METHODS FOR TREATING ELECTRONIC CORRELATION

A. Historical Development and Basic Ideas. Hylleraas' Work on the Helium Atom

It was a characteristic feature of Bohr's classical quantum mechanics that it could never be generalized to give good quantitative results for systems containing more than one electron. The extension from $N = 1$ to $N = 2, 3, \ldots$ came first with modern wave mechanics and Heisenberg's discovery in 1926 of the exchange phenomenon in the He-atom, which, with the "identity

principle," introduced a new concept without any correspondence in either classical physics or classical quantum mechanics. The new symmetry principle was used by Heitler and London in 1927 in an investigation of the H_2 molecule to give a quantum-mechanical explanation of the nature of the covalent chemical bond.

Both the He atom and the H_2 molecule are two-electron systems, and it is evident that, even if one could draw very important qualitative conclusions from the symmetry considerations, the quantitative results must represent only a first rough approximation as long as the Coulomb repulsion e^2/r_{12} was not properly taken into account. The first investigations of the Coulomb correlation were undertaken by Hylleraas, who in an excellent series of papers on the He problem (Hylleraas 1928, 1929, 1930) developed three quantum-mechanical methods for treating correlation in many-electron systems, which have been of fundamental importance for the entire development in this field. In treating the ground state of He and the He-like ions (H^-, Li^+, Be^{2+}, B^{3+}, etc.), Hylleraas could also by numerical methods show that the Schrödinger equation in the two-electron configuration space with small relativistic corrections actually gave a complete agreement between the theoretical energy values and experimental experience. Even if the numerical computations are very impressive, the main importance of Hylleraas' papers lies definitely in the new theoretical methods introduced. The value of Hylleraas' pioneering work can hence hardly be overestimated, and it is therefore very fortunate that these classical papers are now available also in collected form.[12]

A characteristic feature of the two-electron problem is that the total wave function may be factorized into a space part and a spin part:

$$
\begin{aligned}
{}^1\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) &= \Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)\{\alpha(\zeta_1)\beta(\zeta_2) - \alpha(\zeta_2)\beta(\zeta_1)\}/\sqrt{2} \\
{}^3\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) &= \Phi(\boldsymbol{r}_1, \boldsymbol{r}_2) \begin{cases} \alpha(\zeta_1)\alpha(\zeta_2), \\ \{\alpha(\zeta_1)\beta(\zeta_2) + \alpha(\zeta_2)\beta(\zeta_1)\}/\sqrt{2}, \\ \beta(\zeta_1)\beta(\zeta_2) \end{cases}
\end{aligned}
\tag{III.1}
$$

The first function ${}^1\Psi$ represents a singlet with a symmetric space part, and the second function ${}^3\Psi$ represents a triplet having an antisymmetric space part. Because of this separation between

space and spin for $N = 2$, the main interest can be concentrated on the space functions. In the original papers about two-electron systems (He, H_2, etc.) very little is therefore usually said about the spin functions, and the spin properties have to be implicitly understood. With this limitation, the treatment of the two-electron systems gives a great deal of information about the correlation effects.

The three basic methods introduced by Hylleraas in his work on the He series have in modern terminology obtained the following names: (a) Superposition of configurations; (b) Correlated wave functions; (c) Different orbitals for different spins. The first two approaches are developed almost to the full extent, whereas the last method is at least sketched in the 1929 paper.

The method of "superposition of configurations" described in the first paper (1928) implies that, after choosing a complete basic set of one-electron functions $\psi_k(\boldsymbol{r}_1)$ one can develop the space function in Eq. III.1 in the form:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{kl} C_{kl}\psi_k(\boldsymbol{r}_1)\psi_l(\boldsymbol{r}_2) \qquad \text{(III.2)}$$

with $C_{kl} = C_{lk}$. The coefficients in this expansion are then found by means of the variation principle (Eq. II.7). Hylleraas pointed carefully out the importance of having a really *complete* set $\{\psi_k\}$, that hydrogen-like functions could be used only if one included the continuum and that, from the practical point of view, it was better to use a set which was entirely discrete. Hylleraas reported the result $E = -2.8992$ at.u. which is to be compared with the "exact" value $E = -2.9037$ at.u. The energy values are here expressed in the modified atomic unit:

$$1 \text{ at.u.}_Z = \frac{e^2}{a_{0,Z}} = 2hcR_\infty\left(1 + \frac{m}{M_Z}\right)^{-1} \qquad \text{(III.3)}$$

The outcome was certainly good but, according to Hylleraas' opinion, the series (Eq. III.2) converged too slowly. In 1929, Hylleraas tried instead to introduce the interelectronic distance r_{12} in the wave function itself, which is then called a "correlated wave function." In treating the ^1S ground state, he actually used the

expansion

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-\frac{1}{2}(r_1+r_2)} \sum_{nlm=0}^{\infty} C_{n,2l,m}(r_1+r_2)^n (r_1-r_2)^{2l} r_{12}{}^m \quad \text{(III.4)}$$

with the additional assumption that he could also "scale" the right-hand member. This was the first time the important scaling procedure (see Section II.C(3)) was described in the literature. The result of the numerical work was extremely good, $E = -2.90324$ at.u., and the r_{12} method was hence considered as an excellent tool for treating the Coulomb correlation.

In the preliminary discussions in the 1929 paper (Eq. 11), Hylleraas also discussed some lower approximations and pointed out the importance of a configuration where there exist one "inner" electron and one "outer" electron. In modern terminology, this corresponds to a splitting of the closed shell $(1s)^2$ into an open shell $(1s', 1s'')$, or to the use of "different orbitals for different electrons." Hylleraas reported the good result $E = -2.8754$ at.u. for such a configuration, but pointed also out that a "correlated wave function" of the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = (1s', 1s'')\, e^{+0.05 r_{12}} \quad \text{(III.5)}$$

where the symbol $(1s', 1s'')$ stands for a symmetrized product of two ordinary $1s$ functions with different effective charges, would give the energy $E = -2.8994$ at.u., which is better than the value obtained by Eq.III.2 using eleven configurations.

Hylleraas' work was the beginning of a series of investigations on the He problem which are still going on. A more detailed report will be given in a special section on the applications. In conclusion we will only give a summary of Hylleraas' first results in comparison to the SCF value, some later results, and the best known eigenvalue (Kinoshita 1957), since they give an idea of the immediate strength of the different methods.

Taking up the idea of "correlated wave functions" containing r_{12}, James and Coolidge (1933) made a careful study of the H_2 problem and, after a great deal of numerical work, they obtained finally an energy value in complete agreement with experience. This was another successful test of the validity of the Schrödinger

TABLE IV. Unrelativistic Energy for the Ground State of He in Modified Atomic Units (Eq. III.3)

Symbol	Method	Hylleraas' result	Best result obtained so far.
SCF	Hartree-Fock $(1s)^2$		-2.8617 [a]
c	Open shell $(1s', 1s'')$	-2.8754	-2.8779 [b]
a	Superposition of configurations	-2.8992	-2.9012 [b]
c_b	Open shell with correlation factor	-2.8994	-2.9020 [c]
b	Correlated wave function	-2.9032	-2.9037 [d]

[a] Green *et al.* (1954).
[b] Shull and Löwdin (1958).
[c] Löwdin and Rédei (1958).
[d] Kinoshita (1957). Compare also Pekeris (1958).

equation in the two-electron configuration space, and hence there is good reasons for believing that this equation really forms a reliable basis for the theoretical treatment of the electronic structure of matter.

B. Wigner's Study of the Alkali Metals

The study of the two-electron systems was greatly simplified by the fact that the total wave function could be factorized into a space part and a spin part according to Eq. III.1. For $N = 3, 4, \ldots$, such a separation of space and spin is no longer possible, and an explicit treatment of the spin is actually needed in considering correlation effects. This question of the connection between space and spin in an antisymmetric spin function is a rather complicated problem, which has been brought to a simple solution first during the last few years.

An estimate of the magnitude of the correlation energy for a many-electron system was urgently required, however, particularly in the study of the cohesive energy of the alkali metals carried out by Wigner and Seitz by means of the "cellular method". This problem was treated by Wigner in two classical papers (Wigner 1934, 1938), where he used the idea that the correlation energy comes mainly from the Coulomb repulsion between particles having antiparallel spins and that the proper wave function should hence

have a form where the movement of each particle depends on the positions of all the other electrons with opposite spins.

Leaving the question of pure spin states entirely aside, Wigner studied a system containing an even number of electrons ($N = 2n$) by considering the product of two determinants built up from orbitals only

$$\begin{vmatrix} \psi_1(\boldsymbol{r}_1) & \psi_1(\boldsymbol{r}_2) & \dots & \psi_1(\boldsymbol{r}_n) \\ \psi_2(\boldsymbol{r}_1) & \psi_2(\boldsymbol{r}_2) & \dots & \psi_2(\boldsymbol{r}_n) \\ \dots & \dots & \dots & \dots \\ \psi_n(\boldsymbol{r}_1) & \psi_n(\boldsymbol{r}_2) & \dots & \psi_n(\boldsymbol{r}_n) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(\boldsymbol{r}_{n+1}) & \psi_1(\boldsymbol{r}_{n+2}) & \dots & \psi_1(\boldsymbol{r}_N) \\ \psi_2(\boldsymbol{r}_{n+1}) & \psi_2(\boldsymbol{r}_{n+2}) & \dots & \psi_2(\boldsymbol{r}_N) \\ \dots & \dots & \dots & \dots \\ \psi_n(\boldsymbol{r}_{n+1}) & \psi_n(\boldsymbol{r}_{n+2}) & \dots & \psi_n(\boldsymbol{r}_N) \end{vmatrix} \tag{III.6}$$

Here the electronic space coordinates $\boldsymbol{r}_1, \boldsymbol{r}_2, \dots, \boldsymbol{r}_n$ refer to electrons of one spin, whereas $\boldsymbol{r}_{n+1}, \boldsymbol{r}_{n+2}, \dots, \boldsymbol{r}_N$ refer to the electrons of opposite spin. Since there are no spin coordinates, such a function cannot fulfill the general antisymmetric requirement (Eq. II.2), but all exchange effects coming from the Pauli principle will still be included, since all orbitals of a given spin are considered in the same determinant in Eq. III.6. The wave function, Eq. III.6, has therefore the same energy as the Hartree-Fock function, Eq. II.38. Wigner then considered the following modified form

$$\begin{vmatrix} \psi_1(\boldsymbol{r}_1; \boldsymbol{r}_{n+1}, \boldsymbol{r}_{n+2}, \dots, \boldsymbol{r}_N) & \dots & \psi_1(\boldsymbol{r}_n; \boldsymbol{r}_{n+1}, \boldsymbol{r}_{n+2}, \dots, \boldsymbol{r}_N) \\ \dots & \dots & \dots \\ \psi_n(\boldsymbol{r}_1; \boldsymbol{r}_{n+1}, \boldsymbol{r}_{n+2}, \dots, \boldsymbol{r}_N) & \dots & \psi_n(\boldsymbol{r}_n; \boldsymbol{r}_{n+1}, \boldsymbol{r}_{n+2}, \dots, \boldsymbol{r}_N) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(\boldsymbol{r}_{n+1}) & \dots & \psi_1(\boldsymbol{r}_N) \\ \dots & \dots & \dots \\ \psi_n(\boldsymbol{r}_{n+1}) & \dots & \psi_n(\boldsymbol{r}_N) \end{vmatrix} \tag{III.7}$$

where, in the first determinant, he introduced instead of the orbitals $\psi_k(\boldsymbol{r}_i)$, the more complicated functions

$$\psi_k(\boldsymbol{r}_i; \boldsymbol{r}_{n+1}, \boldsymbol{r}_{n+2}, \dots, \boldsymbol{r}_N) \tag{III.8}$$

describing the Coulomb correlation. Expressing the trial function (Eq. III.8) in the form

$$\psi_k(\boldsymbol{r}_i; \boldsymbol{r}_{n+1}, \dots, \boldsymbol{r}_N) = \psi_k(\boldsymbol{r}_i) \left\{ 1 + \sum_{p=n+1}^{N} f_k(\boldsymbol{r}_p - \boldsymbol{r}_i) \right\} \tag{III.9}$$

the functions $f_1, f_2, \dots, f_n$ could be determined by the variation

principle. This leads to an improvement of the Hartree-Fock energy, and at least part of the correlation energy will hence be obtained. Wigner points out in a footnote that, even if the form of Eq. III.7 does not correspond to a pure spin state but to a mixture between several states, the importance of the singlet will still be dominating.

The calculations based on Eq. III.7 are essentially valid only for high-electron densities, but Wigner completes the study with some results for a free-electron gas with low density in a uniform positive background. If the density is so low that the kinetic energy is negligible, the electrons will, according to Wigner, form a body-centered cubic lattice with the electrostatic energy

$$-0.746\frac{e^2}{r_s} \tag{III.10}$$

where r_s is the radius of a sphere the volume of which corresponds to the average space available for each electron, so that

$$\tfrac{4}{3}\pi r_s^3 = V/N \tag{III.11}$$

where V is the total volume. In order to get the correlation energy, one should subtract the exchange energy $-0.458\ e^2/r_s$ from the total electrostatic energy, Eq. III.10, which gives the result $-0.288\ e^2/r_s$. Joining the results for high and low electron densities, Wigner finally obtained the correlation energy formula

$$-0.288\frac{e^2}{r_s + 5.1a_{0,H}} \tag{III.12}$$

where $a_{0,H}$ is the first Bohr-radius or the atomic unit of length. Applying this formula to the alkali metals, one obtains for the correlation energy per doubly filled orbital:

Li	Na	K
−1.89	−1.73	−1.58 ev

The figures are absolutely considerably higher than the values for s orbitals given in Table I and Eq. II.83 but lower than the values for p orbitals discussed in connection with Table II.

(1) *Accuracy of Wigner's Formula: Criticism of "Uniform Positive Background" Model*

Wigner's study of the correlation energy in the alkali metals was a pioneering work of great importance, and the degree of difficulty of this field is perhaps best demonstrated by the fact that, during the last two decades, little improvement has been achieved in his correlation formula III.12. The formula is nevertheless rather crude, and Wigner himself estimates the overall accuracy to be within 20 per cent.

Wigner's study of the correlation effects for high-electron densities is closely connected to the standard methods described in Section III.E., and the main errors come from the restricted form of the wave function (Eq. III.7) and the fact that this function does not represent a pure spin state. Hence, Wigner obtains only an upper bound for the correlation energy in this case.

The treatment of low-electron densities in Wigner's theory is of an entirely different character, since it is based on a model where the discrete nuclei are replaced by a *uniform positive background.* This model has been severely criticized by Slater (1956), who has pointed out that it leads to a wrong behavior of the correlation energy for separated atoms, since this quantity goes to zero for $r_s \to \infty$ instead of approaching the constant limit discussed in connection with Eq. II.90; see Figure 3. It is not clear how much this discrepancy will influence formula III.12 for the r_s values of actual interest, but it may now even be doubtful whether there exists such a simple relation expressing the total correlation energy as a function of the electron density only.

Wigner's formula is open to criticism also on another point, since he assumes the existence of a stationary electron state where the density is so low that the kinetic energy may be neglected. This is in contradiction to the virial theorem (Eq. II.15), which tells us that the kinetic energy can never be neglected in comparison to the potential energy and that the latter quantity is compensated by the former to fifty per cent. A reexamination of the low density case would hence definitely be a problem of essential interest.

C. Brief Survey of Current Situation

Before making a detailed description of the methods now in use to determine correlation effects, i.e., to obtain wave functions of higher accuracy than the HF scheme, we will try to give a very brief survey of the current situation in the field.

Except for the fundamental investigations by Hylleraas and by Wigner, the progress in the correlation studies was fairly slow during the first twenty-five years of modern wave mechanics, as is shown by Yoshizumi's bibliography. We see from the list that the year 1950 represented a turning point of the interest, and a great deal of investigations on the correlation problem were then started. One of the main reasons was certainly the construction of the modern electronic computers which made it possible to carry out the laborious calculations which are always connected with the solutions of many-particle problems. The development since 1950 has so far been almost explosive, and one can expect that still more interest will be devoted to this field during the next decade. A diagrammatic survey of the most important current methods for treating correlation effects is given in Figure 4, and here we will make some short comments.

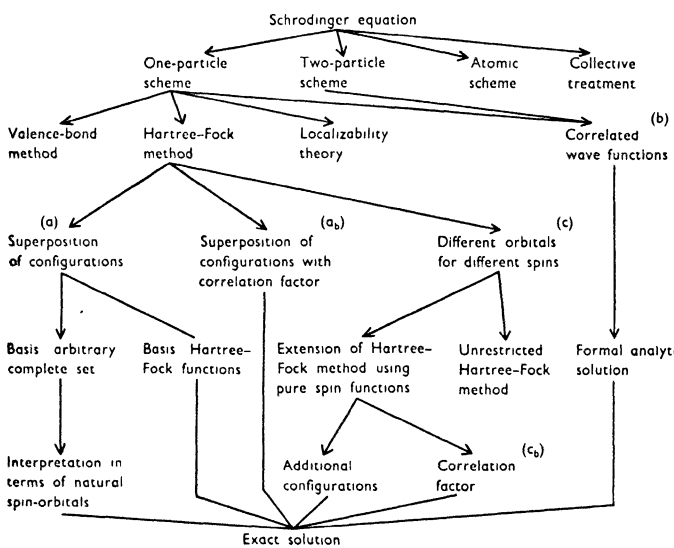


Fig. 4. Survey of current methods for treating correlation effects.

Because of the success of the r_{12} method in the applications, one had almost universally in the literature adopted the idea of the necessity of introducing the interelectronic distances r_{ij} explicitly in the total wave function (see, e.g., Coulson 1938). It was therefore essential for the development that Slater,[39] Boys, and some other authors at about 1950 started emphasizing the fact that a wave function of any desired accuracy could be obtained by *superposition of configurations*, i.e., by summing a series of Slater determinants (Eq. II.38) built up from a complete basic one-electron set. Numerical applications on atoms and molecules were started by means of the new modern electronic computers, and the results have been very encouraging. It is true that a wave function delivered by the machine may be the sum of a very large number of determinants, but the result may afterwards be mathematically simplified and physically interpreted by means of *natural orbitals*.[22,17]

There has been a great deal of discussion in the literature concerning the theoretical background for the method of *correlated wave functions* containing r_{ij}. The main interest has been concentrated on the old helium problem, and the question has been whether the expansions introduced by Hylleraas really converge towards a solution to the Schrödinger equation, and very important results have here recently been obtained by Kinoshita (1957), to whom we also would like to refer for complete references. One has also discussed the analytic character of the total wave function and the existence of logarithmic singularities (see, e.g., Hylleraas and Midtdal 1956), but Kinoshita points out that the logarithmic terms are not necessarily required by the structure of the Schrödinger equation itself.

For systems containing three or more electrons very little is so far known about the foundation for the method of correlated wave functions, and research on this problem would be highly desirable. It seems as if one could expect good energy results by means of a wave function being a product of a properly scaled Hartree-Fock function and a "correlation factor" containing the interelectronic distances r_{ij} (Krisement 1957), but too little is known about the limits of accuracy of such an approach.

On the helium problem, the connection between the method of correlated wave function and the method of superposition of configurations has also been investigated in detail.[8]

For two-electron systems (He, H_2) the method with different orbitals for different electrons was thoroughly discussed at the Shelter Island Conference in 1951 (Kotani 1951, Taylor and Parr 1952, Mulliken 1952). A generalization of this method to many-electron systems has now been given (Löwdin 1954, 1955, Itoh and Yoshizumi 1955) and is called the method with *different orbitals for different spins.*

In this approach, the correlation error is diminished by letting electrons with different spins try to avoid each other, which means that the electrons with a certain spin are localized in another part of space than the electrons with opposite spin. Closely related to this idea is the *localizability theory* of the electrons in atoms and molecules (Daudel 1953, 1954, 1955, 1956), in which the space is divided into loges in such a way that the probability for finding a single electron with a certain spin within each loge is as large as possible. This partitioning of the space leads to a convenient geometrical description of the system.

The method of superposition of configurations as well as the method of different orbitals for different spins belong within the framework of the one-electron scheme, but, as soon as one introduces the interelectronic distance r_{ij}, a two-electron element has been accepted in the theory. In treating the covalent chemical bond and other properties related to electron pairs, it may actually seem more natural to consider two-electron functions as the fundamental building stones of the total wave function, and such a two-electron scheme has also been successfully developed (Hurley, Lennard-Jones, and Pople 1953, Schmid 1953).

The idea of constructing a good wave function of a many-particle system by means of an exact treatment of the two-particle correlation is also underlying the methods recently developed by Brueckner and his collaborators for studying nuclei and free-electron systems. The effective two-particle reaction operator and the self-consistency conditions introduced in this connection may be considered as generalizations of the Hartree-Fock scheme.

For a chemist, a molecule or crystal is always built up by atoms or ions, and the corresponding idea of constructing the total wave function by means of the atomic components goes back to Heitler, London, and Rumer. Recently this approach has been taken up again under the name of *atoms in molecules* (Moffit 1951, Pariser 1953, Pariser and Parr 1953), and, since the wrong asymptotic behavior of the molecular energy curves for the ground state and lower excited states for separated atoms is corrected by means of atomic spectroscopic data, the method is essentially a semiempirical device for treating certain correlation effects (Arai 1957).

An entirely different approach to the correlation problem is taken in the *plasma model* (Bohm and Pines 1953, Pines 1954, 1955), in which the electrons in a metal are approximated by a free-electron gas moving in a uniform positive background. According to classical discharge theory, such a plasma is characterized by an oscillatory behavior having a frequency

$$w_p = (4\pi n_0 e^2/m)^{\frac{1}{2}}$$

where n_0 is the average electron density. By means of rather elaborate field theoretical methods, the collective motions of the electrons have been studied on a quantum mechanical basis. The plasma model has given very important contributions to the knowledge of the effectiveness of the electronic screening actions in metals, but, because of the assumption of the uniform positive background, its treatment of the correlation energy is open to the same criticism as Wigner's theory; see Section III.B(1).

In the three following sections we will try to sketch the mathematical foundation for the three approaches which are most closely connected with the Hartree-Fock scheme, namely the methods of superposition of configurations (a), correlated wave functions (b), and different orbitals for different spins (c). We will also discuss their main physical implications.

D. Superposition of Configurations

(1) *Arbitrary Complete Basic Set*

The mathematical background of the method of superposition of configurations is quite simple and straightforward, and we will

here summarize the main lines. Let us introduce a certain orthonormal and complete set of discrete one-electron functions or spin orbitals $\{\psi_k(\boldsymbol{x})\}$ as a basis, and let us assume that every normalizable function $\psi(\boldsymbol{x})$ of a single electronic coordinate $\boldsymbol{x} = (\boldsymbol{r}, \zeta)$ may be expanded in this set:

$$\psi(\boldsymbol{x}) = \sum_{k=1}^{\infty} c_k \psi_k(\boldsymbol{x}) \tag{III.13}$$

The validity of such an expansion theorem has been carefully studied in mathematics, and there is no need for going into details here.

If we instead have a normalizable function $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2)$ of two electronic coordinates, we can first consider $\boldsymbol{x}_2$ as a fix parameter and expand according to Eq. III.13 with respect to $\boldsymbol{x}_1$. The coefficients $c_k = c_k(\boldsymbol{x}_2)$ are apparently normalizable functions of $\boldsymbol{x}_2$, and, by expanding once more with respect to $\boldsymbol{x}_2$, we obtain

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \sum_{k=1}^{\infty} c_k(\boldsymbol{x}_2)\, \psi_k(\boldsymbol{x}_1) = \sum_{k,l=1}^{\infty} c_{kl}\, \psi_k(\boldsymbol{x}_1)\, \psi_l(\boldsymbol{x}_2) \tag{III.14}$$

For a normalizable function $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ of N electronic coordinates, we have similarly

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \sum_{k_1,k_2,\ldots,k_N=1}^{\infty} c(k_1 k_2 \ldots k_N)\, \psi_{k_1}(\boldsymbol{x}_1)\, \psi_{k_2}(\boldsymbol{x}_2) \ldots \psi_{k_N}(\boldsymbol{x}_N) \tag{III.15}$$

Let us now assume that the given wave function Ψ is antisymmetric and obeys Eq. II.2. Applying the operator $(N!)^{-\frac{1}{2}}A$ defined by Eq. II.16 to both members of Eq. III.15, we get directly

$$\begin{aligned}
\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) &= (N!)^{-\frac{1}{2}} A \Psi \\
&= (N!)^{-1} \sum_{k_1 k_2 \ldots k_N=1}^{\infty} c(k_1 k_2 \ldots k_N) \sum_P (-1)^p P \psi_{k_1}(\boldsymbol{x}_1) \psi_{k_2}(\boldsymbol{x}_2) \ldots \psi_{k_N}(\boldsymbol{x}_N) \\
&= (N!)^{-1} \sum_{k_1 k_2 \ldots k_N=1}^{\infty} c(k_1 k_2 \ldots k_N) \det\{\psi_{k_1}, \psi_{k_2}, \ldots, \psi_{k_N}\} \qquad \text{(III.16)} \\
&= \sum_{k_1 < k_2 < \ldots < k_N} c(k_1 k_2 \ldots k_N) \det\{\psi_{k_1}, \psi_{k_2}, \ldots, \psi_{k_N}\}
\end{aligned}$$

This gives the basic theorem in the method of superposition of configurations:

> *Every normalizable antisymmetric wave function can be expressed as the sum of a series of Slater determinants built up from a complete basic set of one-electron functions.*

We see immediately the connection with the one-electron scheme, but we note that the emphasis is here on the word "complete," whereas, in the Hartree-Fock approximation, one is looking for a finite set of "best" spin orbitals.

