

Order and Disorder in Binary Solid Solutions

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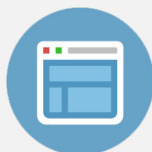
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of "thermal quantum jumps" is quite unnecessary.

In conclusion it may be said that there is agreement between experimental and theoretical specific heats of crystals, within the uncertainty in the latter. This uncertainty is, nevertheless, quite large, and it is hoped that in the near future

the experimental data presented above can be compared with a more precise theory.

The writer wishes to thank Professor W. M. Latimer for his assistance in obtaining the sample of diamonds and for his interest and advice throughout the investigation.

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Order and Disorder in Binary Solid Solutions*

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A theory of order and disorder in solid solutions, based upon a direct evaluation of the crystalline partition function, is described. As in the theory of Bethe, the fluctuation in energy within states of a fixed degree of order, is taken into account. The method promises to be of use in the study of other cooperative phenomena.

I

IT has been found that the atoms of certain solid solutions, although distributed at random among the lattice sites of the crystal at high temperatures, tend to arrange themselves into an ordered structure or superlattice at low temperatures. Moreover, there exists a critical temperature, analogous to the Curie temperature in ferromagnetism, below which the ordering process first begins to set in. Experimental evidence for the existence of order in such alloys as Cu-Au and Cu-Zn is provided by x-ray analysis of their crystal structure, and by the observation of discontinuities in certain of their physical constants or in their derivatives, which occur at the critical temperature.

Bragg and Williams¹ have treated the problem of order and disorder from the theoretical standpoint. Their theory accounts for the existence of a critical temperature and provides an approximate description of the influence of order on the thermodynamic functions of binary solid solutions. In the development of the theory they assume that the energy of the crystal is determined by its degree of long range order.

* The outlines of the present theory were sketched by the author at the Symposium on the Structure of Metallic Phases, held by the department of physics of Cornell University, July 1, 1937.

¹ Bragg and Williams, *Proc. Roy. Soc. London* **A145**, 699 (1934); **151**, 540 (1935); **152**, 231 (1935).

It was pointed out by Bethe² that a given degree of order includes many crystalline configurations of different energy. Bethe developed a more elaborate theory in which the fluctuations in energy were taken into account. His theory, later extensively applied by Peierls,³ yields results which are more nearly in accord with experiment than does the theory of Bragg and Williams.

We shall describe here an alternative theory of order and disorder, essentially equivalent to Bethe's in its degree of approximation, but somewhat less unwieldy in form. It is based upon a straightforward evaluation of the partition function of the crystal by the methods of statistical mechanics. The method of calculation bears a certain resemblance to that of the Heisenberg theory of ferromagnetism. However, the convergence difficulties, encountered by the ferromagnetism theory at low temperatures, do not arise, at least for solid solutions of rational composition. We believe that the theory may prove useful not only in the study of order and disorder in solids, but also in the treatment of cooperative phenomena in general.

II

We consider a binary solid solution containing equal numbers, N , of atoms of the components

² Bethe, *Proc. Roy. Soc. London* **A150**, 552 (1935).

³ Peierls, *Proc. Roy. Soc. London* **A154**, 207 (1936).

We suppose that the crystal is built up of two interpenetrating simple lattices, a and b , as for example, a body-centered cubic structure. Each lattice point of a has z nearest neighbor sites on lattice b , and each point of b has an equal number of nearest neighbor sites on a . In enumerating the microscopic states of the crystal we must consider the possible distributions of the N atoms of type 1 and the N atoms of type 2 among the sites of the two lattices, a and b . We shall refer to each such distribution as a configuration of the crystal. We shall make the assumption that the partition function associated with lattice vibrations is the same for all configurations of the crystal. With this simplification the partition function may be expressed as the product of two factors, one arising from configuration and the other from lattice vibrations. Correspondingly, the thermodynamic functions split up into a configurational term and a lattice vibrational term. The latter may be calculated in the usual manner by the methods of Debye and of Born and Kármán.⁴ We shall be interested here only in the configurational contributions.

