DISCONTINUITIES IN THE ENERGY AND SPECIFIC HEAT

A. BIJL

DISCONTINUITIES
IN THE ENERGY AND SPECIFIC HEAT

kast dissertaties

DISCONTINUITIES IN THE ENERGY AND SPECIFIC HEAT

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INTRODUCTION.

In the last few years our knowledge about caloric properties of many substances has been increased considerably.

In particular it has been shown that many solid bodies show abnormally large specific heats in some small temperature regions. Such an anomaly will be indicated by the term: *transition point* or *transition region*.

The transition points may be of a very different character. In some cases the specific heat becomes very large but can still be represented as a continuous function of temperature; in other cases there is a discontinuity in the energy, accompanied occasionnally by an anomaly in the specific heat or by hysteresis effects, or both at the same time; in very few cases the specific heat is discontinuous and the energy continuous.

Parallel with the exploration of these types of transitions progress has been made in explaining their mechanism. Here the most succesful theories are the theory of Pauling ¹) explaining the caloric anomalies in crystals which contain polyatomic ions and the theory of Johansson and Linde, which shows that the thermal anomalies of alloys can be understood by admitting a transition from an ordered to a disordered state.

In the following pages we will try to arrive at a provisional answer to the question: „What predictions can be made from the type of a transition as to the mechanism by which it is caused."

The method applied here was already given in a paper published in 1934 ²). In the second part of this previous work some mistakes had been made, so that its value for the problem considered was but small. Therefore the present work is given without reference to the former.

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¹) L. Pauling, Phys. Rev. **36**, 430, 1930.

²) A. Bijl, Physica **1**, 1125, 1934.

CHAPTER I.

The order-disorder transitions.

§ 1. *The transition of Cu-Au alloy.*

It will be useful first to discuss the newer theories about transition points. As these theories have been developed in particular for the order-disorder transitions, we shall limit ourselves to these. For a short survey of the experimental facts we shall follow the description of the phenomena as given by Johansson and Linde.[1]

A Debye-Scherrer photograph of a wire of *Cu-Au* alloy (50 at. % *Au*) shows marked superstructure lines, when the wire has been sufficiently annealed between 300° C. and 400° C.

These lines disappear when the wire is heated above 420° C. and appear again after sufficiently slow cooling.

The superstructure lines of the lower temperature form belong to spacings which are about double the spacings of the high temperature form. The high temperature form is cubic face centered and the unit cell contains, therefore, four atoms. If we take a unit cell in which two *Au* and two *Cu* atoms are present and build up a crystal by repeating this unit cell with a fixed configuration of the *Cu* and *Au* atoms the crystal thus obtained must show the observed superstructure lines. So the change in the structure is probably due to an ordering of the gold and copper atoms.

It is easily seen that the unit cell of the ordered form has no longer cubical symmetry but has an axis of symmetry which is perpendicular to the lattice planes which contain two equal

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[1] C. H. Johansson and J. O. Linde, Ann. Phys. **25**, 1, 1936. See for complete references pag. 47 of that article.

atoms of the same unit cell. Parallel with this loss of cubical symmetry is observed a tetragonal deformation, which appears with decreasing temperature at about 400° C., but increases still more at lower temperatures.

The electrical resistance of the alloy determined at rising temperatures increases abnormally, but continuously, from about 250° C. up to 420° C., and increases very rapidly — probably with a discontinuity — at this temperature. Above 420° C. the resistance curve is again „normal"; it is a linear function of temperature.

When the resistance is measured at falling temperatures another curve is obtained. The curve from 420° C. till 400° C. is a smooth continuation of the high temperature curve; at 400° C. there is a sudden decrease and below 400° C. it is about the same as the one obtained with rising temperatures.

Measurements of the specific heat show a strong increase in the specific heat from about 300° C. to 400° C. The determinations of the specific heat by Sykes and others [1]) for some other alloys do not show the hysteresis effects. It would be very remarkable if a hysteresis in the resistance were not accompanied by a hysteresis in caloric properties too. So we may at this moment anticipate that more accurate determinations will show a similar behaviour of resistance and specific heat.