Every selection of N one-electron indices $k_1 < k_2 < k_3 \ldots < k_N$ is called an *ordered configuration* K, and the function

$$\Psi_K(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = (N!)^{-\frac{1}{2}} \det \{\psi_{k_1}, \psi_{k_2}, \ldots, \psi_{k_N}\} \quad \text{(III.17)}$$

is the normalized Slater determinant belonging to this configuration. In the $(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$-space, the functions Ψ_K taken for all ordered configurations form an orthonormal set. Introducing the notation $C_K = (N!)^{\frac{1}{2}} c(k_1, k_2, k_3, \ldots, k_N)$, we can write Eq. III.16 in the form

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = \sum_K C_K \Psi_K(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \quad \text{(III.18)}$$

The coefficients C_K for a solution to the Schrödinger equation (Eq. II.1) may now be determined by the variation principle (Eq. II.7) which leads to an infinite system of linear equations

$$\sum_L (H_{KL} - E\delta_{KL}) C_L = 0 \quad \text{(III.19)}$$

where

$$H_{KL} = \int \Psi_K^* H_{\text{op}} \Psi_L(dx) \quad \text{(III.20)}$$

are the matrix elements of the Hamiltonian with respect to the basic Slater determinants (Eq. III.17). The system III.19 has normalizable solutions only for such values of the energy E as are roots to the secular equation:

$$\det \{H_{KL} - E\delta_{KL}\} = 0 \quad \text{(III.21)}$$

In principle, the method of superposition of configurations is

thus very simple, but let us now see how it works in the applications. So far, no practical method has been devised for solving an infinite secular equation of the type of Eq. III.21 and the best thing one can do is to truncate the basic set and try to estimate the remainder. Even in such a case the numerical work becomes formidable for, if the one-electron set contains M functions $\psi_1, \psi_2, \ldots, \psi_M$ with $M > N$, the number of possible configurations is given by the binomial coefficient ${}^{M}C_{N}$, which is quickly increasing with M. Even with a rather modest finite basis $\psi_1, \psi_2, \ldots, \psi_M$, the order of the secular equation III.21 becomes enormously large. If the secular equation is to be solved by the help of only ordinary desk machines, it is usually convenient to forget about the determinant (Eq. III.21) and to determine the eigenvalues directly from the matrix (H_{KL}) by iterative procedures based on Eq. III.19, and with the aid of an electronic computer several approaches are possible.

In the numerical work there is also another key problem, namely the calculation of the matrix elements H_{KL}, the number of which is

$$\frac{1}{2}\binom{M}{N}^2 + \frac{1}{2}\binom{M}{N} \qquad \text{(III.22)}$$

There seems to be a certain "complementarity" between the degree of difficulty in evaluating H_{KL} for various one-electron sets $\{\psi_k\}$ and the order of the secular equation needed to obtain a certain accuracy in the result. The work carried out in getting extensive tables of "molecular integrals" has also been of essential value for facilitating the calculation of the matrix elements H_{KL}.

(a) *Treatment of Ground State and Lower Excited States. Upper and Lower Bounds for the Eigenvalues. Accuracy of the Wave Functions.* It is evident that a method using a finite truncated basis $\psi_1, \psi_2, \ldots, \psi_M$ instead of an infinite complete set $\{\psi_k\}$ must have its danger and that very easily mathematical complications could occur. The situation is certainly very delicate, and research on this point would be of value. The point is that, as long as the set is complete, one can always describe the wave function in the form of Eq. III.18 but with the truncation, the question of how good the approximation rendered by the finite set will be, follows immediately. We will here consider some criteria for the accuracy.

Let us assume that we are first interested in only the *ground state* of a system. By means of a truncated set, we can get higher and higher accuracy of the wave function Φ and the energy, by successively increasing the number M of functions in the basis and by carrying out a proper scaling for every M value under consideration. The accuracy of the approximation may be tested by comparing the energy obtained with an experimental (or semiempirical) value or, still better, pure theoretically, by considering the smallness of the width

$$(\Delta H)^2 = \int |H\Phi - \langle H\rangle\Phi|^2 (dx) = \langle H^2\rangle - \langle H\rangle^2 \qquad \text{(III.23)}$$

which is vanishing only for the exact solution. By means of the width and a rough estimate of the value E_1 of the first excited level, Temple[40] has found also a lower bound for E_0:

$$\langle H\rangle - (\Delta H)^2/(E_1 - \langle H\rangle) \leqq E_0 \leqq \langle H\rangle \qquad \text{(III.24)}$$

provided that the approximation is at least so good that $\langle H\rangle_{\text{Av}} < E_1$. A simple proof will be given below. The difficulty in the use of formula III.24 lies in the evaluation of $\langle H^2\rangle$.

A test of the accuracy of the approximate wave function Φ_0 for the ground state has been given by Eckart[3] by considering the mean square deviation from the exact eigenfunction Ψ_0:

$$\varepsilon = \int |\Phi_0 - \Psi_0|^2 (dx) \qquad \text{(III.25)}$$

We note that this quantity has a meaning in this connection, only if Ψ_0 has been multiplied in advance by a phase factor $e^{i\alpha}$ chosen so that the overlap integral

$$S = \int \Phi_0^* \Psi_0 (dx)$$

becomes real and positive.* Expanding Φ_0 in the complete set of the eigenfunctions Ψ_k, we obtain $\Phi_0 = \sum_k c_k \Psi_k$, where $\sum_k |c_k|^2 = 1$ and further

* The importance of this phase convention may be seen from the special case $\Phi_0 = -\Psi_0$, which gives $\varepsilon = 4$ instead of $\varepsilon = 0$.

$$\langle H-E_0\rangle = \sum_{k=0}^{\infty} (E_k-E_0)\,|c_k|^2 \geqq (E_1-E_0)\sum_{k=1}^{\infty}|c_k|^2$$
$$= (E_1-E_0)\,(1-c_0{}^2) \qquad \text{(III.26)}$$

Since $\varepsilon = 2(1-S)$ and $S = c_0 = 1-\frac{1}{2}\varepsilon$ is a real quantity, we get finally Eckart's formula:

$$\varepsilon \leqq (\langle H\rangle - E_0)/(E_1-E_0) \qquad \text{(III.27)}$$

where we have neglected a term $\varepsilon^2/4$. This criterion is extremely valuable, particularly if an accurate value of E_0 is known, e.g., from experiments; *cf.* Section II.D(4). If this is not the case, one may still get an upper bound for the numerator from Eq. III.24, leading to the relation

$$\varepsilon \leqq (\Delta H)^2/\{E_1-\langle H\rangle\}^2 \qquad \text{(III.28)}$$

where only a rough estimate of E_1 is needed.

Let us now turn our interest to the *excited states*. The energies $E_1, E_2, \ldots$ of these levels are given by the higher roots to the secular equation (Eq. III.21) based on a complete set, and one can, of course, expect to get at least approximate energy values by means of a truncated set. In order to derive upper and lower bounds for the eigenvalues, we will consider the operator

$$\Omega = (H-E_i)(H-E_j)$$

where E_i and E_j are two neighboring eigenvalues, i.e., $j = i\pm 1$. The operator Ω has the same eigenfunctions as H, and its eigenvalues ω_k are

$$\omega_k = (E_k-E_i)(E_k-E_j)$$

i.e., $\omega_i = \omega_j = 0$, whereas all the others are positive. Application of the variation principle to Ω gives $\langle\Omega\rangle \geqq 0$, or

$$\{\langle H\rangle - E_i\}\{\langle H\rangle - E_j\} \leqq (\Delta H)^2 \qquad \text{(III.29)}$$

Provided that the approximation Φ_i is at least so good that $E_{i-1} < \langle H\rangle_{\text{Av}} < E_{i+1}$, we thus obtain by repeated use of this inequality for $j = i-1$ and $j = i+1$, respectively:

$$\langle H\rangle - (\Delta H)^2/(E_{i+1}-\langle H\rangle) \leqq E_i \leqq \langle H\rangle + (\Delta H)^2/(\langle H\rangle - E_{i-1}) \qquad \text{(III.30)}$$

This formula gives us upper and lower bounds for the eigenvalue E_i, provided that $\langle H^2 \rangle$ has been evaluated and that at least rough estimates of the neighboring eigenvalues are known. Formula III.24 is contained as a special case by taking the left-hand part for $i = 0$.

Most of our present theory of molecular and nuclear spectra is based on the assumption that even a fairly small truncated set will provide reasonably good approximations for the lowest energy levels. One has often believed that, if a truncated set is determined to describe the ground state with high accuracy, it will describe at least the closest lying excited state with about the same accuracy. Actual calculations on the He-problem (Shull and Löwdin, to be published) have shown that this assumption may be entirely wrong, and that a truncated set which is excellent for the ground state may give a surprisingly poor result for even the lowest excited level of the same symmetry type.

The reason for this complication of the theory is evident: the truncated set may contain certain variable parameters, and, if these are carefully adjusted to render the best possible description of a specific state, they may become rather unsuitable for the description of another state. According to Section II.C(3), a truncated set should, e.g., always contain a scale factor as a variable parameter and, if this quantity is fitted to the ground state, it may give a basic set which is rather "out of scale" for even the first excited state. Since the virial theorem is not satisfied for this state, the corresponding total energy may be comparatively poorly reproduced. This implies that in treating excited states, it is desirable to have reliable criteria for the accuracy of both energies and wave functions.

Let us now consider the possibilities for deriving an eigenfunction for a particular excited state. The straightforward application of the variation principle (Eq. II.7) is complicated by the additional requirement that the wave function Ψ_k for the state k must be orthogonal to the exact eigenfunctions $\Psi_0, \Psi_1, \Psi_2, \ldots, \Psi_{k-1}$ for all the lower states although these are not usually known. One must therefore try to proceed by way of the secular equation (Eq. III.21). A well-known theorem[15, 25] says that, if a truncated

set of order M is extended by one more function to the order $(M+1)$, the roots of the orginal secular equation will separate the roots of the extended secular equation. By enlarging the set to be infinite and complete, one can then show that the exact eigenvalues must be lower bounds for the roots of the truncated secular equations. This implies also that the pth root J_p of the secular equation of order M is an upper bound for the pth exact eigenvalue E_p:

$$E_p \leqq J_p \tag{III.31}$$

see Figure 5. The corresponding wave function Φ_p is not necessarily

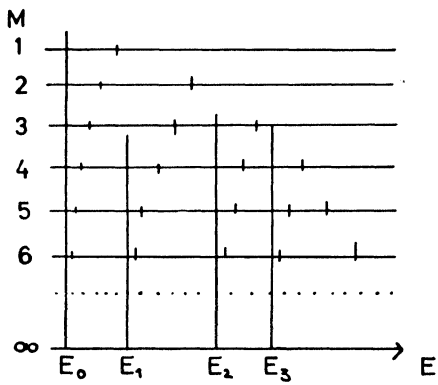


Fig. 5. Graphical illustration of separation theorem; all roots are assumed to be nondegenerate.

orthogonal to the exact eigenfunctions $\Psi_0, \Psi_1, \ldots, \Psi_{p-1}$ but only to the approximate eigenfunctions $\Phi_0, \Phi_1, \ldots, \Phi_{p-1}$, which means that the previously mentioned complicated orthogonality requirement has been removed. One could now try to get better and better approximations for E_k by minimizing J_k, and it seems plausible that if $J_k = E_k$, then $\Phi_k = \Psi_k$. In this connection, it seems also important to find a criterion for the accuracy of the wave function in terms of the difference $(J_k - E_k)$, and such a relation of type III.27 has recently been derived.[33]

The approximate wave functions Φ_k associated with the truncated set of order M fulfil the relations

$$\int \Phi_k^* H \Phi_l (dx) = J_k \delta_{kl}, \qquad \int \Phi_k^* \Phi_l (dx) = \delta_{kl} \tag{III.32}$$

and they may be expanded in the complete set formed by the exact eigenfunctions Ψ_l, so that

$$\Phi_k = \sum_l \Psi_l c_{lk}$$

where $\sum_l |c_{lk}|^2 = 1$. In comparing Φ_k and Ψ_k, we will choose the phase factor of Ψ_k, so that the integral

$$\int \Phi_k^* \Psi_k(dx) = c_{kk}$$

becomes real and positive. For the mean square deviation, we then obtain

$$\varepsilon_k = \int |\Phi_k - \Psi_k|^2 \, (dx) = 2(1-c_{kk}) \tag{III.33}$$

i.e.,

$$c_{kk} = 1 - \tfrac{1}{2}\varepsilon_k$$

and

$$1 - c_{kk}^2 = \varepsilon_k + \varepsilon_k^2/4$$

By means of an Eckart-type procedure we get directly

$$\begin{aligned} J_k - E_k &= \int \Phi_k^* (H - E_k) \Phi_k (dx) = \sum_{l=0}^{\infty} (E_l - E_k) |c_{lk}|^2 \\ &= \sum_{l=0}^{k-1} + \sum_{l=k+1}^{\infty} \geqq \sum_{l=0}^{k-1} (E_l - E_k)|c_{lk}|^2 + (E_{k+1} - E_k) \{1 - c_{kk}^2 - \sum_{l=0}^{k-1} |c_{lk}|^2\} \\ &= -\sum_{l=0}^{k-1} (E_{k+1} - E_l) |c_{lk}|^2 + (E_{k+1} - E_k)(1 - c_{kk}^2) \end{aligned}$$

or

$$1 - c_{kk}^2 \leqq \frac{J_k - E_k + \sum_{l=0}^{k-1} (E_{k+1} - E_l) |c_{lk}|^2}{E_{k+1} - E_k} \tag{III.34}$$

We note that all the overlap integrals

$$c_{lk} = \int \Psi_l^* \Phi_k (dx)$$

for $l = 0, 1, 2, \ldots, k-1$ are contained in the right-hand member, and the problem is now to estimate these quantities in terms of the difference $(J_k - E_k)$.

Let us consider the auxiliary function Ξ, defined by the relation

$$\Xi = \sum_{\alpha} \Phi_{\alpha} \mu_{\alpha} = \sum_{l} \Psi_{l} d_{l} \tag{III.35}$$

where $\mu_0, \mu_1, \mu_2, \ldots, \mu_k$ are a set of multipliers subject to the condition $\sum_{\alpha} |\mu_{\alpha}|^2 = 1$. For the coefficients d_l, we have $d_l = \sum_{\alpha} c_{l\alpha} \mu_{\alpha}$ and further $\sum_{l} |d_l|^2 = 1$. Let us choose these multipliers so that

$$d_0 = d_1 = d_2 = \ldots = d_{k-1} = 0 \tag{III.36}$$

Using Eq. III.32 and the properties of Ψ_l, we then obtain

$$\int \Xi^* H \Xi (dx) = \sum_{\alpha=0}^{k} J_{\alpha} |\mu_{\alpha}|^2 = \sum_{l=0}^{\infty} E_l |d_l|^2 \geqq E_k \tag{III.37}$$

or

$$\sum_{l=0}^{k-1} (E_k - J_l) |\mu_l|^2 \leqq (J_{k-} - E_k) |\mu_k|^2 \tag{III.38}$$

Let us assume that the approximation is at least so good that all values $J_0 \leqq J_1 \leqq \ldots \leqq J_{k-1}$ are definitely less than E_k. All terms in the left-hand member of the inequality are then positive (or vanishing) which for each one of them leads to the relation

$$\left| \frac{\mu_l}{\mu_k} \right|^2 \leqq \frac{J_{k-} - E_k}{E_k - J_l} \qquad l = 0, 1, \ldots, k-1 \tag{III.39}$$

But from the condition $d_l = 0$ follows

$$c_{lk} = -\sum_{\beta=0}^{k-1} c_{l\beta} \mu_{\beta} / \mu_k$$

and hence also

$$|c_{lk}| \leqq \sum_{l=0}^{k-1} \left| \frac{\mu_l}{\mu_k} \right| \leqq [J_k - E_k]^{\frac{1}{2}} A \tag{III.40}$$

where

$$A = \sum_{l=0}^{k-1} [E_k - J_l]^{-\frac{1}{2}}$$

This implies that the absolute values of the overlap integrals $|c_{lk}|$ are vanishing as $A[J_k - E_k]^{\frac{1}{2}}$ for $J_k \to E_k$, ensuring automatic orthogonality between the function Φ_k and all the lower exact eigenfunctions $\Psi_0, \Psi_1, \ldots, \Psi_{k-1}$ when $J_k = E_k$. Substituting this

relation into Eq. III.34 we finally obtain

$$1-c_{kk}^2 \leqq \frac{J_k-E_k}{E_{k+1}-E_k}\left\{1+A^2\sum_{l=0}^{k-1}(E_{k+1}-E_l)\right\} \qquad \text{(III.41)}$$

which gives the upper bound desired. The estimates used in this derivation have been rather rough, and the proportionality factor in this inequality can certainly be refined. For us it is essential, however, that an upper bound for the mean square error ε_k which is proportional to the difference (J_k-E_k) has been found. The result implies that, in using truncated sets, one may use different sets for treating different states, provided only that one minimizes the appropriate root of the associated secular equation.

(b) *Extension of the Scaling Procedure.* In the method of superposition of configurations based on a truncated set, there is an extension of the scaling procedure previously discussed in Section II.C(3) which immediately presents itself. Let us assume that we have solved the secular equation (Eq. III.21) and obtained the solution $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ in the form of Eq. III.18 with fixed numerical coefficients C_K. If the virial theorem (Eq. II.15) is not satisfied, we can then consider the scaled trial function

$$\begin{aligned}\Psi_\eta(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) &= \eta^{3N/2}\Psi(\eta\boldsymbol{x}_1, \eta\boldsymbol{x}_2, \ldots, \eta\boldsymbol{x}_N)\\ &= \eta^{3N/2}\sum_K C_K\Psi_K(\eta\boldsymbol{x}_1, \eta\boldsymbol{x}_2, \ldots, \eta\boldsymbol{x}_N)\end{aligned} \qquad \text{(III.42)}$$

where $\eta\boldsymbol{x}_i = (\eta\boldsymbol{r}_i, \zeta_i)$. By using formula II.25, we can then determine a value $\eta = \eta_1$ so that the virial theorem is fulfilled, and this will also render a certain improvement of the energy. We note, however, that this energy is not the best which can be obtained by starting from the scaled basic set $\psi_1(\eta_1\boldsymbol{x}), \psi_2(\eta_1\boldsymbol{x}), \ldots$ since the coefficients C_K have not been independently varied for the value $\eta = \eta_1$. Solution of the secular equation (Eqs. III.21 and III.19) leads to other coefficients $C_K(\eta_1)$ and a lower energy, but the resulting total wave function may not satisfy the virial theorem. Using Eq. II.25 again, we get a new scale factor $\eta = \eta_2$, for which we can repeat the solution. In this way we obtain an iterative procedure which converges towards the optimum scale factor η_{opt} connected with optimum coefficients $C_K(\eta_{\text{opt}})$.

It may happen that many steps are needed before this iteration process converges, and the repeated numerical solution of Eqs. III.21 and III.18 becomes then a very tedious affair. In such a case, it is usually better to try to plot the approximate eigenvalue $E(\eta)$ as a function of the scale factor η, particularly since one can use the value of the derivative $\partial E/\partial\eta$, too. The linear system (Eq. III.19) may be written in matrix form $\boldsymbol{HC} = E\boldsymbol{C}$ and from this and the normalization condition $\boldsymbol{C}^\dagger\boldsymbol{C} = \mathbf{1}$ follows

$$E = \boldsymbol{C}^\dagger\boldsymbol{H}\boldsymbol{C} \tag{III.43}$$

Differentiating with respect to η, using $\boldsymbol{HC} = E\boldsymbol{C}$ and the normalization condition, we obtain

$$\frac{\partial E}{\partial\eta} = \boldsymbol{C}^\dagger\frac{\partial \boldsymbol{H}}{\partial\eta}\boldsymbol{C} = \boldsymbol{C}^\dagger(2\eta\boldsymbol{T}+\boldsymbol{V})\boldsymbol{C} = 2\eta\langle T\rangle_\eta + \langle V\rangle_\eta \tag{III.44}$$

which is a generalization of the Hellman-Feynman theorem. This implies that relation II.24 is valid even when we consider the variation of the coefficients C_K with η, but the expectation values $\langle T\rangle_\eta$ and $\langle V\rangle_\eta$ are functions of η just because of their dependence of these quantities. This is the reason why Eq. II.25 does not give the optimum value of η directly, and we will instead use Eq. III.44 for determining the value of $\partial E/\partial\eta$ for the η value under consideration. After determining the values of $E(\eta)$ and $E_\eta(\eta)$ for a few trial values, one can easily find the actual minimum point by *interpolation* and this process is often faster than the iteration procedure based on Eq. II.25. The choice of method depends, of course, also on the type of numerical equipment available.

(c) *Remainder Problem. A Numerical Method for Solving Secular Equations of High Order.* All the difficulties connected with the choice of a suitable truncated basic set will disappear, if one goes over to a complete basis. The virial theorem for example, will be fulfilled automatically for all the states, and the scaling becomes irrelevant. It is definitely very difficult to handle an infinite matrix (H_{KL}) numerically, but one could try to divide the complete basis into two parts: the truncated basis $\psi_1, \psi_2, \ldots, \psi_M$, and the *remainder* set $\psi_{M+1}, \psi_{M+2}, \ldots$. The configurations K could then be divided into two subsets (a) and (b), depending on whether the

constituting functions all belong to the truncated basis or whether at least one function comes from the remainder set. Let us now write eq. III.19 in the matrix form

$$\boldsymbol{H}\boldsymbol{C} = E\boldsymbol{C} \tag{III.45}$$

where $\boldsymbol{H}$ is the energy matrix (H_{KL}) and $\boldsymbol{C}$ is a vector formed by the coefficients C_K in expansion III.18. The division of the configurations into two groups corresponds to a partitioning of $\boldsymbol{H}$ and $\boldsymbol{C}$:

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{H}_{aa} & \boldsymbol{H}_{ab} \\ \boldsymbol{H}_{ba} & \boldsymbol{H}_{bb} \end{pmatrix}, \qquad \boldsymbol{C} = \begin{pmatrix} \boldsymbol{C}_a \\ \boldsymbol{C}_b \end{pmatrix} \tag{III.46}$$

and Eq. III.45 may then be written in the form

$$\begin{aligned} \boldsymbol{H}_{aa}\boldsymbol{C}_a + \boldsymbol{H}_{ab}\boldsymbol{C}_b &= E\boldsymbol{C}_a \\ \boldsymbol{H}_{ba}\boldsymbol{C}_a + \boldsymbol{H}_{bb}\boldsymbol{C}_b &= E\boldsymbol{C}_b \end{aligned} \tag{III.47}$$

Solving $\boldsymbol{C}_b$ from the last equation, we obtain

$$\boldsymbol{C}_b = (E \cdot \mathbf{1}_{bb} - \boldsymbol{H}_{bb})^{-1}\boldsymbol{H}_{ba}\boldsymbol{C}_a$$

and substitution of this expression into the first equation gives finally

$$\{\boldsymbol{H}_{aa} + \boldsymbol{H}_{ab}(E \cdot \mathbf{1}_{bb} - \boldsymbol{H}_{bb})^{-1}\boldsymbol{H}_{ba}\}\boldsymbol{C}_a = E\boldsymbol{C}_a \tag{III.48}$$

This is an eigenvalue problem of the form of Eq. III.45 referring to the truncated basis only, and the influence of the remainder set is seen by the additional term in the energy matrix. The relation III.48 corresponds to a solution of the secular equation by means of a modified perturbation theory,[19] and the problem is complicated by the fact that the extra term in Eq. III.48 contains the energy parameter E, which leads to an iteration procedure. So far no one has investigated the remainder problem in detail, but Eq. III.48 certainly provides a good starting point.

The partitioning method also furnishes an excellent tool for the numerical solution of secular equations of any order.[18] In such a case, one chooses the subset (a) to consist of a single function and, since C_a is then simply a number, Eq. III.48 gives

$$\begin{aligned} E &= f(E) \\ f(E) &\equiv H_{aa} + \boldsymbol{H}_{ab}(E \cdot \mathbf{1}_{bb} - \boldsymbol{H}_{bb})^{-1}\boldsymbol{H}_{ba} \end{aligned} \tag{III.49}$$

provided that $C_a \neq 0$. The function $y = F(E) \equiv E - f(E)$ has only single roots, which are identical with the eigenvalues to Eq. III.21 independent of their degree of degeneracy. Only in the accidental case when $C_a = 0$ will an eigenvalue not show up when solving the equation $F(E) = 0$. The asymptotes to the curve $y = F(E)$ are represented by the line $y = E - H_{aa}$ and the vertical lines by $E = h_b$, where h_b are the eigenvalues to $\boldsymbol{H}_{bb}$ which are not simultaneously eigenvalues to $\boldsymbol{H}$. The typical behavior of the function $y = F(E)$ is illustrated in Figure 6.

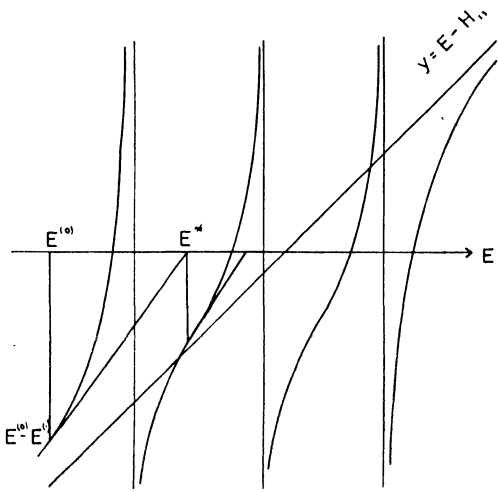


Fig. 6. Typical behavior of the function $y = F(E) \equiv E - f(E)$. The Newton-Raphson construction shows that the second-order process based on Eqs. III.51 and III.53 does not always converge towards the eigenvalue lying closest to $E^{(0)}$.