The various configurations of the crystal may be partially characterized by a parameter, s , called the long range order, which is defined as follows.

$$s = (N_1^{(a)} - N_1^{(b)})/N, \quad (1)$$

where $N_1^{(a)}$ is the number of atoms of type 1 situated on lattice a , and $N_1^{(b)}$ the number on lattice b . We remark that $N_1^{(a)}$ is equal to $N_2^{(b)}$, the number of atoms of type 2 on lattice b , and that $N_1^{(b)}$ is equal to $N_2^{(a)}$, the number of type 2 on a . Further, since $N_1^{(a)} + N_1^{(b)} = N$, we may write

$$\begin{aligned} N_1^{(a)} &= N_2^{(b)} = N(1+s)/2, \\ N_1^{(b)} &= N_2^{(a)} = N(1-s)/2. \end{aligned} \quad (2)$$

We notice that when s has the values, ± 1 , the crystal is in a completely ordered state with all atoms of type 1 on one of the lattices and all atoms of type 2 on the other lattice. On the other hand, when s is zero, each type of atom is randomly distributed between the two lattices.

In the theory of Bragg and Williams the energy of the crystal was assumed to be determined by the long range order, s . As was

pointed out by Bethe, this assumption is equivalent to ignoring the influence of configurational fluctuations on the value of the partition function. If the interaction of pairs of atoms which are not nearest neighbors can be neglected, the energy may be expressed as a linear function of a parameter, p , which is a measure of the local order of the crystal.

$$\begin{aligned} E &= E_0 - 2N\alpha kT(1-p), \\ \alpha &= zV_0/2kT, \\ V_0 &= (V_{11} + V_{22})/2 - V_{12}, \end{aligned} \quad (3)$$

where V_{11} , V_{22} , and V_{12} are the mutual energies of the indicated types of nearest neighbor pair, and p is given by,

$$p = (2/Nz) \sum_{a=1}^N \nu_a n_a, \quad (4)$$

where ν_a is the number of atoms of type 1 occupying lattice point a , either zero or unity, and n_a is the number of sites of lattice b , neighboring site a , which are occupied by atoms of type 1, a number ranging from zero to z . The parameter, p , may be alternatively expressed in the form,

$$p = (1/Nz) \sum_{a,b} \langle n \rangle \nu_a \nu_b, \quad (5)$$

where ν_b is the number of atoms of type 1 occupying site b , and the sum extends over all pairs of a and b sites which are neighbors. The constant, E_0 , is the energy of the two pure crystals, 1 and 2, before mixing, provided there is no change in the lattice parameters on mixing. We remark that Bethe's local order parameter, σ , is equal to $1-2p$. It is immaterial whether we work with the variable σ or p . The parameter, σ , has the intuitive advantage of vanishing when the average environment of any lattice point is randomly distributed between atoms of the two types. Specification of a pair of values, (s, p) does not of course completely characterize the configuration of the crystal. We shall designate by $\omega(s, p)$ the number of different configurations corresponding to the pair of values of the order parameters (s, p) .

By statistical mechanics, the free energy, F , of the crystal is related to the partition function, $f(\beta)$, in the following manner.

$$F = -(1/\beta) \log f(\beta), \quad (6)$$

⁴ See R. H. Fowler, *Statistical Mechanics*, Chap. IV (Cambridge University Press, 1936).

where β is equal to $1/kT$. We shall find it convenient to calculate the configurational partition function for a fixed value of the long range order, s , and then to minimize the free energy with respect to s . The configurational partition function for a fixed s may be written as follows.

$$f(\beta, s) = \sum_{p=0}^{1-s} \omega(s, p) e^{-2N\alpha(p-1)}, \quad (7)$$

where the sum extends from 0 to $1-s$, the maximum value of p . The total number of configurations included by a fixed s for all values of p is readily seen to be the product of the number of ways the N sites of lattice a may be distributed among $N_1^{(a)}$ atoms of type 1 and $N_2^{(a)}$ atoms of type 2, by the number of ways the N sites of lattice b may be distributed among $N_1^{(b)}$ atoms 1 and $N_2^{(b)}$ atoms 2. We distribute the sites among the atoms rather than the atoms among the sites in order to avoid distinguishing between configurations which differ only by the interchange of atoms of the same type. We may therefore write,

$$\sum_{p=0}^{1-s} \omega(s, p) = \left[\frac{N!}{N_1^{(a)}! N_2^{(a)}!} \right] \left[\frac{N!}{N_1^{(b)}! N_2^{(b)}!} \right]. \quad (8)$$

It is convenient to define a distribution function, $\varphi(p)$, which is normalized to unity.

$$\sum_{p=0}^{1-s} \varphi(p) = 1; \quad (9)$$

$$\varphi(p) = \frac{N_1^{(a)}! N_2^{(a)}! N_1^{(b)}! N_2^{(b)}!}{N!^2} \omega(s, p).$$

Making use of Eqs. (2) and (9), we may write (7) in the following form.