Although the transition of the *Cu-Au* system shows many finer details, the facts mentioned above permit us a description of the transition in the following way:

At very high temperatures the different metal atoms are divided at random over the lattice points. There is, however, a tendency towards an ordered arrangement of the atoms. At about 400° C. this process of ordering shows a discontinuity, so that below the transition temperature large ordered regions exist in the crystal, which are indicated by a low electrical resistance and superstructure lines in the X-ray pattern. At still lower temperatures this process is completed, and causes a further decrease in the electrical resistance, an excess specific heat and a shortening of the tetragonal axis.

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[1]) C. Sykes and F. W. Jones, Proc. roy. Soc. **157**, 213, 1936.

With rising temperature the process goes in the reverse direction. It is, however, impossible to obtain the transition at the same temperature; we must distinguish three temperatures:

$$T_a, \quad T_m \quad \text{and} \quad T_b \quad (T_a > T_m > T_b).$$

T_m is the temperature where both phases are in equilibrium, i.e. where their thermic potentials are equal, but between T_m and T_a the lower temperature phase does not pass into the more stable „disordered" phase and similarly between T_m and T_b the disordered phase does not pass into the ordered one.

In conclusion, it seems justified to consider the process of ordening as a process, in which the phase transition is merely an incident, and we must ask ourselves whether such incidents are inherent or not in the mechanism of the ordering.

§ 2. *The theory of Bragg and Williams.*

Some years ago Borelius [1]) described the phenomena observed at the order-disorder transitions by representing the free energy of an alloy as a function of the „degree of order". The actual degree of order in the crystal is fixed by the condition that the free energy is a minimum. As a measure for the degree of disorder was used the deviation of the electrical resistance from an extrapolation of the low temperature part of the resistance curve. This choice was justified by the fact that the electrical resistance is very sensitive to deviations of the lattice from periodicity.

Borelius could show that the introduction of the degree of order as an „inner parameter" of the substance was sufficient to represent in a formal way the experimental data known at that time. He could also invalidate the criticism which had been raised against the experimental results of Borelius, Johansson and Linde and show that these were due to wrong interpretation of the thermodynamic theory of transitions. Recently similar misunderstandings proved to exist about the concept of „transition point" of the second order, intro-

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[1]) G. Borelius, Ann. Phys. **20**, 57, 1934; **24**, 489, 1935.

duced by Keesom and Ehrenfest[1]). Although these difficulties have not yet disappeared entirely[2]) they have been thoroughly discussed so that it seems permitted to omit their discussion here.

Bragg and Williams[3]) made the first attempt to solve the problem of the transition of alloys with the aid of the methods of statistical mechanics. They calculated the energy and entropy as a function of the „degree of order" using some assumptions which we shall presently mention.

The degree of order was defined by comparing the arrangement of the atoms in the crystal with the arrangement in a perfectly ordered crystal. We suppose that in the ordered crystal N lattice points are occupied by atoms of the same kind. If in the real crystal these lattice points are occupied by $\frac{1}{2}N(1+\sigma)$ atoms of this kind and $\frac{1}{2}N(1-\sigma)$ atoms of the other kind, and if in an entirely random distribution of the atoms these numbers would be both $\frac{1}{2}N$, we may call σ the „degree of order" of the lattice.

This definition of degree of order has some minor inconveniences. By replacing every atom of a crystal by an atom of the other kind, σ changes sign so that it may be as well negative as positive. Moreover, if there is perfect order in most parts of the crystal but in such a way that these parts do not fit with each other, the value of σ is still zero according to the definition.

Bragg and Williams first try to derive a relation between the degree of order and the energy of a crystal. They observe that in a perfectly ordered crystal some energy is required to interchange the places of two unequal atoms. In a completely disordered crystal we must expect, however, that this interchange will cause on the average no increase in energy.

It is therefore assumed that an interchange of two unequal

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[1]) W. H. Keesom, Communications Kamerlingh Onnes Laboratory, Leiden, Suppl. 85a; P. Ehrenfest, Suppl. 85b.

[2]) Cf. E. Justi and H. Nitka, Phys. Zs. **38**, 302, 1937.

[3]) W. L. Bragg and E. J. Williams, Proc. roy. Soc. **145**, 699, 1934; **151**, 540, 1935.

atoms requires a certain energy which depends only on the degree of order in the crystal. This is equivalent to the assumption that every atom which fits into the ordered lattice — which we may call a „right" atom — has a certain energy differing from the energy of an atom not fitting into the ordered lattice — i.e. a „wrong" atom — by an amount only dependent on the degree of order.