In order to solve Eq. III.49, one can try to use the formula $E^{(k+1)} = f\{E^{(k)}\}$, which leads to a first-order iteration procedure. Starting from a trial value $E^{(0)}$, one obtains a series $E^{(1)}$, $E^{(2)}$, $E^{(3)}$, . . . which may be convergent or divergent. In both cases, one can go over to a second-order iteration process, which is most easily derived by solving the equation $F(E) = 0$ by means of Newton-Raphson's formula

$$E^* = E^{(0)} - F\{E^{(0)}\}/F'\{E^{(0)}\} \qquad \text{(III.50)}$$

Practically, the solution is carried out by choosing $C_a = 1$ and by strating from an arbitrary trial value $E^{(0)}$; the vector $\boldsymbol{C}_b^{(0)}$ is then determined by solving the linear system

$$(\boldsymbol{H}_{bb} - E^{(0)} \cdot \mathbf{1}_{bb})\boldsymbol{C}_b^{(0)} = -\boldsymbol{H}_{ba} \tag{III.51}$$

Application of the first formula III.47 and Eq. III.50 gives further

$$E^{(1)} = f\{E^{(0)}\} = H_{aa} + \boldsymbol{H}_{ab}\boldsymbol{C}_b^{(0)} \tag{III.52}$$

and

$$E^* = \frac{\boldsymbol{C}^{(0)\dagger}\boldsymbol{H}\boldsymbol{C}^{(0)}}{\boldsymbol{C}^{(0)\dagger}\boldsymbol{C}^{(0)}} \tag{III.53}$$

where $\boldsymbol{C}^{(0)}$ is the vector having the components $C_a = 1$ and $\boldsymbol{C}_b^{(0)}$. Equation III.53 shows a close connection between the variational expression and the Newton-Raphson procedure for solving the equation $F(E) = E - f(E) = 0$. It should be observed that repeated use of Eq. III.53 does not necessarily converge towards the eigenvalue lying closest to $E^{(0)}$; see Figure 6. In using the method numerically, it may therefore be feasible to keep the general shape of the curve $y = F(E)$ in mind. We note further that

$$\begin{aligned} y^{(0)} &= E^{(0)} - E^{(1)} = -\{(H_{aa} - E^{(0)})C_a + \boldsymbol{H}_{ab}\boldsymbol{C}_b^{(0)}\} \\ y'^{(0)} &= \boldsymbol{C}^{(0)\dagger}\boldsymbol{C}^{(0)} = 1 + \boldsymbol{C}_b^{(0)\dagger}\boldsymbol{C}_b^{(0)} \geqq 1 \end{aligned} \tag{III.54}$$

Since the iteration procedure is of the second order, the convergence is anyway extremely rapid. The method is valid both for nondegenerate and degenerate eigenvalues, which are all represented by distinct roots to $F(E) = 0$, and may be used for evaluating all eigenvalues and eigenfunctions. It becomes particularly simple for the ground state.

In conclusion, we observe that the elementary partitioning method described in this section is of value not only for numerical purposes and for estimating the remainder but also for studying theoretical problems connected with conventional perturbation theory and with Brueckner's approximation for treating many-particle systems.

(2) *Different Types of Complete Sets. Importance of the Continuum in Using Hydrogen-like Orbitals*

The method of superposition of configurations is essentially based on the assumption that the basic orbitals form a *complete* set. The most popular basis used so far in the literature is certainly formed by the hydrogen-like functions, which set contains a discrete and a continuous part. The discrete subset corresponds physically to the bound states of an electron around a proton, whereas the continuous part corresponds to a free electron scattered by a proton, or classically to the elliptic and hyperbolic orbits, respectively, in a central-field problem.

The dangerous point in using the hydrogen-like functions is that the discrete subset is by no means complete: in order to expand an arbitrary normalizable one-electron wave function correctly in hydrogen-like orbitals, it is *necessary* to include the part associated with the continuum which will then give normalizable contributions to the expansion in the form of "wave packets." Using arguments from perturbation theory, some authors have tried to conclude that these contributions must be small, since the functions involved have high orbital energies, but this result is definitely wrong. It is easily shown that the large energy differences in the perturbation theory denominators are actually balanced by strong interaction matrix elements in the numerators. Actual examples have also shown that the contributions from the continuum are usually appreciable; see Section III.D(4a).

The discrete hydrogen-like orbitals (nlm) are given by the formula:

$$(nlm) = -2(\eta^3/n^4)^{\frac{1}{2}} \{(n+l)!\}^{-\frac{1}{2}} \{(n-l-1)!\}^{\frac{1}{2}} \times (2\eta r/n)^l e^{-\eta r/n} L_{n+l}^{2l+1}(2\eta r/n)\, Y_{lm}(\theta, \varphi) \tag{III.55}$$

where L_{n+l}^{2l+1} are the Laguerre functions of order $(2l+1)$, η is a scale factor or "effective charge," and Y_{lm} are the spherical harmonics. It was pointed out by Schrödinger[32] in 1926 in the foundation of modern quantum mechanics that the discrete set (Eq. III.55) would not provide a sufficient basis for perturbation theory, since it is not complete. The continuum can, of course, be included, but

the calculations are usually rather cumbersome. Schrödinger suggested therefore that, instead of Eq. III.55, one should use the discrete set which is obtained by omitting the principal quantum number n in the variable $2\eta r/n$, i.e., the set

$$-2(\eta^3/n)^{\frac{1}{2}}\{(n+l)!\}^{-\frac{1}{2}}\{(n-l-1)!\}^{+\frac{1}{2}} \times (2\eta r)^l e^{-\eta r} L_{n+l}^{2l+1}(2\eta r)\, Y_{lm}(\theta, \varphi) \tag{III.56}$$

It is easily shown that, even if this set is not orthogonal, it is *complete*. For practical purposes, this set has been used successfully by Schrödinger and other authors.*

Formal mathematical arguments tell us that we have to use a complete set like III.56 in order to obtain correct results, but we can now also bring in a physical point of view. Let us consider an atomic system which is subject to a small perturbation causing only a slight rearrangement of the electronic cloud. It is clear that it is very difficult to describe such a small deformation of the electronic system by means of the discrete set, Eq. III.55, since, with increasing principal quantum numbers n, the hydrogen-like orbitals (nlm) get more and more extended over the space and soon have their significant regions outside the system under consideration. The remedy comes from the inclusion of the continuum, or from the use of a set like Eq. III.56 which remains localized within the important region.

It has been suggested (Shull and Löwdin 1955) that, instead of the set III.56, one should use the complete discrete set

$$\overline{(nlm)} = (2\eta)^{\frac{3}{2}}\{(n+l+1)!\}^{-\frac{1}{2}}\{(n-l-1)!\}^{+\frac{1}{2}} \times (2\eta r)^l e^{-\eta r} L_{n+l+1}^{2l+2}(2\eta r)\, Y_{lm}(\theta, \varphi) \tag{III.57}$$

containing the Laguerre functions of order $(2l+2)$, since this set is orthogonal within ordinary space.** It has now been used successfully in several applications (Shull and Löwdin 1955, 1956, Holøien 1956, Hirschfelder and Löwdin 1957, Shull and Löwdin 1958).

* Refs. 4, 13, 28, and several others.

** Hylleraas mentioned the possibility of using the $(2l+2)$ order functions in a footnote in ref. 14, but he did not give any explicit formulas or numerical results.

Comparing the two sets III.57 and III.55 for the same value of the "effective charge" η, we find $\overline{1s} = 1s$, whereas all the other functions $(\overline{nl})$ may be expanded in the functions (nl) and the associated continuum. In studying the function $(\overline{2s})$, it has, e.g., been observed (Shull and Löwdin 1955, 1958) that the discrete functions (nl) give a contribution of only 56.501 per cent, which implies that the remaining 43.499 per cent must come from the hydrogen-like continuum. The importance of the continuum part can hence hardly be enough emphasized.

Unfortunately, the omission of the hydrogen-like continuum has in the literature led to several misleading conclusions and wrong results, and this question is still being discussed in connection with the correlation problem (Taylor and Parr 1952, Gerhauser and Matsen 1955).

In mathematics there is a large number of complete sets of one-particle functions given, and many of those may be convenient for physical applications. With the development of the modern electronic computers, there has been a trend to use such sets as render particularly simple matrix elements H_{KL} of the energy, and the accuracy desired has then been obtained by choosing the truncated set larger and larger. Here we would like to mention the use of Gaussian wave functions (Boys 1950, Meckler 1953) and the use of the exponential radial set (Boys 1955), i.e., respectively

$$\exp(-k\eta r^2) \quad \text{and} \quad \exp(-k\eta r) \tag{III.58}$$

($k = 1, 2, 3, \ldots$). It is clear that, in using such sets without direct physical connection with the problem, the total wave function may be represented by a very slowly convergent expansion in configurations, which it is difficult to interpret. This problem will be treated in the next section.

All the complete sets mentioned here are referred to a certain origin and, in an atomic application, this point may conveniently be chosen to coincide with the nucleus. In a molecular problem, this problem is more difficult: one may use a single complete set as in the "united atom model," or one may introduce a complete set at every nucleus or at certain suitably chosen points ("floating-point" wave functions). If more than one complete set is intro-

duced, the total basic set will be *overcomplete* and the corresponding secular equation will be identically vanishing, as in all cases with linear dependencies among the basic functions; the calculation of the matrix elements H_{KL} is also complicated by an overlap or non-orthogonality problem for pair of functions associated with different nuclei. All these difficulties may be removed by a refinement of the total basis by means of an orthogonalization procedure, and, for a more detailed description of this process, we will refer to another review article.*

(3) *Natural Spin Orbitals*

If the basic set $\{\psi_k\}$ is chosen complete, the virial theorem will be automatically fulfilled and no scaling is necessary. In such a case, the wave function under consideration may certainly be expressed in the form of Eq. III.18, but, if the basis is chosen without particular reference to the physical conditions of the problem, the series of determinants may be extremely slowly convergent with a corresponding difficulty in interpreting the results. It therefore seems tempting to ask whether there exists any basic set of spin orbitals $\{\chi_k\}$ which leads to a most "rapid convergency" in the expansion, Eq. III.18, of the wave function for a specific state (Slater 1951).

A certain answer may be found (Löwdin 1955) by considering the first-order density matrix $\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1)$ defined by Eq. II.9. By means of the basis $\{\psi_k\}$ and formula III.14, this matrix may be expressed in the form

$$\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1) = \sum_{kl} \psi_k^*(\boldsymbol{x}'_1)\,\psi_l(\boldsymbol{x}_1)\gamma_{lk} \qquad \text{(III.59)}$$

where the coefficients γ_{lk} form a hermitean matrix, which may be found from the coefficients C_K in expansion III.18 by carrying out the integrations in Eq. II.9. For the diagonal elements, one obtains the simple formula

$$\gamma_{kk} = \sum_{K}^{(k)} |C_K|^2 \qquad \text{(III.60)}$$

where the summation goes over all configurations K containing the

* See ref. 17, particularly sec. 3.2.

specific index k. The element γ_{kk} may be interpreted as the *occupation number* for the spin orbital $\psi_k(\boldsymbol{x})$, and we note that it depends only on the given state characterized by the wave function $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$ and the spin orbital $\psi_k(\boldsymbol{x})$ under consideration.

The occupation numbers have some important properties. The normalization condition (Eq. II.5) gives $\sum_K |C_K|^2 = 1$, and Eq. III.60 leads hence to the inequality

$$0 \leqq \gamma_{kk} \leqq 1 \tag{III.61}$$

This theorem follows from the antisymmetry requirement (Eq. II.2) and is thus an expression for Pauli's exclusion principle. In the naive formulation of this principle, each spin orbital could be either empty or fully occupied by one electron which then would exclude any other electron from entering the same orbital. This simple model has been mathematically formulated in the Hartree-Fock scheme based on Eq. II.38, where the form of the first-order density matrix $\rho(\boldsymbol{x}'_1, \boldsymbol{x}_1)$ indicates that each one of the Hartree-Fock functions $\psi_1, \psi_2, \ldots, \psi_N$ is fully occupied by one electron.

In order to try to approach the HF scheme as much as possible, we will now introduce the basic orthonormal set $\{\chi_k\}$ which has *maximum occupation numbers*. Let $\boldsymbol{U}$ be the unitary matrix which brings the hermitean matrix (γ_{ik}) to diagonal form:

$$\boldsymbol{U}^\dagger \boldsymbol{\gamma} \boldsymbol{U} = \boldsymbol{n} = \text{diagonal matrix} \tag{III.62}$$

Introducing the vector set $\boldsymbol{\chi}$ by the matrix formula $\boldsymbol{\chi} = \boldsymbol{\psi}\boldsymbol{U}$ or

$$\chi_k = \sum_\alpha \psi_\alpha U_{\alpha k} \tag{III.63}$$

we obtain

$$\boldsymbol{\gamma} = \boldsymbol{U}\boldsymbol{n}\boldsymbol{U}^\dagger, \qquad \boldsymbol{\psi} = \boldsymbol{\chi}\boldsymbol{U}^\dagger$$

and finally

$$\gamma(\boldsymbol{x}'_1|\boldsymbol{x}_1) = \sum_k \chi_k^*(\boldsymbol{x}'_1)\,\chi_k(\boldsymbol{x}_1) n_k \tag{III.64}$$

The basic set χ_k defined by Eq. III.63 has thus the occupation numbers n_k, and the extremum properties follow then from the fact that $n_1, n_2, n_3, \ldots$ (with $n_1 \geqq n_2 \geqq n_3 \ldots$) are the *eigenvalues* of the matrix (γ_{ik}).

The functions $\chi_1, \chi_2, \chi_3, \ldots$ will, in the following, be called the

natural spin orbitals associated with the state under consideration. The first function χ_1 is the spin orbital which has the highest occupation number possible, the second function χ_2 has the same property within the class of orbitals orthogonal to χ_1, the third function has the same property within the class of orbitals orthogonal to χ_1 and χ_2, etc.

If the relation $\psi = \chi U^\dagger$ is substituted into Eq. III.8, we obtain an expansion of Ψ into configurations of the natural spin orbitals

$$\Psi(x_1, x_2, \ldots, x_N) = (N!)^{-\frac{1}{2}} \sum_K A_K \det \{\chi_{k_1}, \chi_{k_2}, \ldots, \chi_{k_N}\} \quad \text{(III.65)}$$

which will be called the *natural expansion*. This series is characterized by a most "rapid convergency" in the following sense: according to an elementary theorem* for the eigenvalues of an hermitean matrix, the sum of the r highest eigenvalues is always larger than the sum of any r diagonal elements, which gives

$$\sum_{k=1}^{r} n_k \geqq \sum_{k=(1)}^{(r)} \gamma_{kk} \quad \text{(III.66)}$$

where the sum $k = (1) \ldots (r)$ indicates that we can take any r indices. By using Eq. III.60 and Eq. III.65 we then obtain

$$\sum_{k=1}^{r} \sum_{K}^{(k)} |A_K|^2 \geqq \sum_{k=(1)}^{(r)} \sum_{K}^{(k)} |C_K|^2 \quad \text{(III.67)}$$

which expresses the optimum convergency property of the natural expansion. The relation III.67 is quite general, but more specialized theorems may also be obtained as will be shown below.

(a) *Case of Two-Electron Systems.* In the important case of two-electron systems ($N = 2$), the properties of the natural spin orbitals and the natural expansion (Eq. III.65) have been investigated in greater detail (Löwdin and Shull 1956). The situation is here simplified by the fact that space and spin may be exactly separated according to Eq. III.1. If the truncated basis contains M one-electron functions, the singlet and triplet wave functions contain respectively $M(M+1)/2$ and $M(M-1)/2$ configurations, but

* This theorem is easily derived from the separation theorem quoted in Section III.D(1a); see Figure 5.

the transformation to natural orbitals reduced the number of terms to M and $M/2$, respectively.

The natural expansion has here also another important optimum convergency property. If this expansion is interrupted after r terms, the renormalized truncated function Ψ_r has the smallest total deviation from the "exact solution"

$$\int |\Psi_{\text{exact}} - \Psi_r|^2 \, dx_1 \, dx_2 \tag{III.68}$$

of all functions built up by configurations selected from any finite basic set or order r. The result implies that, for $N = 2$, the first natural spin orbital is closely related to but not necessarily identical with the corresponding Hartree-Fock function.

Calculations of the ^1S ground state of He (Shull and Löwdin 1958) have given the occupation numbers for the first natural spin orbitals as shown in Table V. These results show that the

TABLE V. Occupation Numbers for the First Natural Spin Orbitals in the ^1S Ground State of the He atom (Shull and Löwdin 1958)

Type	k	n_k	Total
s	1	0.991 863	
	2	3 849	
	3	54	
	4	5	0.995 771
p	1	0.003 896	
	2	136	
	3	4	0.004 036
d	1	0.000 180	
	2	4	0.000 184
f	1	0.000 009	0.000 009
		Sum =	1.000 000

Coulomb repulsion is breaking up the closed shell $(1s)^2$, since it is energetically cheaper to have a small fraction (0.8137 %) of the electrons in the first natural spin orbital χ_1 excited to the higher

spin orbitals. The spectroscopic one-electron symbols could apparently here conveniently be replaced by notations of the type

$$(\chi_1)^{2n_1}(\chi_2)^{2n_2}(\chi_3)^{2n_3}\ldots \qquad \text{(III.69)}$$

The first orbital χ_1 is very closely related to the ordinary SCF function, which is also shown by comparing the total energy of the wave function $(\chi_1)^2$ with the Hartree-Fock energy:

$$\begin{array}{ll} (\chi_1)^2 & -2.861\ 530\ \text{at.u.}_{\text{He}} \\ \text{SCF} & -2.861\ 673\ \text{at.u.}_{\text{He}} \end{array} \qquad \text{(III.70)}$$

The first excited orbitals are characterized by being localized mainly within the same region of space as χ_1. The function χ_{nl} has $(n-l-1)$ nodes but is otherwise not particularly hydrogen-like; it may be expanded in the standard hydrogen-like functions only if a considerable contribution from the continuum is included.

In the He problem, the use of natural spin orbitals greatly facilitates the total wave function. Let us for a moment consider a restricted basis consisting of only six s functions of the type III.57 for $\eta = 2.2$, which altogether form 21 configurations. The corresponding 21-term wave function has the energy $-2.878\ 962$ at.u.$_{\text{He}}$, which is very close to the estimated radial limit -2.87900. By going over to natural spin orbitals, one obtains a 6-term function with the same energy and, by neglecting the two highest natural spin orbitals, one obtains further a 4-term function with the energy -2.878928 at.u.$_{\text{He}}$ which is almost as good.

The results reported in Table V were calculated by means of a basis consisting of four s functions, three p functions, two d functions, and one f function of the type of Eq. III.57 for $\eta = 2.2$. The corresponding 20-term function had an energy of -2.901231 at.u.$_{\text{He}}$, and, by going over to natural spin orbitals, one obtains a 10-term function with the same energy.

Similar calculations for the ground state of the H_2 molecule are now in progress, and we hope that they will lead to a simple but at the same time accurate treatment of the chemical bond.

The problem of the interaction between two hydrogen atoms a and b in their ground state at large internuclear separation R has also been treated (Hirschfelder and Löwdin, 1958), and the inter-

pretation of the result was carried out in terms of natural orbitals. The natural expansion may in this case be written

$$\Psi = (1s)^2 \left\{ 1 - \frac{3}{R^6} \sum_{n=2} \lambda_{np}{}^2 \right\} - \frac{\sqrt{6}}{R^3} \Theta_{11} \sum_{n=2} \lambda_{np} \chi_{np}(r_{a1}) \chi_{np}(r_{b2}) \quad \text{(III.71)}$$

where Θ_{11} is an angular function. A basis of four p functions of the type of Eq. III.57 gave the following eigenvalues λ_{np}:

$$\begin{aligned} \lambda_{2p} &= +1.110\,371, & \lambda_{4p} &= +0.000\,541, \\ \lambda_{3p} &= +0.014\,029, & \lambda_{5p} &= +0.000\,059 \end{aligned} \quad \text{(III.72)}$$

With this basis, one gets for the constant in the London dispersion energy formula $E = -B_6/R_6$:

$$B_6 = 6.499\,003 \quad \text{(III.73)}$$

in close agreement with the best value reported.[28] The values λ_{4p} and λ_{5p} are fairly small and, neglecting them, one obtains with only two natural orbitals $B_6 = 6.498\,988$, which is almost as good as Eq. III.73. With only a single natural orbital χ_{2p}, one gets finally $B_6 = 6.497066$, which is still a very good approximation.

The natural orbitals χ_{2p} and χ_{3p} are, in contrast to the hydrogen-like functions, localized within approximately the same region around the nucleus as the 1s orbital. This means that the polarization caused by the long-range interaction is associated mainly with an angular deformation of the electronic cloud on each atom. If χ_{2p} and χ_{3p} are expanded in the standard hydrogen-like functions, an appreciable contribution will again come from the continuum.

The occupation numbers for the three basic orbitals 1s, χ_{2p}, and χ_{3p} are finally given by the formulas:

$$\begin{aligned} n_{1s} &= 1 - \frac{6}{R^6} (\lambda_{2p}{}^2 + \lambda_{3p}{}^2) \\ n_{2p} &= \frac{6}{R^6} \lambda_{2p}{}^2 \\ n_{3p} &= \frac{6}{R^6} \lambda_{3p}{}^2 \end{aligned} \quad \text{(III.74)}$$

showing how the electronic polarization is a function of the interatomic distance R.

(4) *Hartree-Fock Functions as Basis*

In the method of superposition of configurations, considerable simplifications can be obtained in the matrix elements H_{KL}, if the basis is chosen to consist of the *ordinary and virtual Hartree-Fock functions*, i.e., of the occupied or unoccupied eigenfunctions to the effective Hamiltonian (Eq. II.47). This depends on the so-called Brillouin's theorem which says that all the matrix elements for the total energy between the Hartree-Fock function (Eq. II.38) and the singly excited configurations will vanish identically (Brillouin 1933, Møller and Plesset 1934). Since the Hartree-Fock function itself will then interact directly only with doubly excited configurations, the secular equation can conveniently be solved by perturbation theory, and the method has therefore recently been suggested for practical applications (Nesbet 1955). In using this approach, however, one has to be careful about also including such Hartree-Fock functions associated with the continuum as are needed for the completeness of the basis.

From the practical point of view, it may be more feasible to avoid the introduction of the virtual Hartree-Fock functions of discrete and continuous type and to use only the ordinary SCF functions $\psi_1, \psi_2, \psi_3, \ldots, \psi_N$. In order to obtain a complete basis, we will then add a conveniently chosen discrete subset $\varphi_{N+1}, \varphi_{N+2}, \varphi_{N+3}, \ldots$ of functions orthogonal to the SCF functions so that

$$\int \varphi_i^* \psi_k \, dx = 0 \qquad k = 1, 2, \ldots, N \qquad \text{(III.75)}$$

This may be accomplished, e.g., by starting from a complete set φ_i which is then orthogonalized with respect to the functions $\psi_1, \psi_2, \ldots, \psi_N$ by means of the Schmidt procedure. Our basis consists now of the functions

$$\psi_1, \psi_2, \psi_3, \ldots, \psi_N, \varphi_{N+1}, \varphi_{N+2}, \ldots \qquad \text{(III.76)}$$

from which we build up all possible configurations.

Let us consider the principal determinant Ψ_{SCF} and the singly excited determinant $\Psi_{\text{SCF}}\binom{i}{k}$ obtained by replacing ψ_k by φ_i:

$$\Psi_{\text{SCF}} = (N!)^{-\frac{1}{2}} \det \{\psi_1, \psi_2, \ldots, \psi_k, \ldots, \psi_N\}$$
$$\Psi_{\text{SCF}}\binom{i}{k} = (N!)^{-\frac{1}{2}} \det \{\psi_1, \psi_2, \ldots, \varphi_i, \ldots, \psi_N\} \tag{III.77}$$

For their matrix element with respect to the Hamiltonian II.3 or II.4, one obtains directly

$$\begin{aligned}\int \Psi^*_{\text{SCF}}\binom{i}{k} H_{\text{op}} \Psi_{\text{SCF}}\,(dx) &= \int \varphi_i^*(\boldsymbol{x}_1)\, H_1 \psi_k(\boldsymbol{x}_1)\, d\boldsymbol{x}_1 \\ &+ \sum_{l=1}^{N} \left\{ \int \varphi_i^*(1)\, \psi_l^*(2) \frac{e^2}{r_{12}} \psi_k(1)\, \psi_l(2)\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2 \right. \\ &\left. - \int \varphi_i^*(1)\, \psi_l^*(2) \frac{e^2}{r_{12}} \psi_k(2)\, \psi_l(1)\, d\boldsymbol{x}_1\, d\boldsymbol{x}_2 \right\} \\ &= \int \varphi_i^*(1) \left\{ H_1 + e^2 \int \frac{\rho(2,2) - \rho(2,1) P_{12}}{r_{12}}\, d\boldsymbol{x}_2 \right\} \psi_k(1)\, d\boldsymbol{x}_1 \\ &= \int \varphi_i^*(1)\, H_{\text{eff}}(1)\, \psi_k(1)\, d\boldsymbol{x}_1 = \varepsilon_k \int \varphi_i^*(1)\, \psi_k(1)\, d\boldsymbol{x}_1 = 0 \end{aligned} \tag{III.78}$$

where we have used Eqs. II.4, II.47, II.46, and III.75. Hence we have found that, in using the basic set III.76, the matrix elements between the fundamental SCF determinant and all singly excited configurations will vanish identically, which is a simple generalization of Brillouin's theorem.

The only nonvanishing matrix elements H_{KL} associated with the SCF determinant will thus be the diagonal element, which is identical with the Hartree-Fock energy, and the interaction elements with the doubly excited determinants

$$\Psi_{\text{SCF}}\binom{ij}{kl}$$

that is

$$\int \Psi^*_{\text{SCF}}\binom{ij}{kl} H_{\text{op}} \Psi_{\text{SCF}}\,(dx) = \left(\varphi_i \varphi_j \left| \frac{e^2}{r_{12}} \right| \psi_k \psi_l\right) - \left(\varphi_i \varphi_j \left| \frac{e^2}{r_{12}} \right| \psi_l \psi_k\right) \tag{III.79}$$

All matrix elements connected with triply and more highly excited states are also vanishing.