$$e^{-2N\alpha f(\beta, s)} = \left[\frac{N!}{[N(1+s)/2]! [N(1-s)/2]!} \right]^2 \times \sum_{p=0}^{1-s} e^{-2N\alpha p} \varphi(p). \quad (10)$$

The sum in (10) may be expressed in terms of the semi-invariants of Thiele,⁵ which are conveniently used to characterize a distribution function by its moments. The semi-invariants

⁵ See A. Fisher, *Mathematical Theory of Probability*, Vol. I, second edition (Macmillan, 1922).

are defined as follows,

$$\exp \left[\sum_{n=1}^{\infty} (\lambda_n/n!) x^n \right] = \sum_{n=0}^{\infty} (M_n/n!) x^n, \quad (11)$$

$$M_n = \sum_{p=0}^{1-s} p^n \varphi(p).$$

By logarithmic differentiation the λ_n may be shown to satisfy the following set of linear equations, in which the moments M_n of the distribution function appear as coefficients.

$$\sum_{m=1}^n \binom{n-1}{m-1} \lambda_m M_{n-m} = M_n; \quad n=1, 2, \dots \quad (12)$$

Solution of these equations for the first three λ_n yields,

$$\begin{aligned} \lambda_1 &= M_1, \\ \lambda_2 &= M_2 - M_1^2, \\ \lambda_3 &= M_3 - 3M_1M_2 + 2M_1^3. \end{aligned} \quad (13)$$

By expansion in series and comparison with Eq. (11), it is readily verified that the sum in (10) may be expressed in the form,

$$\sum_{p=0}^{1-s} e^{-2N\alpha p} \varphi(p) = \exp \left[\sum_{n=1}^{\infty} ((-2N\alpha)^n/n!) \lambda_n \right]. \quad (14)$$

Using Eqs. (6), (10), and (14), and approximating the factorials of large numbers by Stirling's formula, we obtain the following expression for the configurational free energy of the crystal,

$$\begin{aligned} -F(s)/kT &= N[2 \log 2 - (1+s) \log (1+s) \\ &\quad - (1-s) \log (1-s)] + \sum_{n=1}^{\infty} ((-2N\alpha)^n/n!) \lambda_n \\ &\quad + 2N\alpha. \end{aligned} \quad (15)$$

The equilibrium value of the long range order corresponds to a minimum in the free energy, $F(s)$, and is to be determined by the condition;

$$\partial F(s)/\partial s = 0. \quad (16)$$

Before proceeding to the calculation of the moments of the distribution function, we remark the retention of only the term involving λ_1 amounts to assuming $\varphi(p)$ to have the form of a delta function, $\delta(p-\lambda_1)$. This leads to the Bragg and Williams approximation. Retention of the first two terms, involving λ_1 and λ_2 is equivalent to assuming that $(p-\lambda_1)/\lambda_2^{1/2}$ has a continuous

range of values between $-\infty$ and $+\infty$, and that $\varphi(p)$ is Gaussian in form.

$$\varphi(p) = (1/(\pi\lambda_2)^{1/2})e^{-(p-\lambda_1)^2/2\lambda_2}. \quad (17)$$

Since we shall find by calculation that $1/\lambda_2^{1/2}$ is of the order, $N^{1/2}$, the error involved in assuming the infinite interval for $(p-\lambda_1)/\lambda_2^{1/2}$ is of negligible order. The Gaussian form for $\varphi(p)$ proves itself to be a rather good approximation, and, as we shall show, leads to results in substantial agreement with those obtained by the more complicated method of Bethe.

For the calculation of the moments of the distribution function we make use of the following relations.

$$\sum_{a=1}^N \nu_a = N_1^{(a)}; \quad \sum_{b=1}^N \nu_b = N_1^{(b)}; \quad \sum_{a=1}^N n_a = zN_1^{(b)}. \quad (18)$$

A calculation, the details of which are given in the appendix, leads to the result,

$$\begin{aligned} \lambda_1 &= (1-s^2)/2, \\ \lambda_2 &= (1-s^2)^2/4Nz, \\ \lambda_3 &= s^2(1-s^2)^2/2N^2z^2. \end{aligned} \quad (19)$$

In the expressions for the thermodynamic functions of the crystal we shall retain only the terms in λ_1 and λ_2 . The reader may ascertain with a little calculation that the term in λ_3 makes only very small contributions. We obtain for the free energy,

$$\begin{aligned} -F(s)/NkT &= 2 \log 2 - (1+s) \log(1+s) \\ &\quad - (1-s) \log(1-s) + \alpha(1+s^2) \\ &\quad + \alpha^2(1-s^2)^2/2z + \dots \end{aligned} \quad (20)$$