This assumption is more specialized by assuming that the relation between the above mentioned energy difference or interchange energy V and the degree of order σ can be represented by:

$$V = -\alpha\sigma. \tag{1}$$

V is the derivative of the energy U (calculated per atom) with respect to σ. So we have:

$$U = -\tfrac{1}{2}\alpha\sigma^2. \tag{2}$$

This form of the relation between U and σ is not justified by Bragg and Williams. It is, of course, impossible to do this as long as no more special information is available about the forces which tend to produce an ordered arrangement. The only thing which is rather certain is that U is a monotonic function of σ; the results deduced from (2) can, however, not be regarded as rigourous.

For the determination of the equilibrium value of σ we must also know the relation between the entropy per atom, S, and σ.

A natural extension of the above mentioned assumption is to suppose that to every division of $\frac{1}{2}N(1+\sigma)$ „right" atoms of the same kind over their possible lattice points, corresponds the same energy. The expression for S is than readily obtained by the calculation of the number of different arrangements of $\frac{1}{2}N(1+\sigma)$ atoms over N lattice points. The number of possible configurations W of the crystal is the square of this number, as there are two independent superlattices. The entropy is equal to $k \log W$, and is obtained in the form: [1])

$$S = f(\sigma). \tag{3}$$

The equilibrium value of σ is now determined by the condition that the free energy F is a minimum as a function of σ. Therefore:

$$\frac{\partial F}{\partial \sigma} = 0, \text{ or:}$$

$$\alpha \sigma = T \frac{\partial f}{\partial \sigma}. \tag{4}$$

With this equation the problem of determining the degree of order and the energy as a function of temperature is in principe solved.

It has been remarked by Fowler [2]) that the theory of Bragg and Williams is very similar to the Weiss theory of ferromagnetism. There is, in fact, so much analogy between the theories that both become identical in their algebraïc form if the ferromagnetic theory is applied to magnetic atoms for which only two directions of the magnetic moments are allowed.

In the Weiss theory the elementary magnets are directed by an „effective" field $H_{eff.}$ which contains a term proportional to the magnetisation already obtained:

$$H_{eff.} = H_{ext.} + bI/I_\infty, \tag{5}$$

where $H_{ext.}$ is the external field and I/I_∞ is the magnetisation divided by the saturated magnetisation.

The absolute value of the work done in turning one magnet is equal to

$$V = 2\mu\, H_{eff.} = 2\mu\, H_{ext.} + 2b\mu\, I/I_\infty. \tag{6}$$

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[1]) The introduction of Gibbs' entropy in Borelius paper (l.c.), corresponds to this entropy.

[2]) R. H. Fowler, Proc. roy. Soc. **151**, 1, 1935.

This energy can be compared with the „interchange" energy in (1) if $H_{ext.}$ is zero and I/I_∞ is called the degree of order of the elementary magnets. The entropy of a state with magnetisation is likewise found by considering the number of ways in which $(1 + I/I_\infty)\, N/2$ elementary magnets out of N can be directed along the lines of force. So this entropy is the same function of I/I_∞ in the ferromagnetic case as it is of σ in the treatment of Bragg and Williams.

As is known, the Weiss theory leads to the existence of a sharp Curie point, and so does also the theory of Bragg and Williams. These authors drew attention to the fact that this result depends on the special assumption (1). They made therefore clear that also the existence of a Curie point in the ferromagnetic case is not certain from a theoretical point of view, as there is no reason to expect that the relation (6) gives the exact expression for the energy required to turn an elementary magnet.

Our conclussion must be that the theory of Bragg and Williams gives a valuable qualitative discussion about the transition point, but that it cannot give definite information regarding the physical conditions necessary for the existence of a Curie point.

§ 3. *The theorie of Bethe and Peierls.*

Bethe [1]) and after him Peierls [2]) gave another discussion of the same problem. They first introduced some hypotheses which simplified the physical model of the alloy and made it suitable for exact calculations. In this way they avoided the necessity of using assumptions which could neither be proved nor disproved on the basis of their model.

Bethe first gives an interesting discussion of the definition of the concept „degree of order". In the same way as indicated by Peierls he introduced two different concepts of order, viz. „short range" and „long range" order.

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[1]) H. A. Bethe, Proc. roy. Soc. **150**, 552, 1935.

[2]) R. Peierls, Proc. roy. Soc. **154**, 207, 1935.