In order to solve the secular equation, we will now use the partitioning method discussed in Section III.D(1c). Choosing the subset (a) to contain only the SCF-determinant and using Eq. III.49, we obtain

$$E = E_{\mathrm{HF}} + \boldsymbol{H}_{ab}(E \cdot \mathbf{1}_{bb} - \boldsymbol{H}_{bb})^{-1}\boldsymbol{H}_{ba} \qquad \text{(III.80)}$$

which gives us an implicit equation for the correlation energy to be solved by iteration using Eqs. III.51 and III.53. The practical usefulness of this approach depends upon the possibility of evaluating the matrix elements involved; it is clear that the present numerical functions are hardly accurate enough for this purpose, but good analytical SCF functions will probably soon be available.

(5) *Use of Projection Operators in the Method of Superposition of Configurations*

If the system under consideration has certain symmetry properties, it is always possible to simplify the secular equation (Eq. III.21) by means of group theory, which is definitely a strong tool in this connection. Even more essential simplifications may often be gained, however, by introducing the symmetry considerations at a still earlier stage, namely in connection with the choice of the basic set. In treating a state of given symmetry, it is no longer necessary that the basis is entirely complete—it is instead better that it is "symmetry adapted." Such a symmetry-adapted basis can be obtained from a complete set by means of projection operators which may be of group theoretical or still more elementary nature. This manner of proceeding makes it possible to construct directly a set of reduced secular equations—one for each symmetry type existing in the system. Here we will discuss a very naive approach.*

Let us consider a general energy degeneracy, which may be described by an auxiliary operator Λ commuting with H, so that

$$\Lambda H = H\Lambda \qquad \text{(III.81)}$$

For the sake of simplicity, we will assume that Λ has only a finite number of eigenvalues λ_l such that

$$\Lambda\Theta_l = \lambda_l\Theta_l \qquad \text{(III.82)}$$

* See ref. 17, particularly Section 3.1 and ref. 22.

for $l = 1, 2, 3, \ldots, n$, where Θ_l is the associated eigenfunction. If Θ is an arbitrary trial function associated with the subspace defined by the set Θ_l, it may be expanded in the form

$$\Theta = \sum_{l=1}^{n} \Theta_l a_l \tag{III.83}$$

The problem is now to construct an operator O_k, which, applied to Θ, selects only the term corresponding to $l = k$:

$$O_k \Theta = \Theta_k a_k \tag{III.84}$$

i.e., which takes out the "projection" of the function on the eigenstate k of the operator Λ. One can visualize the expansion problem (Eq. III.83) by thinking about a Hilbert space spanned by the basic vectors $\Theta_1, \Theta_2, \Theta_3, \ldots, \Theta_n$ in which it is required to resolve an arbitrary vector into components along the axes; see Figure 7.

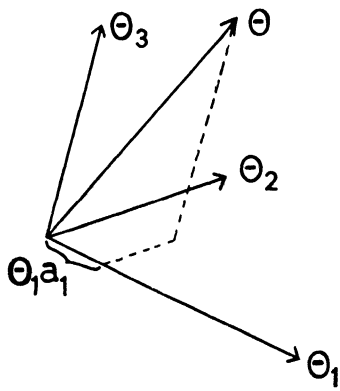


Fig. 7. Resolution of arbitrary vector Θ in a Hilbert space into components along certain axes characterized by the basic vectors $\Theta_1, \Theta_2, \Theta_3, \ldots$ by means of successive projections.

Geometrically this is done by carrying out a series of projections parallel to the axes, and the operator O in the left-hand side of Eq. III.84, is therefore called a *projection operator*. We note that repeated use of O would not change the result, which leads to the relation

$$O^2 = O \tag{III.85}$$

characteristic for the projection operators.[27] The analytical form of

O is now easily constructed; according to Eq. III.82, one has $(\Lambda-\lambda_p)\Theta_p \equiv 0$, which means that the factor $(\Lambda-\lambda_p)$ annihilates the term in Eq. III.83 for $l = p$, the product $(\Lambda-\lambda_p)(\Lambda-\lambda_q)$ annihilates the terms for $l = p$ and $l = q$, etc.; it is then clear that the product operator

$$O_k = \prod_{l=1,2,\ldots,n}^{(l\neq k)} \frac{\Lambda-\lambda_l}{\lambda_k-\lambda_l} \tag{III.86}$$

has the selective property (Eq. III.84) desired. The denominator has here been chosen so that the term for $l = k$ will survive the operation in an unchanged form. We note that, according to Eqs. III.82 and III.84, one obtains $(\Lambda-\lambda_k)O_k \equiv 0$. Since the factors in Eq. III.86 may be written in the form

$$(\Lambda-\lambda_l)/(\lambda_k-\lambda_l) = 1+(\Lambda-\lambda_k)/(\lambda_k-\lambda_l) \tag{III.87}$$

one can then easily prove the two relations

$$O_k^2 = O_k, \qquad O_k O_l = 0, \qquad k \neq l \tag{III.88}$$

showing the projection operator character of Eq. III.86. From Eqs. III.83 and III.84 follows

$$\sum_{k=1}^{n} O_k = 1 \tag{III.89}$$

which is a trivial "resolution of the identity" for a finite Hilbert subspace.

So far we have not made any assumptions about the properties of the operator Λ, but we will now assume that Λ is either self-adjoint or commutes with its hermitean adjoint operator $\Lambda^\dagger$, so that

$$\Lambda\Lambda^\dagger = \Lambda^\dagger\Lambda \tag{III.90}$$

This is a relation fulfilled by the operators corresponding to physical observables and by the unitary operators associated with the basic symmetry operations. It is then easily shown that the functions Θ_l are (or may be chosen to be) simultaneous eigenfunctions to the operators Λ and $\Lambda^\dagger$ belonging to the eigenvalues λ_l and λ_l^*, respectively, and further that eigenfunctions associated with different eigenvalues are automatically orthogonal. In such a case, the operators O_k describe *orthogonal projections*. The selection effect of the operator $O_k^\dagger$ is identical with that of O_k, i.e., the operator is

essentially self-adjoint, and Eq. III.88 may be replaced by the relation

$$O_k^\dagger O_l = O_k \delta_{kl} \tag{III.91}$$

which is of essential importance for the development of the theory.

In solving the eigenvalue problem for the energy operator H_{op}, we have previously always introduced a *complete* basic set Ψ_l, in which the eigenfunction has been expanded:

$$\Psi = \sum_l \Psi_l C_l \tag{III.92}$$

However, if A commutes with H according to Eq. III.81, it is possible to determine the coefficients C_l so that Ψ turns out to be also an eigenfunction to A associated with the eigenvalue λ_k. This implies $O_k\Psi = \Psi$ and, by letting O_k operate on the relation III.92, we hence obtain

$$\Psi = O\Psi = \sum_l (O_k\Psi_l)C_l \tag{III.93}$$

showing that it is also possible to expand Ψ into the set Θ_{k1}, Θ_{k2}, Θ_{k3}, . . ., defined by

$$\Theta_{kl} = O_k\Psi_l \tag{III.94}$$

which consists solely of eigenfunctions to A belonging to the eigenvalue λ_k. This manner of proceeding has previously been used in deriving the relation III.16, which forms the basis for the method of superposition of configurations with the only difference that the antisymmetrization operator (Eq. II.16) is not expressed in product form.

The subset Θ_{k1}, Θ_{k2}, Θ_{k3}, . . . formed from the complete set by means of the projection operator O_k is called A-adapted or symmetry-adapted in the case when A is a symmetry operator. From Eqs. III.81 and III.86 it follows that the projection operators O_k commute with H and, using this property, the quantum-mechanical "turn-over rule," and Eq. III.91, we obtain

$$\begin{aligned} &\int \Theta_{km}^* H_{\text{op}} \Theta_{ln}(dx) = \int (O_k\Psi_m)^* H_{\text{op}} (O_l\Psi_n)(dx) \\ &= \int \Psi_m^* O_k^\dagger H_{\text{op}} O_l \Psi_n(dx) = \int \Psi_m^* H_{\text{op}} (O_k^\dagger O_l)\Psi_n(dx) \\ &= \delta_{kl} \int \Psi_m^* H_{\text{op}} O_l \Psi_n(dx) \end{aligned} \tag{III.95}$$

which shows that two Λ-adapted sets $\Theta_{k1}, \Theta_{k2}, \Theta_{k3}, \ldots$ and $\Theta_{l1}, \Theta_{l2}, \Theta_{l3}, \ldots$ for $k \neq l$ are not only orthogonal but also non-interacting with respect to H_{op}. This theorem supplements the expansion theorem III.93 and indicates that a considerable simplification of the secular equation must be possible.

In the following, we will consider a certain eigenvalue λ and drop the lower index k. Expanding each one of the functions Θ_m $(= \Theta_{km})$ in the complete set Ψ_μ, we obtain

$$\Theta_m = O\Psi_m = \sum_\mu \Psi_\mu \alpha_{\mu m} \tag{III.96}$$

where $\alpha_{\mu m}$ are the matrix elements of the operator O:

$$\alpha_{\mu m} = \int \Psi_\mu^* O \Psi_m (dx) \tag{III.97}$$

forming the discrete and hermitean matrix $\boldsymbol{\alpha}$. From Eq. III.85 follows immediately the relation

$$\boldsymbol{\alpha}^2 = \boldsymbol{\alpha} \tag{III.98}$$

showing that $\boldsymbol{\alpha}$ has only the eigenvalues 0 and 1, both being highly degenerate. Writing Eq. III.98 in the form $\boldsymbol{\alpha}\boldsymbol{\alpha}_\nu = \boldsymbol{\alpha}_\nu$, we find that each one of the column vectors $\boldsymbol{\alpha}_\nu$ of the matrix $\boldsymbol{\alpha} = (\boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, \boldsymbol{\alpha}_3, \ldots)$ is an eigenvector associated with the eigenvalue 1; not all of these are necessarily linearly independent, of course.

Since Θ_m is expressed as a single sum in the basic set, one would expect that the matrix elements of H_{op} with respect to two functions Θ_m and Θ_n would be a double sum. However, using Eq. III.95 for $k = l$, we find

$$\int \Theta_m^* H_{\text{op}} \Theta_n (dx) = \int \Psi_m^* H_{\text{op}} \Theta_n (dx) = \sum_\nu H_{m\nu} \alpha_{\nu n} \tag{III.99}$$

i.e., a single sum, which is a very important simplification.

In order to proceed further, it is now necessary to study the linear dependence of the projected functions $\Theta_1, \Theta_2, \Theta_3, \ldots$ which is done by investigating their overlap matrix

$$\Delta_{\mu\nu} = \int \Theta_\mu^* \Theta_\nu (dx) \tag{III.100}$$

By means of the "turn-over rule" and Eq. III.91, we obtain directly

$$\begin{aligned} \Delta_{\mu\nu} &= \int (O\Psi_\mu)^* (O\Psi_\nu)(dx) = \int \Psi_\mu^* O^\dagger O \Psi_\nu (dx) \\ &= \int \Psi_\mu^* O \Psi_\nu (dx) = \alpha_{\mu\nu} \end{aligned} \tag{III.101}$$

showing that the overlap matrix $\boldsymbol{\Delta}$ is identical with the matrix $\boldsymbol{\alpha}$. This means that the overlap matrix $\boldsymbol{\Delta}$ has also the eigenvalues 0 and 1, the former connected with the existence of linear dependencies among the set Θ_l. The main problem is hence to construct an orthogonal set of Λ-adapted functions which span the particular part of the Hilbert space defined by the functions Θ_l. This can be done in several different ways, but a simple method is provided by the projection operator formalism itself.

Let us consider the functions $\Theta_1, \Theta_2, \Theta_3, \ldots$ successively in order, and let us start by considering the expansions

$$\begin{aligned} \Theta_1 &= O\Psi_1 = \Psi_1 \alpha_{11} + \Psi_2 \alpha_{21} + \Psi_3 \alpha_{31} + \ldots \\ \Theta_2 &= O\Psi_2 = \Psi_1 \alpha_{12} + \Psi_2 \alpha_{22} + \Psi_3 \alpha_{32} + \ldots \end{aligned}$$

If $\alpha_{11} \neq 0$, we will fix the first function Θ_1 having the normalization integral $\Delta_{11} = \alpha_{11}$. It is then possible to determine a multiplier d_{12} so that $\alpha_{12} + \alpha_{11} d_{12} = 0$. Putting $\alpha'_{l2} = \alpha_{l2} + \alpha_{l1} d_{12}$ for $l \geqq 2$, we then obtain

$$\Theta'_2 = O(\Psi_2 + \Psi_1 d_{12}) = 0 + \Psi_2 \alpha'_{22} + \Psi_3 \alpha'_{32} + \ldots \tag{III.102}$$

The function Θ'_2 obtained by eliminating Ψ_1 in the expansion of Θ_2 is automatically orthogonal to Θ_1 for, using the "turn-over rule" and Eq. III.91, we get

$$\begin{aligned} \int \Theta_1^* \Theta'_2 (dx) &= \int (O\Psi_1)^* O(\Psi_2 + \Psi_1 d_{12})(dx) \\ &= \int \Psi_1^* (\Psi_2 \alpha'_{22} + \Psi_3 \alpha'_{32} + \ldots)(dx) = 0 \end{aligned} \tag{III.103}$$

and the question is now only whether Θ'_2 is identically vanishing or not. For the normalization integral, we obtain similarly

$$\begin{aligned} &\int |\Theta'_2|^2 (dx) = \int (\Psi_2^* + \Psi_1^* d_{12}^*) O(\Psi_2 + \Psi_1 d_{12})(dx) \\ &= \int (\Psi_2^* + \Psi_1^* d_{12}^*)(\Psi_2 \alpha'_{22} + \Psi_3 \alpha'_{32} + \ldots)(dx) = \alpha'_{22}, \end{aligned} \tag{III.104}$$

showing that the function is nontrivial if $\alpha'_{22} \neq 0$. However, if

$\alpha'_{22} = 0$, we can conclude that all the higher coefficients α'_{i2} are also vanishing: the function Θ_2 is then proportional to Θ_1 and may be omitted; in such a case, we will proceed in the set Θ_i until we find a function having a nonvanishing normalization integral connected with the coefficient for Ψ_2.

Assuming that $\alpha'_{22} \neq 0$, we will now consider the third function:

$$\Theta_3 = O\Psi_3 = \Psi_1\alpha_{13}+\Psi_2\alpha_{23}+\Psi_3\alpha_{33}+\Psi_4\alpha_{43}+\dots \quad \text{(III.105)}$$

It is possible to eliminate Ψ_1 and Ψ_2 from this expansion by introducing two multipliers d_{13} and d_{23} such that

$$\alpha'_{i3} = \alpha_{i3}+\alpha_{i2}d_{23}+\alpha_{i1}d_{13} \quad \text{(III.106)}$$

fulfilling the conditions $\alpha'_{13} = \alpha'_{23} = 0$. This gives

$$\Theta'_3 = O(\Psi_3+\Psi_2 d_{23}+\Psi_1 d_{13}) = 0+0+\Psi_3\alpha'_{33}+\Psi_4\alpha'_{43}+\dots \quad \text{(III.107)}$$

As before, we can directly show that this function is automatically orthogonal with respect to Θ_1 and Θ'_2 and that the normalization integral is given by the expression

$$\int |\Theta'_3|^2(dx) = \alpha'_{33} \quad \text{(III.108)}$$

If $\alpha'_{33} = 0$, we have $\alpha'_{i3} = 0$, and the function Θ_3 is then a linear combination of the functions Θ_1 and Θ'_2 and should be omitted in the orthogonalization process, which is here simply accomplished by means of the Gaussian elimination technique developed for solving equation systems. The connection between the matrices $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}'$ may be written in the form:

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} & \alpha_{14} & \cdot \\ \alpha_{21} & \alpha_{22} & \alpha_{23} & \alpha_{24} & \cdot \\ \alpha_{31} & \alpha_{32} & \alpha_{33} & \alpha_{34} & \cdot \\ \alpha_{41} & \alpha_{42} & \alpha_{43} & \alpha_{44} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \begin{bmatrix} 1 & d_{12} & d_{13} & d_{14} & \cdot \\ 0 & 1 & d_{23} & d_{24} & \cdot \\ 0 & 0 & 1 & d_{34} & \cdot \\ 0 & 0 & 0 & 1 & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} = \begin{bmatrix} \alpha_{11} & 0 & 0 & 0 & \cdot \\ \alpha_{21} & \alpha'_{22} & 0 & 0 & \cdot \\ \alpha_{31} & \alpha'_{32} & \alpha'_{33} & 0 & \cdot \\ \alpha_{41} & \alpha'_{42} & \alpha'_{43} & \alpha'_{44} & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \quad \text{(III.109)}$$

where we have omitted all columns in the matrix $\boldsymbol{\alpha}$ leading to identically vanishing columns in the matrix $\boldsymbol{\alpha}'$.

The eigenvalue problem with respect to the energy H_{op} is now conveniently solved by means of the orthogonalized Λ-adapted set $\Theta_1, \Theta'_2, \Theta'_3, \dots$ Using the "turn-over rule" and Eq. III.92, we

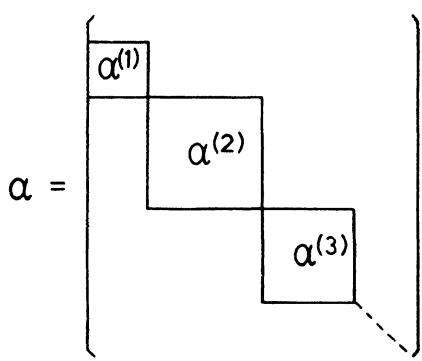
obtain ($m \leqq n$):

$$H'_{mn} = \int \Theta'^{*}_{m} H_{\mathrm{op}} \Theta'_{n}(dx)$$
$$= \int \Big(\sum_{\mu=1}^{m} \Psi_{\mu} d_{\mu m} \Big)^{*} H_{\mathrm{op}} \Big(\sum_{\nu=n} \Psi_{\nu} \alpha'_{\nu n} \Big)(dx) \qquad \text{(III.110)}$$
$$= \sum_{\mu=1}^{m} \sum_{\nu=n} d_{m\mu}^{\dagger} H_{\mu\nu} \alpha'_{\nu n}$$

The single sum in Eq. III.99 is here replaced by the sum of m such single sums, depending on the orthogonalization. The eigenvalue problem (Eq. III.21) is in this way reduced to the form

$$\det \{H'_{mn} - E\alpha'_{mm}\delta_{mn}\} = 0 \qquad \text{(III.111)}$$

and we note that there is an equation of this type associated with each eigenvalue λ_k to A. Hence, the projection operator formalism leads to a splitting of the original secular equation with respect to the various eigenstates of A. The projection operators are here elementarily expressed in the product form (Eq. III.86), but it is clear that exactly the same considerations are valid also for the more complicated group-theoretical projection operators.



In the previous discussion, we have not made any particular assumptions about the basic complete set $\Psi_1, \Psi_2, \Psi_3, \ldots$. However, if the basis is feasibly chosen, the total matrix may appear in partitioned form and consists of a series of submatrices $\boldsymbol{\alpha}^{(1)}, \boldsymbol{\alpha}^{(2)}, \boldsymbol{\alpha}^{(3)}, \ldots$ along the diagonal. In such a case, each one of the matrices

$\alpha^{(i)}$ is idempotent and has only the eigenvalues 0 or 1, which implies that $g_i = \mathrm{Tr}\,\{\alpha^{(i)}\}$ gives the number of linearly independent eigenvectors associated with the matrix. The number g_i may often be found in a still simpler way, as e.g., in the theory of angular momentum, where it is deduced by elementary combinatoric arguments. During such circumstances, it is not even necessary to evaluate the full matrix α, since it is apparently sufficient to calculate only the first g_i columns of $\alpha^{(i)}$ associated with linearly independent projections.

In the case the calculations are based on a truncated set Ψ_1, Ψ_2, Ψ_3, . . . containing adjustable parameters, the Λ splitting is of particular importance, since it permits the investigator to use different values of these parameters for different eigenvalues λ_k—the relation III.95 will anyway be valid. The scale factor η is such a parameter, and the results in Section II.C(3) and III.D(1b) show that, by means of the Λ splitting, it is now possible to get the virial theorem exactly fulfilled for at least one of the eigenfunctions associated with each λ_k.

The projection operator formalism also gives interesting aspects on the correlation problem. Previously one mainly used the secular equation (Eq. III.21) for investigating the symmetry properties of the solutions, and one was often satisfied with those approximate wave functions which were the simplest linear combinations of the basic functions having the correct symmetry. In our opinion, this problem is now better solved by means of the projection operators, and the use of the secular equations can be reserved for handling actual correlation effects. This implies also that, in place of the ordinary Slater determinants (Eq. III.17), we will essentially consider the projections of these functions as our basis.

In the ordinary Hartree-Fock scheme, the total wave function is approximated by a single Slater determinant and, if the system possesses certain symmetry properties, they may impose rather severe restrictions on the occupied spin orbitals; see, e.g., Eq. II.61. These restrictions may be removed and the total energy correspondingly decreased, if instead we approximate the total wave function by means of the first term in the symmetry adapted set, i.e., by the projection of a single determinant. Since in both cases,

the total wave function is essentially a projection of a Hartree product, the projection operator formalism renders a simple tool for introducing at least part of the correlation effects in the independent-particle model. In connection with the spin, this approach will be further discussed in Section III.F.

Symmetry properties which have so far been successfully treated by the projection operator method, include translational symmetry in crystals, cyclic systems, spin, orbital and total angular momenta, and further applications are in progress.*

(6) *Applications to Atoms and Molecules*

To test the accuracy and convenience of the method of superposition of configurations, the problem of the ground state of the helium atom has recently been reexamined by several authors. According to Hylleraas (1928), the total wave function may be expressed in the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \sum_{l=0}^{\infty} P_l(\cos \gamma_{12})\, F_l(r_1, r_2) \qquad \text{(III.112)}$$

where γ_{12} is the angle between the vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$, $P_l(\cos \gamma_{12})$ may be expressed in products of spherical harmonics of the variables (θ_1, φ_1) and (θ_2, φ_2), and $F_l(r_1, r_2)$ may be expanded in products of functions of r_1 and r_2 alone. In particular, the convergence of this "Legendre expansion" has been frequently discussed, and the energy E has been investigated as a function of the highest angular quantum number $l_{\max}$ included. Some results are condensed in Table VI.

It should be observed that all three calculations quoted have been carried out by means of discrete basic sets which are equivalent to Eqs. III.56 and III.57. Shull and Löwdin (1958), and Watson (1956) have determined the best energy by solving a secular equation of type III.21; the former have used the same exponent $\eta_l = \eta_0$ for all terms to obtain the highest degree of simplicity, whereas the latter in one case has chosen $\eta_l = \eta_0 + l$ and, in another case, has varied the exponents freely and even split up single ex-

* See refs. 17, 22, 23, and a series of Technical Notes from the Uppsala Quantum Chemistry Group (1957–58).

TABLE VI. Ground State of the Helium Atom Obtained by Superposition of Configurations[a]

		Solution of secular equation				
l_{max}	Matrix size	$\eta_l = \eta_0$[b]	$\eta_l = \eta_0 + l$[c]	η_l freely varied[d]	Iteration $\eta_l = \eta_0$	Estimated best value[b]
0	10	−2.878 60	−2.878 60	−2.878 86	−2.878 92	−2.879 00
1	16	−2.899 58	−2.899 92	−2.900 25	−2.900 44	−2.900 49
2	19	−2.901 16	−2.902 03	−2.902 35	−2.902 69	−2.902 77
3	20	−2.901 23	−2.902 42	−2.902 74	−2.903 23	−2.903 32
4	—	—	—	—	−2.903 37	—
5					−2.903 43	—
14					−2.903 43	—
					—	−2.903 72

[a] Energy in at. u.$_{He}$ expressed as a function of the highest angular quantum number l_{max} included in expansion III.112 according to various methods.
[b] Method of Shull and Löwdin (1958).
[c] Method of Watson (1956).
[d] Method of Tycko, Thomas, and King (1958).

ponential functions into two-term functions with different exponents.

A somewhat different approach has been used by Tycho, Thomas, and King (1958), who have solved the Schrödinger equation by a modification of the standard iteration procedure, based on the theorem that repeated application of an operator on a trial function of a certain symmetry type will converge towards the eigenfunction having the lowest eigenvalue within this symmetry class. Their final wave function may also be expressed in the form of Eq. III.112 as a superposition of configurations, and the corresponding energy shows that little improvement is gained by adding angular terms having $l > 5$. The reason for the small difference +0.00029 between their best result and the exact value −2.90372 (Kinoshita 1957) remains to be investigated.

The results in Table VI are of considerable interest also for atoms with more than two electrons, since they show the possibilities and limitations of the method of "superposition of configurations," when the latter are built up from one-electron functions

which are products of radial functions and *spherical harmonics*. The convergence of III.112 is comparatively slow, but the results are still encouraging from a chemical point of view (Shull and Löwdin 1958), for the p limit ($l_{max} = 1$) differs from experiment by about only 2 kcal/mole, and the f limit ($l_{max} = 3$) agrees with experiment within a margin of 0.25 kcal/mole. In order to obtain such an accuracy, however, it is necessary to include orbitals of higher angular quantum numbers than those one is conventionally inclined to believe would be of importance.