The equilibrium value of the long range order, s , corresponding to a minimum in the free energy at constant temperature, $(\partial F/\partial s)_\alpha = 0$, is found to satisfy the following transcendental equation,

$$\begin{aligned} s &= \tanh \gamma s \\ \gamma &= \alpha - \alpha^2(1-s^2)/z. \end{aligned} \quad (21)$$

The Bragg and Williams approximation is obtained if the terms in α/z are neglected in Eqs. (20) and (21). We note first of all that Eq. (21) has solutions other than $s=0$, only if α is positive, which we shall see corresponds to a negative energy of mixing. If α is negative there will be a critical solution temperature and separation into two phases. However, treatment

of this case requires the discussion of solutions of arbitrary composition. When α is positive, Eq. (21) has a solution other than $s=0$, only below a certain critical temperature, T_c , corre-

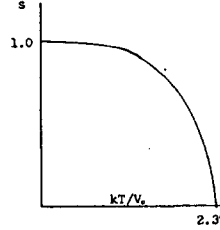


FIG. 1.

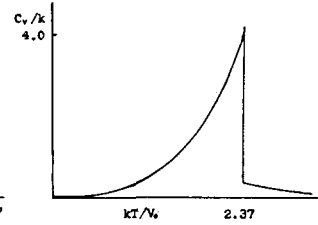


FIG. 2.

sponding to a value of α_c , satisfying the following equation.

$$\begin{aligned} \alpha_c^2 - z\alpha_c + z &= 0, \\ \alpha_c &= (z/2)[1 - (1-4/z)^{1/2}], \\ T_c &= zV_0/2k\alpha_c. \end{aligned} \quad (22)$$

For the simple cubic structure, $z=6$, we find T_c equal to $2.366 V_0/k$, a value which differs only slightly from that of Bethe, $2.372 V_0/k$. In Fig. 1, s is plotted as a function of kT/V_0 for $z=6$. The average or thermodynamic energy, $\bar{E} = \partial(F/T)/\partial(1/T)$ and the entropy, $S = (\bar{E} - F)/T$, may be written in the form,

$$\begin{aligned} \bar{E}/NkT &= -\alpha(1+s^2) - \alpha^2(1-s^2)^2/z, \\ S/Nk &= 2 \log 2 - (1+s) \log(1+s) \\ &\quad - (1-s) \log(1-s) - \alpha^2(1-s^2)^2/2z. \end{aligned} \quad (23)$$

The configurational heat capacity per atom, equal to $(1/2N)(\partial \bar{E}/\partial T)_v$ has the form,

$$\frac{c_v}{k} = \alpha^2 \left[\frac{s^2[1 - (2\alpha/z)(1-s^2)]^2}{\cosh^2 \gamma s - \gamma - 2\alpha^2 s^2/z} + \frac{1}{2z}(1-s^2)^2 \right]. \quad (24)$$

The configurational heat capacity is plotted as a function of kT/V_0 for $z=6$ in Fig. 2. It undergoes a jump at the critical temperature, c_v/k having the value, 4.23 just below T_c , and the value 0.134 just above. The peak of c_v/k is thus higher than Bethe's value, 2.14. The inclusion of the term in λ_3 would lower our value somewhat. The configurational heat capacity does not vanish above the critical temperature, because a certain average degree of local order persists even after the long range order vanishes, and its gradual destruction with increasing temperature contributes to the heat capacity. Since s is a continuous function of the temperature, \bar{E} is also a

continuous function of the temperature. Thus there is no heat of transition, and we have to do with a phase change of the second kind at the critical temperature. In contrast with a phase change of the first kind, there is only one equilibrium phase present at the transition temperature.

It is possible to apply the present theory to face-centered crystals with an atomic ratio, 1 : 3, a case considered by Bragg and Williams and by Peierls, with satisfactory results. The theory may be readily generalized for a crystal constructed of two interpenetrating lattices with any composition instead of the special 1 : 1 atomic ratio considered here. However, when α is positive, certain difficulties are encountered at very low temperatures. They arise from the failure of the series in λ_n to converge rapidly. If the Gaussian approximation, involving only λ_1 and λ_2 is used, the transcendental equation for s fails to have a

nonvanishing solution near the absolute zero, except for the atomic ratio, 1 : 1, treated in the present article. This is analogous to the difficulty encountered in the Heisenberg theory of ferromagnetism, according to which the spontaneous magnetization would vanish at low temperatures. In our case the difficulty may be removed for a region of composition in the neighborhood of the atomic ratio, 1 : 1, by including the term in λ_3 . Outside this region, terms in the λ_n of still higher order are required. The extension of the theory to solid solutions of arbitrary compositions will be discussed in detail at a later time. Its limiting form for vanishing long range order promises to be of use in the theory of liquid solutions.