For atoms with more than two electrons, it is very difficult to obtain such a small absolute error in the energy as in the helium case, but, within an isoelectronic sequence, the relative error will, of course, go down rapidly with increasing atomic number Z. The method of superposition of configurations has been used successfully in a number of applications, particularly by Boys (1950–) and Jucys (1947–), and, for a more detailed survey of the work on atoms, we will refer to the special table on atomic calculations in the bibliography. This is a field of rapid development, where one can expect important new results within the next few years.

In molecular theory, the method of superposition of configurations has more and more taken a leading place during the last eight years. The relative accuracy is reasonable, but we note that, if the helium results are significant also for molecules, one has definitely not yet included orbitals of sufficiently high angular quantum numbers to get the small absolute errors in the binding energy which are ultimately desired. For a bibliographic survey of the development, we will refer to the special molecular tables in Part II, Yoshizumi's bibliographical survey of this problem. One of these tables contains papers on simple molecules of the type LiH, Li_2, H_2O, NH_3, . . . with all (or almost all) electrons treated, and the other contains papers on π electron systems. For comparison, references to corresponding SCF treatments are also given, but it should be observed that for molecules as well as for solid state, the Hartree-Fock approximation is usually brought to "self-consistency" only within the limited framework which is represented by a basis comprised of the orbitals which are conventionally occupied. A great deal of additional work on molecules has been

carried out according to official and unofficial reports, so one can expect several new papers on this topic to appear in the literature very soon. The trend goes towards more and more accurate wave functions, and, since these functions become correspondingly more complicated, it seems now highly desirable to try to simplify them and interpret them, e.g., in terms of natural spin orbitals.

E. Correlated Wave Functions

(1) *Power Series Expansions and Formal Solutions*

(a) *Helium Atom.* If the method of superposition of configurations is based on the use of expansions in orthogonal sets, the method of correlated wave functions has so far been founded on *power series expansions.* The classical example is, of course, Hylleraas' expansion (Eq. III.4) for the ^1S ground state of the He atom, which is a power series in the three variables

$$s = r_1 + r_2, \quad u = r_{12}, \quad t = -r_1 + r_2 \tag{III.113}$$

which will here be rewritten in the somewhat modified form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-\frac{1}{2}s} \sum_{lmn=0}^{\infty} c'_{lmn} s^l u^m t^n \tag{III.114}$$

The energy value $E = -2.90324$ at.u. obtained by Hylleraas by using a 6-term function was extremely good for its time, but there has still been some doubt about the foundation of the approach, since the series III.114 can never be a formal solution to the Schrödinger equation (Bartlett, Gibbons, and Dunn 1935, Coolidge and James 1937). Recent measurements showed a certain discrepancy between the theoretical and experimental results, and an extension of Hylleraas' calculation was also found desirable (Chandrasekar, Elbert, and Herzberg 1953, Chandrasekar and Herzberg 1955, Wilets and Cherry 1956).

An essential improvement of the entire approach has recently been given by Kinoshita (1957), who pointed out that, instead of using Eq. III.113, one could just as well use a power series expansion in the three variables

$$s, \qquad p = u/s, \qquad q = t/u \tag{III.115}$$

which are independent of each other and have the domains $(0, \infty)$,

(0, 1), and (−1, 1), respectively. Because of the identity $s^l p^m q^n = s^{l-m} u^{m-n} t^n$, such a power series corresponds to an expansion in s, u, t of the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = e^{-\frac{1}{2}s} \sum_{lmn=0}^{\infty} c_{lmn} s^{l-m} u^{m-n} t^n \qquad \text{(III.116)}$$

which is essentially an extension of Eq. III.114 but also contains terms in negative powers. Kinoshita has shown that a series of this type could be at least a formal solution to the Schrödinger equation and, by using a 39-term function, he obtained the energy eigenvalue $E = -2.9037225$ at.u., which is in very good agreement with the last experimental results with the necessary relativistic corrections.

A similar method has also been used by Pluvinage (1955), who introduced the three variables

$$s, \quad \rho = u/s, \qquad \tau = -t/s \qquad \text{(III.117)}$$

having the domains (0, ∞), (0, 1), and (−1, ρ) for studying the formal solution of the wave equation; see also Munschy and Pluvinage (1957). Recent calculations by Pluvinage (1957) have given an energy $E = -2.903892$ slightly lower than Kinoshita's value, and, by studying the coefficients for s and u in the expansions of Ψ, he tries to show that it is plausible that his wave function is actually the better one. A detailed comparison of the two methods and their numerical results will certainly be of interest.

A great deal of attention has been paid to the question of the necessity of having logarithmic terms in the expansion (Grönwall 1937, Bartlett 1952, 1955, Fock 1954, Hylleraas 1955), but Kinoshita has pointed out that although such terms may be convenient from the numerical point of view (Hylleraas and Midtdal 1956), they are not necessarily required by the form of the Schrödinger equation itself.

It seems as if an energy value of sufficiently high accuracy has now been found for the helium problem, but we still do not know the actual form of the corresponding exact eigenfunction. In this connection, the mean square deviation $\varepsilon = \int |\Phi - \Psi|^2 (dx)$ and criteria of the Eckart type (Eq. III.27) are not very informative, since ε may turn out to be exceedingly small, even if trial function

Φ differs quite appreciably from the exact eigenfunction Ψ, provided this happens only within volumes which are sufficiently small.[16] Hence, it seems hardly possible to obtain any information about singularities or other peculiarities of the exact wave function by means of either the method of correlated wave functions or the method of superposition of configurations, as long as these are based on the variation principle applied to finite expansions.

It has been pointed out by Bartlett (1955) that a much more sensitive criterion for the local accuracy of an approximate wave function Φ is provided by the "*local energy*" defined by the relation

$$E_{\text{loc}} = H\Phi/\Phi \tag{III.118}$$

which is a function of all electronic coordinates $x_1, x_2, \ldots, x_N$ involved but which reduces to a constant ($= E$) for the exact solution Ψ. Bartlett showed that, even for Hylleraas' best expansion of the type III.114, this test quantity varied from $-\infty$ to $+\infty$, and that it was close to the corresponding expectation value $\langle H \rangle_{\text{Av}}$ only within a small region in space. Bartlett also tried to solve the helium wave equation in a more exact way by introducing a suitably chosen network and by replacing the Laplacian by an adequate difference operator, and this resulted in a wave function having a considerably smaller variation in E_{loc}.

The problem of the analytical form and special properties of the exact wave function is apparently still far from being solved. Kinoshita emphasizes the fact that the existence of formal solutions by itself is not very significant, unless it can be shown that some of them converge towards an actual solution. In a fundamental mathematical work, Kato (1951) has investigated the general conditions for the existence of solutions to the Schrödinger equation for atomic systems and this study has recently been continued (1956). The fact that these basic problems are not yet fully solved even for the simple case of the helium atom shows that the mathematical background for the entire quantum theory of many-particle systems is still rather diffuse. Further research in this field would therefore be of great importance.

In conclusion, we note that similar work has also been carried out on the He-like ions: H^-, Li^+, Be^{2+}, etc, and, for references, we

will refer to a special table on this subject in the bibliography.

(b) *Hydrogen Molecule.* The basic two-electron problem of molecular theory concerns the ground state of the H_2-molecule, and the classical work on correlation was here carried out by James and Coolidge (1933) by using a wave function of the form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{2\pi} e^{-\delta(\xi_1+\xi_2)} \sum_{mnjkp=0}^{\infty} c_{mnjkp}(\xi_1^m \xi_2^n \eta_1^j \eta_2^k u^p + \xi_2^m \xi_1^n \eta_2^j \eta_1^k u^p) \tag{III.119}$$

where ξ and η are elliptic coordinates referred to the two atomic nuclei, a and b:

$$\xi = (r_a+r_b)/R_{ab}\,, \qquad \eta = (r_a-r_b)/R_{ab}\,, \qquad u = 2r_{12}/R_{ab}$$

We note that the power series expansion III.119 is a direct generalization of the Hylleraas form III.114 to which it should go over in the limiting case $R_{ab} = 0$. James and Coolidge obtained a value of the electronic energy, -1.17347 at.u., in excellent agreement with the experimental results available, and their work forms even today the best basis for our understanding of the electronic structure of the chemical bond.

A great deal of work has later been carried out in order to simplify and refine the wave function for the H_2 molecule, and, for a more detailed survey, we will refer to a special table in the bibliography. There is little doubt that, even as to the H_2 molecule, one can in due time expect a similar development as is now going on concerning the He atom, and, since the former is being complicated also by the nuclear motion involved, several new interesting problems will probably appear.

(2) *Method with Correlation Factor*

(a) *Two-Electron Systems*: He-*like Ions and* H_2 *Molecule.* A correlated wave function of the type III.114 or III.116 for helium has not the same high degree of physical visuality as is characteristic for the simple wave function $(1s)^2$ in the one-electron scheme. It is therefore of interest to study whether the correlation effects could be introduced in the latter in a simpler way, e.g., in the form of a "correlation factor" $g(r_{12})$ containing the interelectronic

distance r_{12}:

$$\Psi = u(r_1)\, u(r_2)\, g(r_{12}) \qquad \text{(III.120)}$$

This approach was first sketched by Hylleraas (1929) who pointed out that, by choosing $u = 1s$ and $g = \exp\{\alpha r_{12}\}$, one could obtain the surprisingly good energy $E = -2.8896$ at.u.$_{He}$. Hylleraas also showed[14] (p. 356) that, by choosing the very simple correlation factor $g = 1+\alpha r_{12}$, one could reach the still better energy $E = -2.8912$ at.u.$_{He}$.

In order to demonstrate the possibilities and limitations of this method, we will quote some recent results (Löwdin and Rédei 1958) obtained by using a wave function of the type $u^2(1+\alpha r_{12})$, where u is expressed either as a single exponential or as the sum of two exponentials:

$$u = (A_1 e^{-a_1 r} + A_2 e^{-a_2 r}) \qquad \text{(III.121)}$$

This function is flexible enough to include even the ordinary SCF function.* The results are condensed in Table VII.

TABLE VII. Results Obtained using a Wave Function of the Type $u^2(1+\alpha r_{12})$

u	Scale factor η	$\eta\alpha$	Energy in at.u.$_{He}$
Single exponential	1.6875	0.199	−2.874 84
SCF function	1.0000	0.156	−2.880 71
Single exponential	1.8498	0.366	−2.891 12
Scaled SCF function	1.0958	0.322	−2.895 38
Sum of two exponentials	—	0.3503	−2.898 06

The results show that it is possible to improve the Hartree-Fock energy −2.86167 at.u. considerably by means of a simple correlation factor, but also that it is essential to scale the total function Ψ properly to fulfil the virial theorem. The parameters in the best function u of the form of Eq. III.121 are further given below:

$$\begin{aligned} A_1 &= 2.707\,16, & a_1 &= 1.563\,993 \\ A_2 &= 2.569\,10, & a_2 &= 2.497\,697 \end{aligned} \qquad \text{(III.122)}$$

with the orbital u normalized to 1.

* See refs. 20 and 8; see also Watson (1956).

The function III.120 with more general forms of the functions u and g has also been studied in greater detail by Baber and Hassé (1937) and by Pluvinage (1950). The latter expanded $g(r_{12})$ in a power series in r_{12} and, by studying the formal properties of the wave equation itself, Pluvinage could derive certain general relations for the coefficients. At the Paris molecular symposium in 1957, Roothaan reported that, by expressing u and g in the form

$$u(r) = e^{-\eta r} \sum_{n=0,2} a_n r^n, \qquad g(r_{12}) = 1 - e^{-\alpha r_{12}} \sum_{m=0,3} b_m r^m \qquad \text{(III.123)}$$

and minimizing all parameters, he had been able to reach an energy minimum of $E = -2.90036$ at.u.$_{\text{He}}$.

We note that it is possible to combine the method with correlation factor with the method using superposition of configurations to obtain any accuracy desired by means of comparatively simple wave functions. For a very general class of functions $g(r_{12})$, one can develop the quotient $\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)/g(r_{12})$ according to Eq. III.2 into products of one-electron functions $\psi_k(r)$, which leads to the expansion

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = g(r_{12}) \sum_{kl} C_{kl} \psi_k(r_1) \psi_l(r_2) \qquad \text{(III.124)}$$

where $C_{kl} = C_{lk}$. By means of a suitable linear transformation of the basic set analogous to Eq. III.63, this relation may be brought to the simple form

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = g(r_{12}) \sum_{k=1}^{\infty} \lambda_k \chi_k(r_1) \chi_k(r_2) \qquad \text{(III.125)}$$

of which Eq. III.120 represents the first term. In order to show the

TABLE VIII. Energies of the He-like Ions[a] (in at.u.)

He-like ions	Z	$(u)^2(1+\alpha r_{12})$		Correlated wave function of type III.125				
		α	E	$k_{\max} = 1$	$k_{\max} = 2$	$k_{\max} = 3$	α	Exact
H^-	1		−0.520 50	−0.5174	−0.5262	−0.5264	0.3503	−0.52756
He	2	0.3503	−2.898 06	−2.8973	−2.9020	−2.9023	0.2880	−2.90372
Li^+	3		−7.273 85	−7.2733	−7.2778	−7.2781	0.2689	−7.28040
Be^{2+}	4		−13.649 18	−13.6488	−13.6531	−13.6534	0.2609	−13.65722

[a] See Löwdin and Rédei, 1958.

power of this approach, we will quote some recent results for the He-like ions (Löwdin and Rédei 1958), obtained by using a linear correlation factor $g(r_{12}) = 1+\alpha r_{12}$ and a basis consisting of only three $\overline{(ns)}$ functions of the type III.57. The numerical data are condensed in Table VIII.

In table VII, the values for E_{exact} are estimated from experiments or taken from highly accurate calculations based on correlated power series expansions. The energy values in the column for $k_{\max} = 1$ are associated with wave functions of the type III.120, but, since the α-values are actually optimized for $k_{\max} = 3$, they could probably all be slightly improved. For comparison, we have included the energy values for the best functions $(u)^2(1+\alpha r_{12})$, where u is expressed in the form III.121.

The energy values in the column for $k_{\max} = 3$ are to be compared with the exact eigenvalues and with the results obtained by ordinary superposition of configurations; a study of Table VI for helium shows that, even by including terms up to $l = 3$ and solving a 20-order secular equation, one does not obtain such a good energy as the one provided by the 3-term function used here. A combination of the method using a simple correlation factor and the method of superposition of configurations seems therefore to be a rather powerful tool for the future.

In Section II.D(4c), it was pointed out that, in treating correlation effects in a molecular system, it is of essential importance that the improved wave function leads to an energy curve having correct asymptotic behavior for separated atoms. It has been shown (Frost, Braunstein, and Schwemer 1948) that this condition may be fulfilled by a convenient choice of a correlation factor g. Let us consider the H_2 molecule and a wave function of the type

$$\Psi = (a_1+b_1)(a_2+b_2)g \qquad \text{(III.126)}$$

Since this function may be expanded in the form:

$$\Psi = a_1a_2g(r_{12}) + b_1b_2g(r_{12}) + (a_1b_2+a_2b_1)g(r_{12}) \qquad \text{(III.127)}$$

it is clear that the contributions from the ionic terms ($r_{12} \approx$ atomic dimensions) will vanish in comparison to the covalent terms ($r_{12} \approx R_{ab}$) for separated atoms, provided $g(r_{12})$ increases indef-

initely with increasing r_{12}. The last condition is fulfilled even for the linear factor $g(r_{12}) = 1+\alpha r_{12}$, and the corresponding wave function (Eq. III.126) will then not show any accumulation of two electrons on the same proton and no H^- ions will be formed.

The best energy at the equilibrium distance R_0 of a wave function (Eq. III.126) for scaled 1*s* orbitals and $g = 1+\alpha r_{12}$ has also been calculated by Frost and Braunstein (1951), and their result $E = -1.151$ at.u. is to be compared with the value $E = -1.17347$ at.u. obtained by James and Coolidge. The error $+0.022$ at.u. is almost twice as large as the corresponding figure $+0.0125$ at.u. for the helium atom. Since 0.022 at.u. = 0.60 ev $\approx$ 14 kcal/mole, the accuracy is hardly satisfactory from the chemical point of view. In the case of the hydrogen molecule, it seems hence highly desirable to combine the method using correlation factor with the method of superposition of configurations and to derive a simple wave function of the form III.125.

(b) *Many-Electron Systems: Connection with Wigner's Theory and the Plasma Model.* For a two-electron system, the interelectronic distance could be introduced into the wave function Ψ simply by choosing r_{12} as one of the independent variables. For a many-electron system such an approach is no longer possible, since we have altogether $N(N-1)/2$ interelectronic distances r_{ij} and only $3N$ independent space coordinates. So far, no strict foundation for a generalization of the theory has been developed, but several lines could be followed. Here we will consider only a generalization of the method with correlation factor, which to some extent represents a unification of the r_{ij} idea with the method of superposition of configurations and which, for two-electron systems, was described in the previous section.

Let us consider a system represented by the antisymmetric wave function $\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N)$, and let us assume that $g(r_{ij}) = g(r_{12}, r_{13}, r_{23}, \ldots)$ is a *symmetric function* of all the $N(N-1)/2$ interelectronic distances r_{ij}, nodeless and subject to the condition that the quotient function Ψ/g should still be normalizable. In such a case, Ψ/g is an antisymmetric function of the electronic coordinates $\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N$, which hence may be expanded in the form III.18 so that we obtain the representation

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = g(r_{12}, r_{13}, r_{23}, \ldots) \sum_K C_K \Psi_K(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) \tag{III.128}$$

The function $g(r_{ij})$ is here a correlation factor, and it is clear that, if this function is chosen in different ways, we will have different coefficients C_K in the expansion in the first factor. An important problem is then to try to find forms of the correlation factor which will reduce this expansion as much as possible, and a particular problem is to investigate how good an approximation could be obtained by a single determinant:

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = g(r_{12}, r_{13}, r_{23}, \ldots) \begin{vmatrix} \psi_1(\boldsymbol{x}_1)\, \psi_2(\boldsymbol{x}_1) & \ldots & \psi_N(\boldsymbol{x}_1) \\ \cdots & \cdots & \cdots \\ \psi_1(\boldsymbol{x}_N) \psi_2(\boldsymbol{x}_N) & \ldots & \psi_N(\boldsymbol{x}_N) \end{vmatrix} \tag{III.129}$$

where the orbitals $\psi_1, \psi_2, \ldots, \psi_N$ are, of course, not necessarily restricted to ordinary HF functions associated with the problem or to scaled HF functions. If the function g is chosen to have its smallest value when any $r_{ij} = 0$, the form of Eq. III.129 corresponds to the existence of "Coulomb holes" for both parallel and antiparallel spins. A slight generalization of Eq. III.129 is obtained by letting g be an even and symmetric function of all the $N(N-1)/2$ vectors $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$ instead of only the interelectronic distances $r_{ij} = |\boldsymbol{r}_{ij}|$.

Following the discussion in connection with the expansion III.127, we note that, for a molecular or a solid-state system, the wave function III.129 will lead to a correct asymptotic behavior of the energy for separated atoms, provided that the factor g has been conveniently chosen so that it increases indefinitely when any one of the electrons is taken away from the others. A more detailed study of g may sometimes be necessary in order to ensure that no excessive accumulation of ions will occur when the system is separated into its constituents.

The main advantage of the method with correlation factor, based on Eq. III.128 or Eq. III.129, lies in the fact that it may be applied to any many-electron system. The practical calculation of the energy integrals involved may be fairly cumbersome, but the approach is nevertheless straightforward.

From the point of view of principles, it is interesting to note that the method based on the generalized form of Eq. III.129 seems to be very closely connected both with Wigner's classical theory described in Section III.B and with Bohm and Pines' plasma model (Krisement 1957). Following Krisement, we will replace the various trial functions $f_1, f_2, \ldots, f_n$ in Eq. III.9 by a single average function f, and Wigner's basic wave function (Eq. III.7) takes then the simple form

$$\begin{vmatrix} \psi_1(\boldsymbol{r}_1) & \ldots & \psi_1(\boldsymbol{r}_n) \\ \cdot & \cdot & \cdot \\ \psi_n(\boldsymbol{r}_1) & \ldots & \psi_n(\boldsymbol{r}_n) \end{vmatrix} \cdot \begin{vmatrix} \psi_1(\boldsymbol{r}_{n+1}) & \ldots & \psi_1(\boldsymbol{r}_N) \\ \cdot & \cdot & \cdot \\ \psi_n(\boldsymbol{r}_{n+1}) & \ldots & \psi_n(\boldsymbol{r}_N) \end{vmatrix} \cdot g \qquad \text{(III.130)}$$

where

$$g = \prod_{i=1}^{n} \{1 + \sum_{p=n+1}^{N} f(\boldsymbol{r}_{pi})\} \qquad \text{(III.131)}$$

Since $\boldsymbol{r}_p$ and $\boldsymbol{r}_i$ here refer to electrons having opposite spins, the form III.130 introduces correlation only for electrons with antiparallel spins. It is clear that, by using different functions $f_1, f_2, \ldots, f_n$, one may get a still lower energy, but additional complications will occur, since the wave function III.7 corresponds then to a mixture between different spin types (*cf.* Brickstock and Pople 1953).

Putting Wigner's theory in the simplified form (Eq. III.130), Krisement was able to compare it with the results of the plasma model where, in a first approximation, Pines' wave function may be written in the generalized form (Eq. III.129) with

$$g = \exp\left\{-\sum_{k<k_c} \sum_{ij}{}' \frac{2\pi e^2}{k^2} \frac{e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{ij}}}{\hbar\omega_p}\right\} \qquad \text{(III.132)}$$

The function g describes the collective motions of the electrons; k_c is the cut-off vector for the plasma oscillations and ω_p is the plasma frequency (see Pines 1955, particularly p. 391); see also Section III.C.

This analysis shows that a refinement of the Hartree-Fock method by means of a correlation factor $g(r_{12}, r_{13}, r_{23}, \ldots)$ seems to be possible along several lines, but the numerical work involved

in actual applications of this approach will always be formidable and require electronic computers. The numerical results on He and H_2 show also the rather severe limitations of the best energy obtainable by using the form III.129, whereas any accuracy desired may be achieved by using a wave function of the form III.128.

F. Different Orbitals for Different Spins

(1) *New Method for Constructing Pure Spin Functions. Extended Hartree-Fock Scheme*

The large correlation errors in the conventional Hartree-Fock approximation exemplified by Tables I and II certainly depends on the fact that pairs of electrons of opposite spins are forced together in doubly filled orbitals. This pairing goes back partly to the classical formulation of the Pauli principle, partly to the fact that this procedure permits a simple constuction of pure spin states as discussed in Section II.D(2). It seems therefore highly probable that one could remove at least part of the defects coming from correlation by *letting electrons with different spins occupy different orbitals in space* so that they get a chance to avoid each other in accordance with the influence of the Coulomb repulsion. This implies, of course, that one has to find a new method for constructing pure spin states.

For two-electron systems the basic idea of using different orbitals for different electrons goes back to Hylleraas (1929) and to Eckart (1930) who both used it in treating He. The method was thoroughly discussed at the Shelter Island Conference 1951 in treatments of He and H_2 (Kotani 1951, Taylor and Parr 1952, Mulliken 1952), but the circumstances are here exceptionally simple because of the possibility of separating space and spin according to Eq. III.1.

A generalization of the idea of "different orbitals for different spins" is hence possible, only by an explicit treatment of the spin problem connected.[22] Let us consider a Slater determinant

$$D = (N!)^{-\frac{1}{2}} \det \{\psi_1, \psi_2, \ldots, \psi_N\} \qquad \text{(III.133)}$$

where the spin-orbitals $\psi_1, \psi_2, \ldots, \psi_N$ are assumed to be of either pure α or β character. The fundamental invariant may then be

written in the form of Eq. II.53, i.e., the determinant is characterized by the two space density matrices

$$\rho_+(\boldsymbol{r}_1, \boldsymbol{r}_2), \qquad \rho_-(\boldsymbol{r}_1, \boldsymbol{r}_2) \tag{III.134}$$

As shown in Section II.D(2), the determinant of Eq. III.133 can be brought to correspond to a pure spin state by imposing a certain condition (II.61) on the relation between ρ_+ and ρ_- which corresponds to the pairing of the electrons. If ρ_+ and ρ_- are permitted to vary independently of each other, the determinant is no longer a pure spin state but a mixture of states associated with the quantum numbers

$$S = \tfrac{1}{2}N, \tfrac{1}{2}N-1, \ldots, \tfrac{1}{2}(N_+-N_-) \tag{III.135}$$

For the sake of simplicity, we will first assume that the number of particles is even ($N = 2n$) and that $N_+ = N_- = n$. The determinant of Eq. III.133 is then a mixture of terms:

$$D = \text{singlet} + \text{triplet} + \text{quintet} + \ldots \tag{III.136}$$

associated with $S = 0$, $S = 1$, $S = 2$, ..., respectively. In this series we can always select any pure spin component desired by means of a "projection operator" O, which is very simple to construct according to the general methods outlined in Section III.D (5). If Ψ_S is an eigenfunction to $\boldsymbol{S}^2$, we have $\boldsymbol{S}^2\Psi_S = S(S+1)\Psi_S$, and this relation may be rewritten in the form

$$[1-\boldsymbol{S}^2/S(S+1)]\,\Psi_S \equiv 0 \tag{III.137}$$

showing that the operator $[1-\boldsymbol{S}^2/S(S+1)]$ annihilates the function Ψ_S. The singlet component of Eq. III.136 is hence selected by the operator

$${}^1O = (1-\boldsymbol{S}^2/1\cdot 2)\,(1-\boldsymbol{S}^2/2\cdot 3)\,(1-\boldsymbol{S}^2/3\cdot 4)\ldots \tag{III.138}$$

where the first factor will annihilate the triplet term, the second factor the quintet term, etc., whereas the singlet term will survive the operation in an unchanged form. We note that, according to Eq. III.85, such an operator O fulfills the relation $O^2 = O$ characteristic for the projection operators.

More generally a projection operator ${}^{(2S+1)}O$ for selecting a spin state, associated with the quantum number S and having the multiplicity $(2S+1)$, is given by the formula

$$ {}^{(2S+1)}O = \prod_{k}^{k \neq S} \frac{\{\boldsymbol{S}^2 - k(k+1)\}}{\{S(S+1) - k(k+1)\}}. \tag{III.139} $$

It is now possible to formulate an extension of the conventional Hartree-Fock scheme by considering a wave function ${}^{(2S+1)}\Psi$ which is a pure spin state and which is simply defined by the component of the single Slater determinant Eq. III.133 as has the spin property required:

$$ {}^{(2S+1)}\Psi = {}^{(2S+1)}OD \tag{III.140} $$

Since the operator (Eq. III.139) because of Eq. II.58 does not affect the space functions, the wave function ${}^{(2S+1)}\Psi$ is a pure spin function depending only on the space density matrices $\rho_+(\boldsymbol{r}_1, \boldsymbol{r}_2)$ and $\rho_-(\boldsymbol{r}_1, \boldsymbol{r}_2)$ which now may be varied entirely independent of each other. The best functions $\boldsymbol{\rho}_+$ and $\boldsymbol{\rho}_-$ may again be found by means of the variation principle (Eq. II.7) starting from the expression

$$ \begin{aligned} \langle H_{\text{op}} \rangle_{\text{Av}} &= \frac{\int \Psi^* H_{\text{op}} \Psi (dx)}{\int \Psi^* \Psi (dx)} \\ &= \frac{\int D^* H_{\text{op}} (OD)\ (dx)}{\int D^* OD (dx)} \end{aligned} \tag{III.141} $$

where we have used the turn-over rule and the relation $O^2 = O$. It may be shown that the density matrices associated with the function III.140 can be expressed in terms of $\boldsymbol{\rho}_+$, $\boldsymbol{\rho}_-$, and powers of the matrix $\boldsymbol{\omega} = \boldsymbol{\rho}_+\boldsymbol{\rho}_-$ defined in Eq. II.56. In this way, we are lead to an extension of the Hartree-Fock scheme, where the constraint (Eq. II.61) has been fully removed, and one can hence expect a certain improvement of the energy below the Hartree-Fock level.

So far, no exact application of this extended HF scheme has been carried out, but, by using the helium atom as a typical example, one can get an idea of the possibilities and limitations of this ap-

proach. For a two-electron system, it has been shown (Löwdin and Shull 1956) that, if one uses the expansion of the wave function in terms of natural spin orbitals—see Section III.D(3a)—and includes only the first two terms, the result is equivalent to a (u, v) function, i.e., to a singlet projection of det $\{u\alpha, v\beta\}$ according to Eq. III.140. In this way, one can derive the (u, v) function having maximum overlap with the exact wave function, and the corresponding energy for helium is found to be -2.87792 at.u.$_{He}$ (Shull and Löwdin 1958). We note, however, that even if this figure is far below the HF energy -2.86167 at.u. and rather close to the estimated radial limit -2.87900 at.u., it is still high above the exact eigenvalue -2.90372 at.u.

For atoms, it has been possible during the last few years to program the calculations in the ordinary HF scheme for some electronic computers, and, as soon as one has obtained enough experience in this connection, there will probably be no difficulties in doing the same also for the extended HF scheme sketched in this section. For molecules and crystals, on the other hand, one has probably to be satisfied with comparatively rough approximations for a long time.

The *alternant* MO *method* is an approximate method for evaluating ρ_+ and ρ_- in a molecular system of alternant character (Löwdin 1954, 1955). The method is based on the fact that by suitable linear combination of bonding and antibonding molecular orbitals, one can construct basic orbitals which are semilocalized so that electrons with opposite spins get a possibility of avoiding each other. Applications to the benzene molecule (Itoh and Yoshizumi 1955) have shown that a change of the energy minimum by 2.35 ev is possible in this simple approach, and this result corresponds to about 85 per cent of the lowering found by superposition of configurations (Parr, Craig, and Ross 1950). Further applications have been carried out to acetylene (Yoshizumi and Itoh 1955).

In conclusion we note that the method of alternant molecular orbitals leads to a correct behavior of the energy curve for separated atoms, which is of essential importance in considering correlation effects (see Section II.D(4c)) and in studying magnetic phenomena.

(2) *Higher Approximations. Introduction of Correlation Factor*

The method using "different orbitals for different spins" is evidently a special case of the general extension of the Hartree-Fock scheme by means of projection operators describing various symmetry properties, which was discussed at the end of Section III.D(5). This implies that the basic wave function (Eq. III.140) may be considered as the first term in an infinite expansion (Eq. III.93) of "projected configurations," and that any accuracy desired may be obtained by adding more and more terms in this series. In order to fully describe a system, one can introduce two complete sets of orbitals $\{\psi_k\}$ and $\{\varphi_l\}$ and let $\{\psi_k \alpha\}$ describe the electrons having plus spin and $\{\varphi_l \beta\}$ the electrons having minus spin, so that the combined set $\{\psi_k \alpha, \varphi_l \beta\}$ is complete with respect to any spin orbital and may be used for constructing a set of configurations Ψ_K in the $(x_1, x_2, \ldots, x_N)$-space; see Eq. III.17. If the total wave function Ψ is a pure spin function, we can then take the projection of the configurational expansion III.18 and obtain

$$\Psi(x_1, x_2, \ldots, x_N) = \sum_K C_K O(\Psi_K) \qquad \text{(III.142)}$$

which proves our statement. The ordinary HF scheme is related to the expansion, Eq. III.18, in the same way as the extended HF scheme is related to expansion III.142: in both cases, one is interested in getting a principal term having as good energy as possible.

In Section III.E(2) we discussed the improvement in the convergency of expansion III.18 which could be obtained by introducing a suitably chosen correlation factor $g(r_{12}, r_{13}, r_{23}, \ldots)$, and it is clear that a similar procedure can be carried out also in connection with Eq. III.142, provided that the factor g does not change the symmetry character of the wave function. In complete analogy with Eq. III.128, we hence obtain

$$\Psi(x_1, x_2, \ldots, x_N) = g(r_{12}, r_{13}, r_{23}, \ldots) \sum_K C_K O(\Psi_K) \qquad \text{(III.143)}$$

Again it is an important problem to find such forms of the correlation factor g as will reduce the expansion over the ordered configurations K as much as possible. We will also consider the ap-

proximation furnished by a single term

$$\Psi = gO(D) \tag{III.144}$$

where the spin orbitals in the determinant should give the best energy possible.

The wave function III.144 has a very simple form, and applications to the He-like ions show that one can still expect a surprisingly high accuracy. Let us consider a singlet wave function of the form:

$$\begin{aligned} {}^1\Psi &= (1+\alpha r_{12})\,{}^1O \det\{u\alpha, v\beta\} \\ &= (1+\alpha r_{12})(u, v)(\alpha_1\beta_2 - \alpha_2\beta_1)/2 \end{aligned} \tag{III.145}$$

where $g = 1+\alpha r_{12}$. Approximating the orbitals u and v by single exponentials with different exponents, Chandrasekhar (1944) has investigated H^-, and Green *et al.* (1954) He and Li^+ with very good results, these having recently been further improved (Löwdin and Rédei 1958). The numerical data are given in Table IX. We note that a wave function of the type III.125 for $k_{max} = 2$ is equivalent to the form III.145; the corresponding energy values are taken from Table VIII but, since the α values are actually optimized for $k_{max} = 3$, one can expect that these energies can be slightly improved.

TABLE IX. Energies of the He-like ions for a Wave Function of the Form $(1+\alpha r_{12})(u, v)$ (in at.u.)

He-like ion	Z	u, v = single exponentials	Eq. III.125 for $k_{max} = 2$	E_{exact}
H^-	1	−0.5259 2	− 0.5262	− 0.5275 6
He	2	−2.9014 2	− 2.9020	− 2.9037 2
Li^+	3	−7.2771 8	− 7.2778	− 7.2804 0
Be^{2+}	4	—	−13.6531	−13.6572 2

The data show that, in the case of the He-like ions, a combination of the method using correlation factor and the method with different orbitals for different spins leads to excellent results.

(3) *Unrestricted Hartree-Fock Scheme. Exchange Polarization*

In this section, we will briefly discuss a phenomenon which is closely connected with the correlation problem, namely the *exchange polarization*. It has been pointed out by Slater[35,37] that, in a system with unbalanced spins having $S_z \neq 0$, the electrons with plus spin would be influenced by an exchange potential other than the electrons with negative spin, since the exchange interactions occur only between electrons having parallel spins. One could therefore expect that electrons with different spins would have different orbitals, and this effect would then be of essential importance in treating magnetic effects,[36,38] ferromagnetism, antiferromagnetism, etc.

In the so-called unrestricted Hartree-Fock scheme developed by Slater and collaborators for treating this exchange polarization, the total wave function is approximated by a single determinant where electrons with different spins may have different orbitals. The Hartree-Fock equations become hence particularly simple, since there are no nondiagonal multipliers ε_{kl} arising from the condition II.61 but the total wave function does not usually represent a pure spin state. The basis of the method has been investigated in some detail by Pratt[30] by considering the $(1s)^2 2s$ ground state of the Li atom, and he found that the total energy of the lowest state actually decreases when going from the conventional to the unrestricted Hartree-Fock scheme. The unrestricted Hartree-Fock method has also recently been used in some extensive calculations of the wave functions and energy levels for the Fe atom by Wood and Pratt.[42] In tabulating numerically the different orbitals for different spins, the additional freedom of the unrestricted Hartree-Fock scheme resulted in a small to moderate orbital splitting.

The general idea of using "different orbitals for different spins" seems thus to render an important extension of the entire framework of the independent-particle model. There seem to be essential physical reasons for a comparatively large orbital splitting depending on correlation, since electrons with opposite spins try to avoid each other because of their mutual Coulomb repulsion, and, in systems with unbalanced spins, there may further exist an extra exchange polarization of the type emphasized by Slater.

A common feature of the Hartree-Fock scheme and the two generalizations discussed in Section III.F is that all physical results depend only on the two space density matrices ρ_+ and ρ_-, which implies that the physical and mathematical simplicity of the model is essentially preserved. The differences lie in the treatment of the total spin: in the conventional scheme, the basic determinant is a pure spin function as a consequence of condition II.61, in the unrestricted scheme, the same determinant is a rather undetermined mixture of different spin states, and, in the extended scheme, one considers only the component of the determinant which has the pure spin desired.

If the Coulomb splitting is essential in treating the electronic correlation, the exchange splitting may be of particular importance in investigating magnetic properties. The question is only whether the unrestricted Hartree-Fock scheme provides an accurate enough basis for discussing this exchange polarization. It is natural that the best energy obtainable within the unrestricted scheme may come out lower than in the conventional scheme, since the constraint (Eq. II.61) has been removed in the variation; *cf.* the results by Pratt (1956). With increasing orbital splitting, however, the basic determinant ceases to approximate a pure spin function and goes over into a mixture of different spin states, and increase in orbital splitting now increases the energy. Apparently there are two competing effects, which only partly compensate each other; for a small orbital splitting, there may still be a resulting lowering of the energy, whereas, for a larger splitting, the mixing in of other spin states may become dominating and destroy the improvement. In the unrestricted scheme, there may thus be a limit for the orbital splitting, a limit which is artificial, since it is not caused by any physical reason but comes from a requirement of mathematical convenience.

It should also be observed that there exists an approximation which is "intermediate" between the unrestricted and the extended Hartree-Fock scheme. In starting from the former, the energy is increased by the mixing in of unappropriate spin states, and it can hence be essentially improved by selecting the component of the pure spin desired. It is clear that the energy obtained

in this way can hardly have optimum properties, since the orbitals used correspond not to the pure spin state but to the mixture. The energy is thus better than in the unrestricted scheme but not as good as in the extended scheme. One could also try to use the result as an "intermediate" approximation for the wave function, particularly if the orbital splitting in the unrestricted scheme is assumed to be about the same as in the extended scheme. The few examples available so far indicate, however, that the orbital splitting is usually much larger in the extended scheme than in the unrestricted one.

This means that one has to be extremely careful in making physical interpretations of the results of the unrestricted Hartree-Fock scheme, even if one has selected the pure spin component desired. In many cases, it is probably safer to carry out an additional variation of the orbitals for the specific spin component under consideration, i.e., to go over to the extended Hartree-Fock scheme. In the unrestricted scheme, one has obtained mathematical simplicity at the price of some physical confusion—in the extended scheme, the physical simplicity is restored, but the corresponding Hartree-Fock equations are now more complicated to solve. We probably have to accept these mathematical complications, since it is ultimately the physics of the system we are interested in.

IV. RECENT DEVELOPMENTS; CONCLUDING REMARKS

A. Survey of the Expansion Methods

The methods for solving the electronic Schrödinger equation treated in this survey are all based on the idea that it is possible to expand the exact eigenfunctions in a complete orthonormal set with the expansion coefficients determined by the variational principle—a general procedure which goes back to Ritz.[31] Comparison between the theoretical results obtained and experiment tells us that this approach is practically possible, even if the detailed mathematical properties of the energy operator H_{op} in this connection are not yet understood well enough. So far, very little is known about the existence, singularities, and general analytical character of the exact eigenfunctions, but work on this problem is in progress, particularly on helium.

A weakness of the development in the literature up to now has been that too much effort has been concentrated on the helium problem, whereas more complicated systems have been only scarcely treated. The reason is obvious: it is much easier to test a new method for treating correlation on the ground state of helium, and if the method fails on this simple system, it will certainly not work on a more complicated system either. In treating energy differences in many-electron systems, simple methods will often produce results in excellent agreement with experiment owing to a fortuitous cancellation of errors, but a test on helium will then often reveal the faults of the approach. Even in the future, one can therefore expect that the helium problem will be paid a great deal of interest.

The main method so far for treating correlation in many-electron systems is based on an expansion of configurations of the type III.18:

$$\Psi = \sum_K C_K \Psi_K \tag{IV.1}$$

where Ψ_K is a Slater determinant associated with the ordered configuration K; see Eq. III.17. The approximation represented by the first term $\Psi \approx D$, where D is a single Slater determinant with orbitals adapted to give an optimum energy, is nothing but the conventional Hartree-Fock scheme; for helium, the error involved is about 1.14 ev = 26.30 kcal/mole. To reach higher accuracy, more terms in Eq. IV.1 are needed, but the results in Table VI show that, if the angular dependence of the basic orbitals is expressed in terms of spherical harmonics, the over-all convergence may be fairly slow, and that it may require a rather large number of terms to achieve even a modest "chemical" accuracy of about 1 kcal/mole.

The convergence of Eq. IV.1 may be essentially improved by introducing a correlation factor $g = g(r_{12}, r_{13}, r_{23}, \ldots)$ so that

$$\Psi = g \sum_K C_K \Psi_K, \tag{IV.2}$$

see Eq. III.128. Even the approximation containing only one term $\Psi \approx gD$, is here of interest and may be considered as an extension of the Hartree-Fock scheme by means of a correlation factor. The

over-all accuracy of this method is probably not too high; the figures in Tables VII and VIII indicate that, for helium, the error will be about 0.1 ev $\approx$ 2.3 kcal/mole.

If the wave function Ψ has a symmetry property characterized by a projection operator O, the expansion IV.1 may be replaced by the series

$$\Psi = \sum_K C_K O(\Psi_K) \tag{IV.3}$$

see Eq. III.142. The approximation based on the principal term $\Psi \approx OD$ is of particular interest, since it permits the construction of a generalization of the independent-particle model to include certain correlation effects by using different orbitals for different spins. For helium, the error involved amounts to 0.70 ev $\approx$ 16 kcal/mole, but it may probably be further diminished by introducing also angularly dependent orbitals.

The convergency of expansion IV.3 may also be improved by introducing a correlation factor g:

$$\Psi = g \sum_K C_K O(\Psi_K) \tag{IV.4}$$

see Eq. III.143. The approximation based on the principal term $\Psi \approx gO(D)$ may by convenient choice of g be comparatively accurate; the result for helium is fairly promising and shows an error of only 0.05 ev $\approx$ 1.16 kcal/mole. For comparison, the various data mentioned in this section are condensed in Table X.

TABLE X. Different Expansion Methods and Extended Hartree-Fock Schemes; $g = 1+\alpha r_{12}$

Expansion	Principal term	Helium error [a]
$\Psi = \Sigma_K C_K \Psi_K$	$\Psi \approx D$	26.3
$\Psi = \Sigma_K C_K O(\Psi_K)$	$\Psi \approx O(D)$	16.0
$\Psi = g\Sigma_K C_K \Psi_K$	$\Psi \approx gD$	2.3
$\Psi = g\Sigma_K C_K O(\Psi_K)$	$\Psi \approx gO(D)$	1.2

[a] Helium errors for the extended Hartree-Fock scheme, in kcal/mole.

It is essential for the success of the expansion methods, that they are based on sets which are complete in a mathematical sense. This

means that, if hydrogen-like functions are used, it is necessary to include the continuum; see Section III.D(2). For helium, the neglect of the continuum part will, e.g., cause an error of at least 13.8 kcal/mole—a quite appreciable figure. On the other hand, it is not necessary to choose a basic set having direct physical significance, but, in such a case, it may often be convenient to express the total wave function obtained afterwards in terms of natural spin orbitals; see Section III.D(3). For truncated sets, the scaling is important; see Section II.C(3) and Section III.D(1b).

So far, most of the work carried out has been concentrated on the ground state of the system, but the study of the excited states offers also many interesting and difficult problems; see Section III.D(1a). For the hydrogen atom, the discrete energy spectrum is nicely separated from the continuous part, but, for many-electron systems, it may well happen that some of the discrete eigenvalues may lie embedded in the continuum and correspond to metastable states. The variational principle (Eq. II.7) and the solution of the corresponding secular equation put perhaps too much emphasis on the bound states having discrete energies, and a more unified treatment of both the discrete and continuous states would be highly desirable.

In this review, we have mainly studied the correlation energy connected with the standard unrelativistic Hamiltonian (Eq. II.4). This Hamiltonian may, of course, be refined to include relativistic effects, nuclear motion, etc., which leads not only to improvements in the Hartree-Fock scheme, but also to new correlation effects. The relativistic correlation and the correlation connected with the nuclear motion are probably rather small but may one day become significant.

B. Some Recent Developments: Bohm-Pines' Plasma Model, Brueckner's Approximation

Bohm-Pines' plasma model seems at first sight to be very different from the expansion methods treated here, but in Section III.E(2b) it was shown that it is rather closely connected with the method using correlation factor. Similar to Wigner's formula, it probably gives reasonable values for the correlation energy for the

electron densities found, e.g., in alkali metals, but, for separated atoms, it leads to wrong estimates of this energy, since it is based on an approximation using a uniform positive background instead of the actual nuclei; see Section III.B(1).

The plasma model itself gives an important contribution to the theory of systems containing highly mobile electrons, and particularly its treatment of the screening phenomena is of value. The model has been carefully described in some reviews, and here we would like to refer to Pines (1955). We note that the plasma model has essentially been constructed for treating metals, but it would be interesting to see whether the basic ideas could be applied also to other many-electron systems.

Another approach which looks rather different is Brueckner's approximation for treating many-particle systems in nuclei. This is also an extension of the Hartree-Fock scheme, but its original mathematical language in terms of a formal operator algebra (Brueckner 1954, 1955, Bethe 1956) makes it difficult to see the direct connection with the expansion methods. Starting out from perturbation theory, or still better from condensed formulas of the type of Eq. III.49, it is possible to get a configurational aspect on the effective two-particle interaction operator and to study Brueckner's self-consistency conditions (Rodberg 1958), but it is still not so easy to compare this new approach with the conventional methods (see, e.g., Nesbet 1958). The Brueckner approximation has been developed for nuclei, but it would be interesting if it could be tested also on a simple atomic or molecular system.

C. Variation of the Density Matrix

In Section II.B, we have used the density matrices to simplify the calculations, but the wave functions Ψ are still the fundamental quantities. Relation II.11 shows, however, that the expectation value of the energy $\langle H_{\text{op}} \rangle_{\text{Av}}$ depends only on the second-order density matrix, and we can rewrite it in the form[22]

$$\langle H_{\text{op}} \rangle_{\text{Av}} = \frac{\int \left\{ H_0 + N H_1 + \binom{N}{2} H_{12} \right\} \Gamma(x'_1 x_2 | x_1 x_2) dx_1 dx_2}{\int \Gamma(x_1 x_2 | x_1 x_2) dx_1 dx_2} \qquad \text{(IV.5)}$$

It should be emphasized that not all normalizable hermitean matrices $\Gamma(x'_1 x'_2 \ldots x'_p | x_1 x_2 \ldots x_p)$ having the correct antisymmetry property are necessarily strict density matrices, i.e., are derivable from a wave function Ψ. For instance, for $p = N$, it is a necessary and sufficient condition that the matrix $\boldsymbol{\Gamma}$ is idempotent, so that $\boldsymbol{\Gamma}^2 = \boldsymbol{\Gamma}$, Tr $(\boldsymbol{\Gamma}) = 1$. This means that the Γ-space goes conceptually outside the Ψ-space, which it fully contains. The relation IV.5 has apparently a meaning within the entire Γ-space, independent of whether $\boldsymbol{\Gamma}$ is connected with a wave function or not. The question is only which restrictions one has to impose on $\boldsymbol{\Gamma}$ in order to secure the validity of the inequality

$$\langle H_{\text{op}} \rangle_{\text{Av},\Gamma} \geqq E_0 \tag{IV.6}$$

which then would form the basis for a variational principle in Γ-space. This would, of course, be a very convenient approach, since one could then vary only the second-order density matrix $\Gamma(x'_1 x'_2 | x_1 x_2)$ containing only four electron coordinates x_i instead of the wave function Ψ containing N coordinates. In practice, this method has been tried by Mayer (1955), but his restrictions on $\boldsymbol{\Gamma}$ have been considered too weak (Tredgold 1957).

It is clear that the density matrix formalism renders a considerable simplification of the basis for the quantum theory of many-particle systems. It emphasizes points of essential physical and chemical interests, and it avoids more artificial or conventional ideas, as for instance different types of basic orbitals. The question is, however, whether this formalism can be separated from the wave function idea itself as a fundament. Research on this point is in progress, and one can expect some interesting results within the next few years.

D. Aspects for the Future

In the physics and chemistry of many-particle systems comprising atoms, molecules, solid state, and nuclei, quantum mechanics has given very important contributions to the theory of both a qualitative and quantitative nature. The Hartree-Fock scheme has usually been considered as a rather sophisticated approach, but, if one seriously studies the typical errors listed in Tables I and II and Eqs. II.83 and II.84 it becomes clear that the qualitative aspects

must probably be considered rather dominating and that one has a long way to go before one reaches even a rough "chemical" margin for the error of about 1 kcal/mole, not to speak of spectroscopic accuracy. However, in order to investigate molecular binding, cohesion in solids, elasticity, conductivity, magnetic phenomena, lattice types, etc., it is necessary to try to reach a very high accuracy in the wave function, which implies a still higher accuracy for the energy. This makes it almost compulsory to study the correlation effects in full detail and to consider the independent-particle model only as a first rough approximation.

Table X gives an idea of the strength of the various expansion methods, and it shows that, by using the principal term only, one can hardly expect to reach even the above-mentioned "chemical" margin, even if the wave function $\Psi \approx gO(D)$ is actually very close in the helium case. This means that one has to rely on expansions in complete sets, and the construction of the modern electronic computers has fortunately greatly facilitated the numerical solution of secular equations of high order and the calculation of the matrix elements involved. For atoms, the development will probably go very fast, but, for small molecules one has first to program the conventional Hartree-Fock scheme in a fully self-consistent way for the computers, before the next step can be taken. For large molecules and crystals, the entire situation is much more complicated, and it will hence probably take a rather long time before one can hope to get a detailed understanding of the correlation phenomena in these systems.

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CORRELATION PROBLEM IN MANY-ELECTRON QUANTUM MECHANICS.

II. BIBLIOGRAPHICAL SURVEY OF THE HISTORICAL DEVELOPMENT WITH COMMENTS

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I. INTRODUCTION

The purpose of this bibliography is to give a brief survey of the development of the methods for treating the correlation effects in many-electron systems by listing the most important papers in this field year by year. In accordance with the general outline used in Part I, Section III.C, the following methods will be included:

a. Superposition of configurations.
b. Correlated wave functions containing r_{ij} explicitly.
c. Different orbitals for different electrons (different spins).
d. Plasma model.
e. Brueckner's approximation.
f. Density matrix formalism.
g. Localizability theory.

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The letters a–g will be used in the references as brief symbols for indicating the main method used in a paper, and many papers are further characterized by one line comments. Even articles concerning the general theory for many-particle systems have been included.

In the bibliography, we have tried to concentrate the interest on contributions going beyond the Hartree-Fock approximation, and papers on the self-consistent field method itself have therefore not been included, unless they have also been of value from a more general point of view. However, in our treatment of the correlation effects, the Hartree-Fock scheme represents the natural basic level for study of the further improvements, and it is therefore valuable to make references to this approximation easily available. For atoms, there has been an excellent survey given by Hartree,* and, for solid-state, we would like to refer to some recent reviews.** For molecules, there does not seem to exist something similar so, in a special list, we have tried to report at least the most important papers on molecular applications of the Hartree-Fock scheme.†

At the end of the paper, condensed tables of the higher approximations have been carried out with respect to atomic and molecular systems. For atoms, the tables are arranged after the number of electrons involved, which means that, e.g., $N = 2$ refers to the series of He-like ions: H^-, He, Li^+, Be^{2+}, etc. For molecules, there is a table for H_2, a table for other simple molecules (LiH, BeH^+, H_2O, NH_3, etc.) with all or almost all electrons treated, and finally a special table for the π electron systems; in the two latter cases, the references to the best SCF data available are also contained for comparison.