In conclusion, the writer wishes to express his thanks to Professor H. Bethe of Cornell University and to Professor F. Bitter of the Massachusetts Institute of Technology for many helpful discussions.

APPENDIX

Calculation of the moments

From Eq. (4) we observe that the moment, M_m , of the distribution function, $\varphi(p)$, may be written in the form,

$$M_m = (2/Nz)^m \langle (\sum_{a=1}^N \nu_a n_a)^m \rangle_{AV}, \quad (25)$$

where $_{AV}$ denotes an *a priori* average over all crystalline configurations. Since the *a priori* distributions on the two different lattices a and b are independent, an average of the form, $\langle (f_1(\nu_1 \cdots \nu_N) f_2(n_1 \cdots n_N)) \rangle_{AV}$, may be written as $\langle f_1(\nu_1 \cdots \nu_N) \rangle_{AV} \langle f_2(n_1 \cdots n_N) \rangle_{AV}$, inasmuch as the ν_a refer to atoms on lattice a and the n_a to atoms on lattice b . To avoid confusion, we remark that this is true since we are concerned only with *a priori* averages. It would not be true of statistical-mechanical averages, where the Boltzmann factors, of course, introduce correlation between the distributions on the separate lattices. We shall employ the following sum relations in the subsequent calculations,

$$\sum_{a=1}^N \nu_a^m = rN; \quad \sum_{a=1}^N n_a = zwN, \\ r = N_1^{(a)}/N = (1+s)/2, \quad w = N_1^{(b)}/N = (1-s)/2. \quad (26)$$

These relations follow from Eqs. (2) and (18), and from the fact that $\nu_a^m = \nu_a$ when m is not zero, since the ν_a are either zero or unity.

Since the average values of $\langle \nu_a^m \rangle_{AV}$ and $\langle n_a \rangle_{AV}$ are of course the same for all lattice sites, we obtain by averaging both sides of Eqs. (26),

$$\langle \nu^m \rangle_{AV} = r, \quad \langle n \rangle_{AV} = zw, \quad (27)$$

where $\langle \nu^m \rangle_{AV}$ and $\langle n \rangle_{AV}$ refer to any lattice site. Similarly, $\langle \nu_a \nu_{a'} \rangle_{AV}$ has the same value, $\langle \nu \nu' \rangle_{AV}$, for any pair of sites (not true of $\langle n_a n_{a'} \rangle_{AV}$). Thus we have from Eq. (26),

$$r^2 N^2 = \langle (\sum_{a=1}^N \nu_a)^2 \rangle_{AV} = N \langle \nu \rangle_{AV} + N(N-1) \langle \nu \nu' \rangle_{AV}, \quad (28)$$

$$\langle \nu \nu' \rangle_{AV} = \frac{r(rN-1)}{N-1} = r^2 - \frac{rw}{N} + O\left(\frac{1}{N^2}\right).$$

We shall also require the value of $\langle n^m \rangle_{AV}$, the average of n_a^m for any site a . The number of ways in which a set of z sites of lattice b may be assigned to n atoms of type 1 and the remaining $N-z$ sites to $N_1^{(b)}-n$ atoms of type 1 and

$N_2^{(b)}-z+n$ atoms of type 2 is evidently equal to $\binom{N}{N_1^{(b)}-n}$, while the total number of configurations of lattice b is $\binom{N}{N_1^{(b)}}$. Thus we may write for the normalized probability, $P_z(n)$, of configurations in which the z neighbors of a site of lattice a include n atoms of type 1,

$$P_z(n) = \binom{N}{N_1^{(b)}}^{-1} \binom{N}{N_1^{(b)}-n} \binom{z}{n} \\ = \binom{z}{n} r^{z-n} w^n + O\left(\frac{1}{N}\right). \quad (29)$$

The average value $\langle n^m \rangle_{AV}$ may then be expressed as follows,

$$\langle n^m \rangle_{AV} = \sum_{n=0}^z n^m P_z(n) \\ = [(\partial^m / \partial x^m) (w e^x + r)^z]_{x=0}. \quad (30)$$

The relations stated above suffice for the calculation of M_1 and M_2 . For the higher moments others of a similar nature would be needed.