* D. R. Hartree, *Reports on Progress in Physics* **11**, 113 (1948); this survey is brought up to date in D. R. Hartree, *The Calculation of Atomic Structures*, Wiley and Sons, New York, and Chapman and Hall, London, 1957. See also R. S. Knox, "Bibliography of Atomic Wave Functions," in *Solid State Physics* (Seitz and Turnbull, eds.), Academic Press, New York, 1957, Vol. 4, p. 413.

** J. C. Slater, *Handbuch der Physik*, XIX, *Electrical Conductivity* I, 1 Springer, Berlin, 1956; P.-O. Löwdin, *Adv. Phys.* **5**, 1 (1956); F. Herman, *Revs. Modern Phys.* **30**, 102 (1958).

† In this connection, the author would like to gratefully acknowledge the use of a review by Dr. T. Itoh, *Buturigaku Kaishi* (in Japanese) **12**, 1 (1957).

It is evident that, with a literature of this size, it is almost impossible to give a bibliography which is entirely complete, and it may therefore be found that papers published in more unusual periodicals or papers treating correlation effects more peripherically as well as other contributions may be missing. The field is presently developing very rapidly and it should perhaps be mentioned that the list essentially covers the period up to June 30, 1957 and that only a few papers appearing after this date have actually been included.

The author is greatly indebted to Fil. mag. Jean-Louis Calais and Fil. kand. Anders Fröman for valuable assistance in collecting the material.

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IV. ATOMS

N = number of electrons, G = ground state, E = excited state.

$N = 2$

Hylleraas (1928) He (G)
Hylleraas (1929) He (G)
Hylleraas (1930) H^-, He, Li^+, Be^{2+} (G)
Bartlett *et al.* (1935) He (G)
Baber and Hassé (1937) He (G)
Chandrasekhar (1944) H^- (two papers)
Hylleraas (1949)
Pluvinage (1950) He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+}, F^{7+} (G)

Green *et al.* (1952) He (*G*)
Lennard-Jones and Pople (1952) He (*G*)
Mulliken (1952) He (*G*)
Taylor and Parr (1952) He (*G*)
Luke *et al.* (1952) Li^+ (*G*)
Chandrasekhar *et al.* (1953) He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+} (*G*)
Green *et al.* (1953) He (*G*)
Green *et al.* (1954) (i) H^-, He, Li^+ (*G*)
Green *et al.* (1954) (iii) H^-, He (*G*)
Munschy and Pluvinage (1954) He (*E*)
Plaskett (1954) H^-, He (*G*)
Bartlett (1955) He (*G*)
Chandrasekhar *et al.* (1955) He, Li^+ (*G*)
Gerhauser and Matsen (1955) He (*G*)
Löwdin and Shull (1955) He (*G*)
Mitler (1955) He (*G*)
Munschy (1955) He (*G*, *E*)
Pluvinage (1955) He (*G*)
Shull and Löwdin (1955) He (*G*)
Green *et al.* (1956) H^-, He (*G*)
Holøien (1956) H^-, He, Li^+, Be^{2+}, C^{4+}, O^{6+}, Ne^{8+} (*G*)
Hylleraas and Midtdal (1956) H^-, He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+}, F^{7+}, Ne^{8+}, Na^{9+}, Mg^{10+}, Al^{11+}, Ca^{18+} (*G*)
Löwdin and Shull (1956) He (*G*, *E*)
Schwartz (1956) He (*G*)
Shull and Löwdin (1956) H^-, He, Li^+, Be^{2+}, B^{3+}, C^{4+} (*G*, *E*)
Stewart (1956) Be^{2+} (*G*)
Wilets and Cherry (1956) He, Li^+ (*G*)
Watson (1956) He (*G*)
Arai and Onishi (1957) H^-, He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+} (*G*, *E*)
Hart and Herzberg (1957) H^-, He, Li^+, B^{3+}, O^{6+}, Ne^{8+}, Mg^{10+} (*G*)
Kabir and Salpeter (1957) He (*G*)
Kinoshita (1957) He (*G*)
Mariott and Seaton (1957) He (*G*)
Munschy and Pluvinage (1957) He (*G*)
Pluvinage (1957) He (*G*)
Stewart (1957) H^-, He, Li^+, Be^{2+} (*G*)
Fröman (1958) He, Li^+, Be^{2+}, C^{4+} (*G*)
Gray and Pritchard (1958) H^- (*E*)
Holøien (1958) H^-, He (*G*)
Hurst *et al.* (1958) H^-, He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+}, F^{7+}, Ne^{8+} (*G*)
Hylleraas and Midtdal (1958) H^-, He, Li^+, Be^{2+}, B^{3+}, C^{4+}, N^{5+}, O^{6+}, F^{7+}, Ne^{8+}, Ca^{18+} (*G*)
Löwdin and Redei (1958) H^-, He, Li^+, Be^{2+} (*G*)
Shull and Löwdin (1958) He (*G*)
Tycho *et al.* (1958) He (*G*, *E*)

$N = 3$

Kessler (1955) Li, Be^{+}, B^{2+}, C^{3+} (*G*)
Pratt (1956) Li (*G*)
Arai and Onishi (1957) He^{-}, Li, Be^{+}, B^{2+}, C^{3+}, N^{4+}, O^{5+} (*G*, *E*)
Brigman and Matsen (1957) Li (*G*)
Hurst *et al.* (1958) He^{-}, Li, Be^{+}, B^{2+}, C^{3+}, N^{4+}, O^{5+}, F^{6+}, Ne^{7+} (*G*)

$N = 4$

Boys (1950) Be (*G*, *E*)
Brickstock and Pople (1952) Be (*E*)
Kibartas *et al.* (1956) Be (*G*)
McWeeny (1956)(i) Be (*G*)
Arai and Onishi (1957) Li^{-}, Be, B^{+}, C^{2+}, N^{3+}, O^{4+} (*G*, *E*)

$N = 5$

Boys (1953) B (*G*, *E*)
Glembotskii *et al.* (1956) B (*G*)

$N = 6$

Boys (1953) C (*G*, *E*)
Yilmaz (1955) C, N^{+}, O^{2+}, F^{3+} (*G*)
Bolotin *et al.* (1956) C, N^{+}, O^{2+}, F^{3+}, Ne^{4+} (*G*)

$N = 10$

Bernal and Boys (1952)(ii) F^{-}, Ne, Na^{+} (*G*)
Fröman (1958) F^{-}, Al^{3+} (*G*)

$N = 11$

Gombás (1954) Na (*G*)
Simons (1955) Na (*G*)
Douglas (1956) Si^{3+} (*G*)

$N = 16$

Boys (1954)(i) S (*G*, *E*)

$N = 17$

Boys (1954)(i) S^{-}, Cl (*G*, *E*)

$N = 18$

Boys (1954)(i) Cl^{-} (*G*, *E*)

$N = 19$

Douglas (1956) Ca^{+} (*G*)

$N = 26$

Wood and Pratt (1957) Fe (*G*)

V. THE HYDROGEN MOLECULE

James and Coolidge (1933)
Coulson (1938)
Inui (1938)
Inui (1941)
Coulson and Fischer (1949)
Gurnee and Magee (1950)
Frost and Braunstein (1951)
Kotani (1951)
Mueller and Eyring (1951)
Mulliken (1952)
Bates *et al.* (1953)
Berencz (1954)
Barker *et al.* (1955)
Callen (1955)
Wallis (1955)
Berencz (1956)
Donath *et al.* (1956)
Hurley (1956)(i)

Pitzer (1956)
Arai (1957)
Berencz (1957)
Harris (1957)
D'Hooghe and Rahman (1957)
Rahman (1957)
Barnett *et al.* (1958)
Joy and Parr (1958)

VI. SIMPLE MOLECULES

Molecule	Higher approximations	SCF
Li_2	James (1934) Kotani (1956) Fieschi (1957) Ishiguro *et al.* (1957) Arai *et al.* (1958)	Coulson and Duncanson (1943) Kotani (1956) Faulkner (1957)
N_2	Hurley (1956) (iii)	Scherr (1955)
O_2	Fumi and Parr (1953) Meckler (1953) Kotani (1956) Kotani *et al.* (1957)	Kotani (1956)
HeH^+	Evett (1955) Evett (1956) Hurley (1956) (iiii)	
LiH	Tomita and Fukui (1953) Karo and Olson (1956)	Fischer (1952) Karo and Olson (1956)
BeH^+		Fischer (1952)
BH	Ohno and Itoh (1955) Boys *et al.* (1956)	Sahni (1956)
CH		Higuchi (1954) (i)
NH		Higuchi (1956)
OH	Freeman (1956) Freeman (1958)	Freeman (1956)
FH	Kastler (1953) Hurley (1956) (ii)	Duncan (1955) Allen and Karo (1957) Allen (1957)
CO		Sahni (1953)

Table continued

VI. SIMPLE MOLECULES (*Continued*)

Molecule	Higher approximations	SCF
H_3	Boys *et al.* (1956) Ransil (1957) Kimball and Trulio (1958)	
He_3		Shostak (1955)
H_2O	Boys *et al.* (1956) Funabashi, Magee (1957)	Ellison and Shull (1955)
NH_2		Higuchi (1954) (ii) Higuchi (1956)
CO_2		Mulligan (1951)
O_3		Fischer-Hjalmars (1955) Fischer-Hjalmars (1957)
HCN		Bassompierre (1954)
NH_3	Kaplan (1954) Kaplan (1957)	Higuchi (1956) Duncan (1957)
CH_3		Higuchi (1958)
CH_4	Funabashi and Magee (1957) Mills (1958)	Buckingham and Carter (1956)
CCl_4		Buckingham and Carter (1956)
CF_4		Buckingham and Carter (1956)
SF_6		Duncan (1952)
B_2H_6		Yamazaki (1957)

VII. π-ELECTRON SYSTEMS

Molecule	Higher approximations	SCF
HCN	Iguchi (1955)	
Ethylene	Parr and Crawford (1948) Kolos (1957)	Parr and Crawford (1948)
Acetylene	Nakamura *et al.* (1952) Ross (1952) Serre and Pullman (1953) Yoshizumi and Itoh (1955) Serre (1956)	Nakamura *et al.* (1952) Ross (1952) Serre and Pullman (1953)

Table continued

VII. π-ELECTRON SYSTEMS (*Continued*)

Molecule	Higher approximations	SCF
Diacetylene		Serre (1954)
Allyl radical	Chalvet and Daudel (1952) Moffitt (1953) Levkovits *et al.* (1955) Higuchi (1957) (i) Higuchi (1957) (ii) Hunt *et al.* (1957)	Berthier (1955)
Carbonyl radical		Sidman (1957)
Butadiene	Coulson and Jacobs (1951) Lefèbvre (1953) Pullman (1954) Pullman and Baudet (1954) Nesbet (1955) Pullman and Berthod (1955) Fain and Matsen (1957) Berry (1957)	Parr and Mulliken (1950) Nesbet (1955) Berry (1957)
Cyclo-butadiene	Craig (1950) (ii) McWeeny (1955)	
Benzene	Mayer and Sklar (1938) Craig (1950) (i) Parr, Craig, Ross (1950) Bevan, Craig (1951) McWeeny (1955) Kolos (1957)	Mueller (1954) McWeeny (1956)
Naphthalene	Moser and Lefèbvre (1955)	
Fulvene	Julg and Pullman (1953)	Berthier (1953)
Azulene	Pariser (1956)	
Pyridine	McWeeny and Peacock (1957) McWeeny (1957) (i)	McWeeny (1956)
Pyridazine	McWeeny and Peacock (1957)	
Pyrimidine	McWeeny and Peacock (1957)	
Pyrazine	McWeeny (1957) (i) McWeeny and Peacock (1957)	McWeeny (1957) (i)

THE PROBLEM OF BARRIERS TO INTERNAL ROTATION IN MOLECULES

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I. INTRODUCTION

The study of internal rotation in molecules and of the magnitude and origin of the forces interfering with free internal rotation has interested physical chemists for a good many years. The center of attention has been the rotation of one part of a molecule relative to the rest about a single bond connecting the two parts. A simple example is ethane, in which one CH_3 can rotate with respect to the other about the C—C bond. Historically the absence of isomers due to different orientations led to the idea that such rotation about a single bond must be essentially free. In the 1930's, thermodynamic data gradually provided convincing evidence that in most molecules potential energy barriers had to be surmounted in turning

from one configuration to another.[9, 10, 13] The barriers vary considerably in amount but are not normally large enough to stabilize isomers.

Although these potential barriers are only of the order of a few thousand calories in most circumstances, there are a number of properties which are markedly influenced by them. Thus the heat capacity, entropy, and equilibrium constants contain an appreciable contribution from the hindered rotation. Since statistical mechanics combined with molecular structural data has provided such a highly successful method of calculating heat capacities and entropies for simpler molecules, it is natural to try to extend the method to molecules containing the possibility of hindered rotation. Much effort has been expended in this direction, with the result that a wide class of molecules can be dealt with, provided that the height of the potential barrier is known from empirical sources. A great many molecules of considerable industrial importance are included in this category, notably the simpler hydrocarbons.

The influence of barriers on thermodynamic properties must have importance in determining the rates of various chemical reactions. It seems certain that the activated complex for many reactions will involve the possibility of restricted rotation and that the thermodynamic properties of the complex will therefore be in part determined by the magnitude of the barriers. Whereas at the moment there is no direct way of determining such barriers, any general principles obtained for stable molecules should ultimately be applicable to the activated state. One might then hope to be able to estimate the barriers and the reaction rates *a priori*.

The hindering potentials must be of importance in the question of the flexibility of long-chain molecules such as synthetic polymers and naturally occurring macromolecules such as proteins and nucleic acids. Again, direct information on barriers in these molecules will be difficult to obtain but inferences can presumably be drawn from experiments on simpler analogues.

Recently the subject of conformational analysis[20] has acquired some importance as a branch of organic chemistry. This is the study of the preferred configurations of molecules involving one or more possibilities of internal rotation. A better understanding of the

origin of barriers to internal rotation is required in order to put this subject on a firmer theoretical foundation.

Despite the extensive studies which have been made on a large number of molecules, it is still true that the theory of the origin of these potential barriers is not very far advanced. This provides perhaps the most important reason for the further study of the subject, since it is difficult to be satisfied with a situation where our ignorance of the basic forces within molecules is so evidently exposed to view. Even the experimental determination of numerical values of barriers cannot be regarded as in a satisfactory state. Large numbers of molecules have been examined by one method or another, but the reliability of the results leaves much to be desired. It has been difficult to evolve satisfactory theories of the origin of barriers because of this uncertainty in the values themselves. The application of microwave spectroscopy has provided new methods for determining not only the barriers with greater accuracy, but also the equilibrium configuration and certain other rather detailed pieces of information which are helpful in comparing rival theories of the origin of potential barriers.

This paper will outline briefly various methods of measurement and, in more detail, the microwave methods. Then some of the theories of the origin of the forces will be discussed in the light of existing information.

II. METHODS OF MEASUREMENT OF POTENTIAL BARRIERS

A. Thermodynamic Method

A considerable variety of experimental methods has been applied to the problem of determining numerical values for barriers hindering internal rotation. One of the oldest and most successful has been the comparison of calculated and observed thermodynamic quantities such as heat capacity and entropy.[27] Statistical mechanics provides the theoretical framework for the calculation of thermodynamic quantities of gaseous molecules when the mass, principal moments of inertia, and vibration frequencies are known, at least for molecules showing no internal rotation. The theory has been extended to many cases in which hindered internal rotation is

TABLE I. Some Potential Barriers in kcal/mole

Molecule	$V(\mu$ wave)	V(thermo)	Ref.
CH_3CH_3		2.7–3.0	1
CH_3CH_2F	3.30		2
CH_3CHF_2	3.18		2
CH_3CH_2Cl	3.56	2.7, 4.7	3, 4, 5
CH_3CH_2Br	3.57		3
CH_3OH	1.07	1.6	6, 7
CH_3SH	1.26	1.5	8, 9
CH_3NH_2	1.94	1.9	10, 11
CH_3CHO	1.15	1.0	12, 13
CH_3CFO	1.08		14
CH_3CClO	1.35		15
CH_3COCN	1.27		16
CH_3COOCH_3	1.17		17
$CH_3CH{:}CH_2$	1.98	1.95	18, 19
$CH_3CH{:}CHF$ *trans*	2.20		20
$CH_3CF{:}CH_2$	2.62		21
$CH_3CH{:}C{:}CH_2$	1.59	1.65	22, 23
CH_3COOH	0.48	2.5 ± 0.7	24, 25
CH_3SiH_3	1.70		26
CH_3SiH_2F	1.56		27
CH_3SiHF_2	1.28		28
CH_3CHOCH_2	2.56		29
CH_3ONO_2			30
CH_3GeH_3	1.2		31
CH_3NO_2	.006 (6-fold)	< 0.25	32, 33
CH_3BF_2	.014 (6-fold)		34

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possible. If all the other parameters, including the shape of the barrier, are known from spectroscopic and other data, the height of the potential barrier can be used as an adjustable parameter with which to secure agreement between calculated and observed magnitudes. It is possible to make sufficiently accurate measurements on the heat capacities or third-law entropies of many gases so as to obtain quite accurate values of the hindering potential. However, the method is very vulnerable to errors either in the experimental measurements or particularly in the assignment of vibration frequencies, since it is based on a small difference between two large quantities, and any errors at any point will show up as

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an error in the value of the hindering potential. The method is therefore most reliable for molecules in which a very careful study of the vibration frequencies has been made. Since there are many quite simple molecules in which some uncertainty still exists as to the assignment of vibration frequencies, it is understandable that this is a serious cause for errors in more complicated molecules. It is also necessary that the experimental measurements be adequately corrected for nonideal gas behavior. This was particularly important, for example, in the case of methyl alcohol.

Table I shows some comparisons between the results of the statistical method and the microwave method to be discussed later.

B. Dipole Moment Method

One of the earliest methods for the study of internal rotation is the measurement of the dipole moment of the molecule as a function of temperature.[18] Consider, for example, the classical case of dichloroethane. Here the two CH_2Cl groups can rotate relative to one another but presumably with some hindering potential barrier. Consequently at very low temperatures, one might expect the *trans* form to be the only one present. This would have zero dipole moment. At very high temperatures there might be free rotation, in which case a dipole moment would be exhibited which can be calculated by averaging over the rapid internal rotation. If this picture is correct, one would expect the observed dipole moment to vary with the temperature. This prediction has been born out by observations on a number of molecules of this general type. Although in principle it is possible to get quantitative information about the barrier from such measurements, in practice it is rather difficult. Naturally if there is information suggesting that the shape of the potential barrier is of a simple form governed by a relatively small number of parameters, then there is more chance that dielectric constant measurements can be used to determine the magnitudes of the parameters, whereas if the potential barrier is of complex shape, this procedure is quite difficult

C. Electron Diffraction Method

In theory, electron diffraction measurements on gaseous molecules are somewhat sensitive to the thermal motions of the atoms,

including vibrations and internal rotations. In recent years the introduction of improved rotating sector electron diffraction apparatus has greatly improved the accuracy of this type of measurement, and at least a semiquantitative interpretation of the thermal motions has become possible. By making assumptions regarding the form of the barrier, a careful fitting of the observed electron diffraction data can lead to an estimate of barrier heights, especially when heavy atoms are involved in the motion of the groups.[19, 29] The accuracy so far is not very high.

D. Infrared and Raman Method

In principle, infrared spectroscopy is capable of giving accurate barriers for a wide class of molecules. If the barrier is sufficiently high, there will be several energy levels corresponding to different torsional states of the molecule. Transitions from the ground state to the first or second of these torsional levels will give their energy separation, from which the height of the barrier can be computed if its shape is assumed to be known. In the very simplest cases, such as ethane, transitions between these energy levels are not allowed as fundamentals in the infrared and so cannot be observed. They might, however, be expected to appear in combination with certain other fundamentals, and particularly the two-quantum jump might be expected to appear in combination with any active fundamental. It is difficult to predict the intensity of such combination bands, but presumably they are usually quite weak.

In a number of cases, weak bands have been assigned to such combinations and barrier values calculated from the resulting frequencies. There are four difficulties in the use of this method. The first difficulty is that of observing such combinations because of their relatively weak transition probability. The second difficulty, and the most serious one, is in making an assignment which is certainly valid. From the disagreements between this and other methods in a number of molecules, it appears that misassignments must have been made in a number of cases. Since there are often many possible explanations of weak combination bands, it is easy to understand how such errors can arise. For this reason, it seems imperative that alleged combinations of torsional energy levels

should be checked in a number of ways. For example, corresponding differences tones should be observable and identifiable by their temperature coefficients. In addition, the torsional frequency might be located in combination with more than one fundamental and several isotopic species might be studied as well as the primary species. So extensive a study does not seem to have been made on any molecule as yet.

For molecules in which at least one internal rotating part has a dipole moment component perpendicular to the axis of rotation, there should appear directly in the infrared spectrum transitions between the torsional states. For most cases these would be quite far in the infrared region and therefore more difficult to observe. Nevertheless a few molecules of this type have been studied in this region, and such transitions have been reported.[6]

Another difficulty with the infrared method is that of determining the band center with sufficient accuracy in the presence of the fine structure or band envelopes due to the overall rotation. Even when high resolution equipment is used so that the separate rotation lines are resolved, it is by no means always a simple problem to identify these lines with certainty so that the band center can be unambiguously determined. The final difficulty is one common to almost all methods and that is the effect of the shape of the potential barrier. The infrared method has the advantage that it is applicable to many molecules for which some of the other methods are not suitable. However, in some of these cases especially, barrier shapes are likely to be more complicated than the simple cosine form usually assumed, and, when this complication occurs, there is a corresponding uncertainty in the height of the potential barrier as determined from the infrared torsional frequencies. In especially favorable cases, it may be possible to observe so-called "hot bands" i.e., $v = 1$ to $v = 2$, 2 to 3, etc. This would add information about the shape of the barrier.

Raman spectroscopy can in principle be applied to this problem in much the same manner as infrared spectroscopy. The primary difference is that the selection rules are not the same as for the infrared. In a number of molecules, frequencies have been assigned to combinations or overtones of the fundamental frequency of the

torsional oscillation, but the same difficulties relating to the positive identification of the transition must be reckoned with in the Raman method as in the infrared method. Furthermore, Raman data are usually from the liquid state and may show shifts from gas values.

E. Nuclear Magnetic Resonance Method

In recent years a new technique has become available which is applicable in certain restricted areas to the determination of potential barriers. This is the technique of nuclear magnetic resonance spectroscopy, particularly high resolution NMR. There are actually two applications of this method to the determination of barriers. For barriers sufficiently high, of the order of 15,000 calories or more, it is convenient to consider the various conformations of the molecule as separate isomers of rather short lifetime. The rate of interconversion of the isomers depends upon the height of the potential barrier; the process is essentially a unimolecular reaction. Molecules emerging from a collision with a sufficiently high torsional energy will pass over the potential barrier and may then be stabilized by another collision which removes torsional energy, dropping the molecule into a different minimum of the potential energy curve. The rate of this reaction naturally depends sharply on the temperature in the usual exponential manner. Nuclear magnetic resonance spectroscopy has the property that the appearance of the spectrum of an interconverting set of substances can change as the rate of interconversion increases. At low rates of reaction, in other words relatively long lifetimes for the individual species, the spectrum is that of a superposition of the spectra of the different species. At high rates of reaction or very short lifetimes of the individual species, the observed spectrum is that of the nuclear spin in question in an average environment; that is, an environment which is the average of that encountered in the several species. Consequently, if the potential barrier is in the right range, it is possible by changing the temperature to pass from one of these extreme conditions to the other. From the temperature region in which the transition occurs, an estimate of the

potential barrier may be obtained.[5, 25] This interesting method has so far been applied only to cases in which the rotation is not about a pure single bond, but a bond with considerable double-bond character introduced by resonance with an adjacent multiple bond. Presumably it might also be applied to cases of very strong steric hindrance.

For low barriers this method is not convenient, but in certain cases an alternative has been proposed[1] which does not give the height of the barrier but does give the energy differences between conformational isomers. This method is based on the fact that the averaging over the separate isomeric forms will not be an unweighted average but will depend upon the relative amount of time spent in each form. This relative amount of time will depend upon the difference in energies between the forms and also upon the temperature. In certain cases, a fine structure varying with temperature can appear, due to the unequal population of the separate states. Information about the difference in energy can be obtained from these observations.

F. Dispersion of Sound Method

A very interesting method based on the absorption and dispersion of high frequency sound waves has been applied to a few liquids.[30] Where a molecule has two conformations of different energies separated by a potential barrier of an appropriate height, low frequency sound waves will permit equilibrium to be maintained between the two forms throughout the compression cycle, while at high frequencies, the substance will act like a mixture of two nonreacting molecules. The frequency region of change-over yields the rate of the reaction. From temperature coefficients, the height of the barrier and the energy difference between the two forms can be obtained. So far this method has been practical only for liquids, which is unfortunate because these energies can differ from liquid to vapor.

G. Microwave Intensity Method

With the development of microwave spectroscopy, a powerful new technique for the determination of potential barriers has become available for simple polar molecules. There are actually three

quite different microwave methods, the intensity method and two frequency methods. The intensity method[34] will be discussed first.

It is often found that a given pure rotational transition is accompanied in the microwave spectrum by one or more weaker spectral lines displaced in frequency from the main line but with practically the same Stark patterns as the main line. These can arise from molecules in excited vibrational or torsional states which are undergoing the same change of rotational quantum numbers which is responsible for the main line, the latter coming from molecules in the ground vibrational or torsional state. Since the effective moments of inertia change slightly on vibrational or torsional excitation, these satellite lines are displaced from the main line, usually by shifts which are quite large compared with the resolving power available in the microwave region. Their weaker intensity is due to the lower population of the excited torsional or vibrational state, a population governed by the Boltzmann distribution law. See Fig. 1.