We may calculate M_1 at once, using Eqs. (25) and (27), and obtain the result,

$$M_1 = \frac{2}{NZ} \sum_{a=1}^N \langle \nu_a \rangle_{Av} \langle n_a \rangle_{Av} = \frac{2 \langle \nu \rangle_{Av} \langle n \rangle_{Av}}{s} = (1-s^2)/2. \quad (31)$$

For the moment, M_2 , we may write, by virtue of the independence of averages on the separate lattices,

$$M_2 = \frac{4}{N^2 Z^2} [N \langle (\nu^2)_{Av} - \langle \nu \nu' \rangle_{Av} \rangle \langle n^2 \rangle_{Av} + \langle \nu \nu' \rangle_{Av} \langle (\sum_{a=1}^N n_a)^2 \rangle_{Av}]. \quad (32)$$

From Eq. (30) we find that n is equal to $z^2 r^2 + z r w$. This result together with Eqs. (27), (28), and (32) yields,

$$M_2 = M_1^2 + (4/NZ) r^2 w^2 + O(1/N^2) \\ = M_1^2 + (1-s^2)^2/4NZ + O(1/N^2). \quad (33)$$

The third moment, M_3 , may be obtained in a similar fashion, although the calculation is somewhat more tedious. When substituted in Eqs. (13), the moments so obtained yield Eqs. (19).

The moments may be calculated in another way if p is expressed in the form of Eq. (5). A method analogous to that employed by Van Vleck⁶ in his treatment of the Heisenberg theory of ferromagnetism may then be employed. This method, though somewhat simpler to state, involves about the same amount of computational labor as the one described above.

⁶ J. H. Van Vleck, *Electric and Magnetic Susceptibilities*, Vol. 12, § 78 (Clarendon Press, Oxford, 1932).

FEBRUARY, 1938

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The Electron Diffraction Investigation of the Molecular Structures of Ketene and Thiophosphoryl Chloride¹

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(Received November 23, 1937)

The structures of the gas molecules of ketene and thiophosphoryl chloride have been determined by the diffraction of 57 kilovolt electrons. The interpretation of the photographs was made by the visual method in conjunction with the radial distribution method. The results for ketene are: carbon-carbon distance $1.35 \pm 0.02\text{\AA}$, and carbon-oxygen distance $1.17 \pm 0.02\text{\AA}$. The carbon-hydrogen distance was assumed to be 1.07\AA . The results for thiophosphoryl chloride are: phosphorus-chlorine distance $2.01 \pm 0.02\text{\AA}$, phosphorus-sulphur distance $1.94 \pm 0.03\text{\AA}$, and the Cl-P-Cl angle $107 \pm 3^\circ$. The results are discussed in terms of covalent radii and the resonance of molecules among several electronic structures.

THE apparatus used in this investigation is closely similar to the one described by Brockway³ and used by Pauling, Brockway *et al.* for determining the structures of gas molecules. The electrons were accelerated by a potential of roughly 57 kilovolts. The wave-length of the electrons was 0.0515\AA . This wave-length was found accurately by taking transmission pictures of gold foil, the structure of which is known. In interpreting the photographs we have used the visual method and the radial distribution method. Both of these procedures have been

described by Pauling and Brockway.⁴ Bauer⁵ has developed an analytic method, based on visual measurement, for interpreting photographs. The method consists of differentiating the theoretical scattering curve and setting the derivative equal to zero at each of the measured maxima and minima. The interatomic distances are then obtained by solving a set of simultaneous equations.

The formula used in the visual method for calculating the intensity of the scattered elec-

¹ Presented before the American Chemical Society, Rochester, September, 1937.

² National Research Fellow in chemistry.

³ For a general review of the experimental procedure and a summary of electron diffraction results see L. O. Brockway, *Rev. Mod. Phys.* **8**, 231 (1936).

⁴ The visual method of interpretation, originally developed by R. Wierl, *Ann. d. Physik* **8**, 531 (1931) and **13**, 453 (1932), has been tested and discussed by L. Pauling and L. O. Brockway, *J. Chem. Phys.* **2**, 867 (1934). The radial distribution method was developed, tested and applied to a large number of compounds by L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **57**, 2684 (1935).

⁵ S. H. Bauer, *J. Chem. Phys.* **4**, 406 (1936).