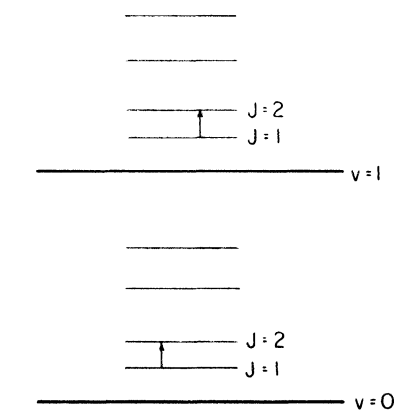

Fig. 1

By measuring the relative intensities of satellite and main lines, the population ratio is obtained, if it can be assumed that the dipole moment and line strength is not appreciably different in the two cases. From the population ratio R, the energy interval ΔE is obtained from the Boltzmann law; i.e.,

$$\Delta E = -RT \ln R/r = h\nu \qquad (1)$$

where r is the ratio of statistical weights of the levels, and ν is the torsional vibration frequency. For high barriers, the barrier height (threefold cosine shape) is approximately

$$V_3 \cong (16/9)\pi^2 I\nu^2 \tag{2}$$

where I is the reduced moment of inertia about the axis of torsion.

This is a method which is very attractive in principle and which has been applied to yield approximate barriers for a number of molecules. There are, however, difficulties in its use. In the first place, it is not easy to measure the intensities of microwave lines with accuracy. There are unsolved problems of saturation, reflections in the wave guide, and variation of detector efficiency with frequency which are presumably reponsible for the fact that measurements made with ordinary wave guide spectrometers are not very reproducible. In addition, both the spectral lines may be split into components by tunnelling from one potential minimum to another and this splitting, even though it is not resolved, can alter the apparent intensity. Furthermore, it is often difficult to find pairs of lines such that neither is obscured by Stark lobes from the other.

Some of these difficulties can be circumvented. In particular a cavity-type Stark effect spectrograph has been built which seems capable of yielding relative intensities of near-by lines to within two or three per cent.[32] Barrier values for acetaldehyde and fluoroethane have been obtained which are in excellent agreement with those from the frequency method described below. From Eq. (1) it can be seen that the error in ν is

$$\delta\nu = -(RT/h)(\delta R/R) \tag{3}$$

so that a 10 per cent error in R results in an absolute error of about 21 wave numbers in ν. This would correspond to an intolerable error in the barrier for most substances. Consequently accurate intensity ratios are a requirement for this method.

H. Microwave Splitting Method

Another and more accurate microwave method makes use of frequency measurements.[1, 11, 16, 28, 31] Acetaldehyde is an example of the class of molecules to which this method has been applied. Here there are three equivalent potential minima because of the

threefold symmetry of the methyl group. Consequently, the lowest or ground torsional energy level is triply degenerate in the high barrier limit. For lower barriers, tunnelling of the hydrogens from one minimum to another causes the level to split into a nondegenerate level. The coupling of angular momentum of the top with that of the rest of the molecule has the effect of causing pure rotational transitions for molecules in the nondegenerate and in the doubly degenerate torsional states to appear at slightly different frequencies, provided that the "framework" part of the molecule (here CHO) is an asymmetric rotor. Consequently, the microwave spectrum consists of doublets. Several theories, using different types of approximation, have been published which permit the barrier to be calculated from the spacing of these doublets and the geometry of the molecule.

The first molecule to be studied in this manner, methyl alcohol, is a rather special case because of the very small moment of inertia of the OH group. Consequently, most of the "doublets" are so widely split that only one member has been observed. Nevertheless a very precise barrier value was obtained from the analysis.

Another early example is nitromethane which is special in two respects. First, the barrier has sixfold symmetry because of the threefold character of the methyl group and the twofold character of the nitro group. Secondly, the barrier turns out to be extremely low, only about 5 small calories. For such a low barrier, it is convenient to treat the coupling between free internal rotation and overall rotation exactly and consider the barrier as a small perturbation.

About twenty-five molecules (all containing a methyl group) have been studied by the doublet splitting method. The barrier values obtained are given in Table I, along with values obtained by the thermodynamic method where available. In several of these molecules, independent barrier values were obtained from a number of spectral lines for each of several isotopic species, with agreement to 5 per cent or better. While some systematic error can still be present (for example, from an error in the stucture*), the

* The method gives V_3/F, where F is a reduced mass of the rotating group and the rest of the molecule. F is not always accurately known.

agreements provide strong support for the validity of this method.

There are several different ways in which quantum mechanics has been applied to the problem of relating the barrier to the frequency separation of the spectroscopic doublets. These are all approximation procedures and each is especially suitable under an appropriate set of circumstances. For example one may use perturbation theory, treating either the coupling of internal and external angular momenta, the molecular asymmetry, or the potential barrier as perturbations. Some of the different treatments have regions of overlap in which they give equivalent results; choice is then usually made on the basis of convenience or familiarity. Extensive numerical tables[8] have been prepared which simplify considerably the calculations.

This microwave technique can give other valuable information as well. For example, by substituting one deuterium atom on the methyl group, the three equilibrium orientations can have two (or three) different sets of moments of inertia whose values will depend on the angles at which equilibrium is attained. By this method it has been conclusively demonstrated that the equilibrium conformations in ethyl chloride, methyl silane, and methyl germane are staggered and that a methyl hydrogen in acetaldehyde is eclipsed by the oxygen.

In principle it should be possible to use the microwave splitting method to obtain barriers in excited vibrational states, and this should be instructive in testing various theories of the origin of hindrance.

I. Nonrigid Treatment

In the frequency doublet method discussed above, the two parts of the molecule are each treated as rigid. As a consequence, this model cannot account for the quite large frequency shifts observed between rotational transitions in the ground torsional state and the corresponding transitions in excited torsional states. There appear to be three effects contributing to these shifts: centrifugal distortion due to the torsional motion, distortion of the two parts by the forces which give rise to the barrier and whose effects change with torsion angle, and finally Coriolis coupling of internal rotation and some of the vibrational normal modes.

Kivelson[14] has given a treatment of the distortion by the barrier forces and centrifugal effects. This has been applied phenomenologically to CH_3SiH_3 (a coaxial symmetric rotor) to fit the set of $J = 0$ to 1 transitions associated with the first few torsional states. One of the parameters involves the barrier height, which was thereby determined.

Unfortunately, sufficient experimental data to permit application of this method is so far available for very few molecules. However, a very detailed treatment of the nonrigidity effects has been made for methyl alcohol.[7]

Although these nonrigidity effects are responsible for the large shifts between ground state and torsional state lines and also influence significantly the splitting of the ground state lines in methyl alcohol, they do not seem to invalidate the determination of barriers for most molecules with the rigid approximations. For one thing, the calculated barrier is not a sensitive function of the splitting.

One very interesting aspect of the nonrigid analysis is that it yields information about the effect of various deformations of the molecule on the barrier height. Too little data of this kind has as yet been analyzed to be conclusive, but the possibility of obtaining such information is very important.

III. EMPIRICAL DISCUSSION OF BARRIER VALUES

From a practical point of view, it would be very desirable to have reliable rules, even if only empirical, which could provide estimates of barrier heights in the absence of experimental data. This would be of obvious use in predicting thermodynamic quantities for stable molecules and would also be most valuable in testing and applying theories of reaction rates. Furthermore, any empirical regularities observed could be helpful in the development of a theoretical treatment of barriers.

Unfortunately, experimental data of sufficient reliability and accuracy are available for an insufficient number of molecules. Nevertheless, some regularities are suggested by the data.

The first of these is that when the symmetry of the two groups at the ends of the axial bond demands a barrier with six equivalent

maxima, the barrier height is very small, in fact negligible from a thermodynamic viewpoint. The only molecules of this class worked out are nitromethane and methyl boron difluoride which have barriers of only a few small calories. In propylene oxide, which has a threefold barrier, the sixfold term seems to be very small. This limited empirical evidence is backed up by the fact that various proposed force laws between the end atoms or bonds also give very small values for sixfold barrier heights. Thermodynamic data has not been reliable for low barriers. A puzzling apparent exception is CF_3SF_5 which is stated[12] to have a barrier of 630 cal despite the fact that it is twelvefold. This probably should be reinvestigated.

The length of the axial bond would be expected on all theories to be important. The barrier height does decline from ethane to methyl silane to methyl germane, but of course the bonded atoms are different. Unfortunately reliable values are not available for dimethyl mercury, dimethyl acetylene, and similar molecules with still longer bonds. An apparent exception is provided by methyl mercaptan and methyl alcohol. The latter, with the shorter axial bond, has the lower barrier.

The effect of substituting other atoms for one or more hydrogens on ethane, methyl silane, and acetaldehyde is interesting. The first point is that the effect is not extremely large; CH_3, Cl, F, CN, where tested, produce changes of only 10 to 30 per cent, so long as the substitution is confined to one end of the molecule. Secondly, the effect is not always to increase the barrier. Thus adding fluorines to methyl silane progressively decreases the barrier, as does replacing the acetyl hydrogen by fluorine on acetaldehyde. On the other hand, addition of one fluorine to ethane increases the barrier but a second fluorine produces little effect. The data available suggests that chlorine always raises the barrier but the values for CH_3CH_2F, CH_3CH_2Cl and CH_3CH_2Br are surprisingly close together.

When larger atoms are substituted at both ends and threefold symmetry is preserved, the limited data suggest that a larger increase is produced. Thus recent infrared data[2] on CF_3CH_2F give *ca.* 4.2 kcal, and electron diffraction data[19] on CCl_3CCl_3 give very roughly 10.8 kcal. However, it is claimed that $SiCl_3SiCl_3$ has only

1 kcal. It may well be that in the ethane derivatives larger atoms at both ends interact by van der Waals repulsion, which must be added to the other forces present in ethane itself, whereas in hexachloro disilane the distance is too great for van der Waals forces to be important.

Microwave studies of equilibrium orientations of methyl groups show that the forces act like repulsions, i.e., the hydrogens are staggered with respect to the atoms at the other end, at least in ethyl chloride, methyl silane, methyl fluorosilane, and methyl germane. Where there are only two attached atoms at one end, one connected by a single, the other by a double bond, as in acetaldehyde, propylene, acetyl fluoride and chloride, one of the methyl hydrogens is opposite the double bond, i.e., eclipsed.

There is some experimental data from nuclear magnetic resonance[5, 25] and sonic[30] observations which indicate that a bond which would be expected to have a partial double bond character because of conjugation with an adjacent double bond will show a barrier intermediate between single and double bond values.

IV. THEORIES OF THE ORIGIN OF BARRIERS

It is generally accepted that the energies of various molecular configurations are calculable in principle from quantum mechanics and arise, for all practical purposes, from the ordinary electrostatic attractions and repulsions of the electrons and nuclei. There is no reason to suspect any new basic forces or anything fundamentally surprising in the origin of barriers. The difficulty is as usual the mathematical impracticability of calculating sufficiently accurate wave functions. The tractable approximations which have been developed for the general problem of molecular energies are lacking both in accuracy and in internal indicators of how bad they may really be. The much simpler problem of calculating bond dissociation energies is in a quite primitive and unsatisfactory state with respect to the ability to make reliable predictions in advance of experimental knowledge. Consequently, it is too much to expect that the same crude approximations can give results of reliability for the considerably smaller energy differences involved in barriers, and no such results have been published.

Nevertheless it is important to be able to give a verbal description of the origin of barrier forces in terms of conventional quantum-mechanical language. Such a description might be of no use for quantitative predictions, but it could at least be plausible and not in conflict with known facts. It would strengthen the belief that a reliable theory only awaited the further refinement of the approximations used.

Although it has not yet led to a satisfactory quantitative explanation of barriers, it is perhaps still worthwhile reviewing briefly the way in which the standard valence-bond method of quantum mechanics has been applied to the problem. As is well known, this method utilizes a considerable number of approximations, some of which are of very dubious validity. If multiple exchange integrals are neglected and the so-called approximation of perfect pairing[24, 33] is used, the energy of any given nuclear configuration has the form

$$E = (1/\Delta)\{Q + \sum I_{ij} \text{ (bonded)} - \tfrac{1}{2}\sum I_{kl} \text{ (nonbonded)}\} \quad (4)$$

Here Q is the Coulomb integral. It is the electrostatic energy of the system of electrons and nuclei, calculated with the electron distribution which is given by the original product-type wave function without exchange, plus their standard kinetic energy. The quantities I_{ij} are the single exchange integrals between pairs of orbitals, bonded or nonbonded. Δ is the normalization integral.

It was shown quite early that this approximation gave at most a very small barrier for ethane, a result thought at that time to be in agreement with experiment. When the existence of a barrier of about 3 kcal became known, Eyring *et al.* reinvestigated the quantum-mechanical theory and considered various higher-order approximations in order to see if any of them could reasonably provide the needed barrier, but they were not successful.

In the original, elementary treatment governed by Eq. 4 above, one might initially expect contributions to the barrier from several sources. There is first the Coulomb integral Q, which will contain angle dependent terms from the electrostatic interaction of the electrons and protons ar the two ends of the molecule. In this treatment the only orbitals used are 1*s* on each H atom and tetra-

hedral sp^3 on the carbons. The filled orbitals on carbon give spherical symmetry, hence no barrier contribution and the interaction between hydrogens is very small because of cancellation of the effect of protons and electrons. The overlapping of the electron clouds from the two ends, which would make a contribution, is believed to be too small, as calculated with existing estimates of 1*s* orbitals. This is believed to be true for the exchange integrals between hydrogens also (*a* in Fig. 2).

The exchange integrals between the two carbon orbitals forming the C—C bond (see *b* in Fig. 2) do not depend on the angle of rotation (χ), i.e., this bond is cylindrically symmetric. The exchange integrals (repulsive) between the tetrahedral C—H orbitals on opposite carbons (*c*) yield nothing as long as the C—H bonds are formed from three equivalent *s*, *p* hybrids with any degree of hydridization. In the same way the repulsions between 1s on H at one end and the carbon C—H on the other (*d*) yield nothing.

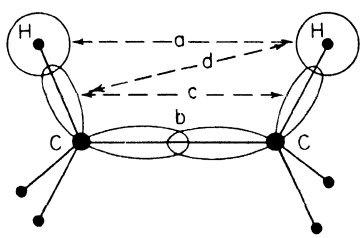

Fig. 2

These statements may not be immediately obvious. The proof is as follows. The sum of the exchange integrals between a hydrogen orbital (U_{1s}) and the three C—H tetrahedrals (*a*, *b*, *c*) on the opposite carbon is proportional to

$$\int U_{1s}(1)\{a(2)\,a(1)+b(2)\,b(1)+c(2)\,c(1)\}U_{1s}(2)\,(1/r_{12})\,d\tau_{12}$$

where r_{12} is the distance between the two electrons. The tetrahedral orbitals can be written (except for normalization) as

$$a = \tfrac{1}{2}s+\frac{2}{\sqrt{6}}p_x-\tfrac{1}{6}\sqrt{3}p_z$$

$$b = \tfrac{1}{2}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y - \tfrac{1}{6}\sqrt{3}p_z$$

$$c = \tfrac{1}{2}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y - \tfrac{1}{6}\sqrt{3}p_z$$

in which s is a $2s$ orbital, p_x, p_y, p_z are the three (real) $2p$ functions, transforming like x, y and z. The z direction is along the C—C axis. Insertion of these expressions causes the expression in brackets to reduce to

$$s(1)\,s(2) + p_x(1)\,p_x(2) + p_y(1)\,p_y(2) + p_z(1)\,p_z(2)$$

which is unchanged by a rotation of x, y axes about the z axis and hence cannot contribute to the barrier. Replacement of U_{1s} by a', b' or c', any one of the carbon C—H orbitals at the other end, yields a similar result.

Eyring and co-workers[3] considered a number of higher approximations. The first was a lack of cylindrical symmetry of the C—C bond so that the C—C bond energy would vary with the internal angle χ. Since the basic valence-bond treatment using s and p orbitals can only be the first term in an expansion in terms of similar functions built from higher energy orbitals, one expects such orbitals as $4f$ to make some contribution. The fact that the basic approximation is known to be poor strengthens the belief that higher orbitals must be rather important. One of the $4f$ functions would be expected to increase the concentration of the electron density along the C—C bond and therefore increase the bond strength. However, this one would also be cylindrically symmetrical. Another $4f$ function has the $\cos 3\chi$ dependence required for a barrier contribution. It would not, however, be likely to add to the bond strength and Eyring's admittedly crude estimates suggested that it could not be important.

Some of the empirical evidence, such as the small effect of changing from H to F, Cl, Br on one end and the apparently small effect on the barrier of bending the C—H bonds, would be understandable in terms of a noncylindrical C—C bond. Further, the crudity of available quantum mechanical methods may be such that this effect is perhaps still a possible one. However, there is one serious

adverse argument: it seems most likely that such a cause would stabilize the opposed configuration, since this would give the greatest overlap of bonding orbitals. It is known that the staggered configuration is the stable one, so the idea of a noncylindrical C—C bond is not favored at the present.

The effect of modifying the orbitals on carbon which form the C—H bonds was next considered. It was pointed out that by mixing into them some *d* character, the three bond orbitals at one carbon no longer would give cylindrical symmetry for the electron density and therefore a barrier could arise from the interaction of these distributions on the two carbons. It is, however, very difficult to estimate how much *d* character could be involved and what it would contribute to the barrier. Eyring's estimate, because of the additional effect of carbon (C—H) orbital-hydrogen interaction (*d* in Fig. 2) (which also no longer vanishes) was that the net result would be small and in the wrong direction. Again the uncertainty of such calculations must be stressed.

Despite the numerical results of Eyring, *et al.*, this idea has been espoused by others.[23]

For example, Pauling[23] has recently advocated the importance of both *d* and *f* functions in the carbon orbitals forming the C—H bonds. He gave a rough semi-quantitative argument for the amount of *d* and *f* character which might be expected on the basis of the improved C—H bond strength they would provide at the price of the promotion energy required. From this he then estimated the contribution of the *f* character to the barrier, considering however, only the interaction of carbon C—H orbitals; i.e., *c* of Fig. 2.

There are several criticisms one might make of the numerical estimates involved in this treatment, so much so that it can hardly be claimed to be more than an order of magnitude estimate. Consequently, it can be tested only on the basis of its ability to make correct qualitative predictions. One of these is that the barrier should be nearly independent of substituents (unless they are bulky or very polar), as seems to be the case. Pauling states that this theory gives the required repulsive configuration, but it should be noted that the related treatment by Eyring gave the opposite configuration, because of the interactions *d* of Fig. 2, which Pauling

does not discuss. If a double bond from carbon to a substituent (as in CH_3CHO) is treated as formed from two tetrahedrals from C with some *f* character, then the equilibrium configuration of the methyl group comes out with H on methyl eclipsing O on CHO as found experimentally. As with presumably all theories, the barrier would be expected to diminish as the axial bond increased in length. This seems to be generally true experimentally, an apparent exception being the pair methyl alcohol-methyl mercaptan.

An interesting question is the effect of unshared pairs of electrons on an axial atom. Pauling states that they appear to contribute little to three fold barriers, basing this on the observed fact that methyl amine with two N—H bonds and one pair has about 2/3 the barrier of ethane while methyl alcohol with one O—H bond and two pairs has approximately one third the ethane value. He explains this by pointing out that the unshared pairs, not forming bonds, have not the same reason to acquire *f* character, without which they will not contribute to a threefold barrier.

It is observed that sixfold barriers are very small. On the above theory, Pauling says that this is due to the fact that *i* orbitals would be required to give a sixfold contribution and these are too high to be much involved. Actually the combination of *f* with *f* and *p* with *g* should give such terms. The absence of a reliable way of making quantitative estimates again detracts from the value of these explanations of known facts.

Another set of terms considered by Eyring, *et al.* consisted of structures having a double bond between carbons. These should be expected to be involved to some small extent—small because they have one less real bond. This is essentially invoking hyperconjugation. These authors did not reach a definite conclusion regarding the importance of these structures and decided that they probably would stabilize the eclipsed configuration, which was not known at that time to be the incorrect one. It is still not simple to make a reliable estimate of the importance of this contribution.

It was also pointed out that ionic structures would contribute to a barrier. Thus a completely ionic structure with bare protons would give a value somewhat larger than the experimental potential. (The calculation is very sensitive to uncertainties in inter-

atomic distances.) It is almost impossible to believe that the C—H bonds are sufficiently ionic for this effect to be the major one in ethane.

Since the elementary quantum-mechanical treatment does not seem to give a high enough barrier, various treatments of the problem have been proposed which use empirical data such as bond dipole moments and steric repulsive forces. These treatments do not introduce any new forces which would not be included in a proper quantum-mechanical analysis, but they attempt to short-circuit these difficult and uncertain calculations.

Thus it has been suggested that the interaction of bond dipoles at opposite ends of the molecule, especially where halogens and other polar groups are involved, contributes strongly to the barrier.[15,18,21] This interaction is not something different from the Coulomb integrals discussed above (if ionic structures are included). Instead of discussing the exact Coulombic interaction of two charge distributions, (as is involved in the Coulomb integrals), the two charge distributions can be described in terms of a net charge, a dipole, quadrupole, etc., all located at some arbitrarily chosen point. Consequently, if the exact interaction has been investigated for any given choice of wave functions (or charge distribution), nothing new can be learned from the use of this expansion. Furthermore, its convergence at these close distances can be doubtful. Its value lies in the possibility of describing this "electrostatic" interaction in terms of a few parameters (bond dipole moment, bond quadrupole moment, etc.) which might somehow be experimentally determined. Unfortunately, no satisfactory independent way of determining these quantities has yet been found. Further, the value of higher moments depend on the origin chosen, if any lower moment is nonvanishing. For all these reasons, attempts to account for barriers by the interaction of dipoles, quadrupoles, octupoles, etc. have to be considered at present as not the whole answer, although surely these so-called electrostatic effects will contribute when polar groups are involved.

Another important approach to the prediction of barriers assumes that direct repulsive forces between the attached atoms are dominant and that these can be predicted from a knowledge of

the repulsive forces between separate spherical atoms, as considered in the kinetic theory of gases.[17] Again, such forces are not something new and different from those included in the quantum-mechanical treatment outlined above. They are primarily repulsions due to exchange interactions of nonbonded electrons; it is only their evaluation that is different.

Since interatomic potentials for H, F, Cl, etc. in the forms which they have in molecules are not directly obtainable from data on gases, the approximation has been used of replacing bonded fluorine by atomic neon, chlorine by argon, etc. Hydrogen presents an especially difficult problem. Data on the mutual repulsion of rare gas atoms are available from gaseous viscosities and also, at closer distances of approach, from direct, atomic beam scattering experiments. There is some suggestion that these figures should be modified in using them to represent bonded halogen atoms, but this in general has not been done.

The most rough consideration of these *steric repulsions* is based on tables of *van der Waals radii*. Pauling[22] has given such a table derived from crystal structure data on the closest distance of approach of nonbonded pairs of atoms. It might well be postulated that important contributions from direct repulsions will occur only when two atoms are separated by less than the sum of their van der Waals radii. However, this is undoubtedly an oversimplication, not only in the use of a radius instead of a force law, but also because it is unreasonable, as has been pointed out by Pauling, to treat the atoms as spherical. Since the conventional van der Waals radius is about .8 A larger than the covalent radius, the radius may be a function of direction with respect to the bond direction so that it can reduce to the covalent radius in the bond direction. The directions of approach of nonbonded atoms within a simple molecule are likely to make fairly small angles with the bond directions, and therefore the repulsions can be expected to be small even when the distance is slightly less than the sum of the van der Waals radii.

At longer distances weak attractions are expected due to induced dipoles and so-called dispersion forces. These are not included in the quantum-mechanical treatment outlined above but could be covered in principle by the inclusion of large numbers of excited

states in which the electrons occupy higher orbitals. In practice, formulas are available for estimating their magnitude.

There is little doubt that there are cases where the electrostatic interaction of polar groups makes an important contribution. Although probably unreliable quantitatively, estimates based on the interaction of bond dipoles show that such effects can be important if there are polar groups on both ends. In the cases where one end is CH_3, it seems much less likely that this is a major effect.

Similarly, examples of barriers arising largely from simple steric hindrance can be found, as for instance in the hindered diphenyls.[35] On the other hand there are many arguments suggesting that this is not the important force in ethane and similar molecules. It would be difficult to understand the relatively slow fall in barrier from ethane to methyl silane to methyl germane on a van der Waals repulsion basis. Furthermore, the small effect of substituting F, Cl, or Br on one end would also seem mysterious. The equilibrium orientation in propylene is opposite to the predictions of one of the quantitative van der Waals theories. Finally, the apparently small effect of bending back the C—H bonds is not in accord with either the electrostatic or van der Waals pictures.

V. CONCLUSION

It must finally be confessed that there is at present no theory which seems to meet the most elementary test—that it be able to make valid predictions of potentially observable facts not now known, predictions not obvious by simple empirical extrapolations from presently known data. Some of the theories do not even fit very well with the facts now known.

Although it is rather certain that electrostatic interactions of polar groups, steric hindrance, and partial double bond character due to conjugation will all be of importance in selected molecules, the explanation of the barrier in ethane probably requires something else. Though far from being proven and certainly not now useful for prediction, the idea that the ethane barrier arises from repulsion of C—H bond orbitals on the carbons, due to their being more concentrated than sp hybrids, seems the most plausible picture available.

It should be noted that this and some of the other proposed explanations would yield similar barrier contributions in other molecules where steric or electrostatic interactions are expected. In any calculations, the basic ethane-like contribution has to be subtracted before the other forces can be considered. This has not been customary.

It is to be hoped that the new sources of accurate barriers now available will yield values for molecules which will enable an ultimate decision to be made on the question of the origin of barriers.

Acknowledgment

It is a pleasure to acknowledge the many helpful discussions which I have had with my students working on the problem of barriers. I should like to thank Dr. Dudley Herschbach and also Dr. Robert Curl for criticism of the manuscript.

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