For the definition of the „short range" degree of order we shall restrict ourselves to such superstructures in which the entirely ordered crystal is already determined if only it is known by which kind of atom one single lattice point is occupied. This would for instance be the case in a body centered alloy, in which the components are present in equal amounts.

We may now compare the nearest neighbours of a given atom with the nearest neighbours of a similar atom in a completely ordered crystal. The number of nearest neighbours which would fit into the ordered crystal is clearly a measure for the degree of order of the crystal considered. We may proceed in the same way for every atom in the crystal. If p is the chance that a pair of nearest neighbours is „ordered" the quantity

$$\sigma = 2p - 1 \tag{7}$$

is called the „degree of short range order". For a completely ordered state σ is unity, for a random distribution of the atoms σ is zero.

In more complicated cases the degree of order can be defined by considering the chance that an atom is of the same kind as an atom occupying the corresponding place in a neighbouring unit cell. This definition is, however, not always useful for physical applications.

The degree of order defined above may considerably differ from zero, while the degree of order defined by Bragg and Williams is still zero. To distinguish it from the former the latter is called by Bethe: „the long range order" of the atoms.

In a qualitative discussion of the problem Bethe concludes that the disappearance of the „long-range" order will be accompanied by a jump in the specific heat, but that above that temperature the short-range order will persist. The decrease of this order with rising temperature will also cause an anomaly in the specific heat above the transition temperature. This is in fact in accordance with the experimental determinations.

The physical assumption which Bethe introduced in his theory is that two neighbours, which are „ordered" will have an energy different from a pair of nearest neighbours, which are not ordered. For instance, if in a cubic body-centered crystal the centre is occupied by the same kind of atom as a corner, this configuration will have an energy V in excess of that of the configuration, in which these lattice points are occupied by different atoms. We shall always assume in this brief discussion that all nearest neighbours in the ideally ordered state are different from each other. Moreover it is assumed that only nearest neighbours interact. Therefore the total energy of the crystal is determined by the number of equal neighbours, i.e. by the degree of „short range" order.

With these assumptions the probability that a certain lattice point (which we shall call the „central" lattice point) is occupied by an atom of a given kind is determined entirely if the configuration of the nearest neighbours of the central lattice point is given. These nearest neighbours of the central lattice point are called the „first shell",

Again the probability for a certain configuration of the central atom and the first shell is determined if the configuration of all the nearest neighbours of the first shell is given. These lattice points are called the „second shell" and so on.

The treatment of Bethe is now an approximation in which the influence of the different shells on the order of the central atom is calculated. The calculation cannot be made by general formulae, and therefore only the influence of the two first shells has been taken into account.

Bethe's calculations are divided into two parts; in the first part he only considers the states in which the long range order is zero; in the second part he considers in more detail the states with non-vanishing long range order.

We shall give here a representation of Bethe's calculation which is due to Mott and Jones. [1]

Let us call the probability that a nearest neighbour of the

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[1] N. F. Mott and H. Jones, Properties of metals and alloys, pag. 28.

central atom is not of the same kind p. The „short range order" is than equal to:

$$\sigma = 1 - 2p.$$

If we only take into account the interaction between the first shell and the central atom the energy difference between the states in which a certain atom of the first shell is equal or unequal to the central atom is V. So the relative probability of these states must be equal to

$$e\,(-V/kT)$$

and we obtain:

$$\frac{p}{1-p} = e\,(-V/kT), \quad \text{or}$$

$$\sigma = \tanh\,(V/2kT). \tag{8}$$

In a similar, but of course more complicated way the configurations of the atoms including the second shell can be investigated. In this second approximation the value of σ differs at the high temperatures only slightly from (7), at low temperatures the deviations are considerable.

In the states with long range order the atoms are divided in „R" atoms (right atoms) and „W" atoms (wrong atoms). The R atoms fit into the ordered lattice, the W atoms do not. Of course there are more R atoms than W atoms. In order to make it possible to treat the states with non-zero long distance order in an analogous way it is assumed that the long distance order has the effect that for an atom of the last shell considered the probality that it shall be a R atom is $1/(1+\varepsilon)$.

Let us call the number of lattice points in the first shell z. Then the relative probalility that in a state in which there are n W atoms in the first shell the central atom is R, which will be called r_n, is equal to:

$$r_n = \binom{z}{n} \varepsilon^n\, e\,(-nV/kT). \tag{9}$$

The factor $e\,(-nV/kT)$ is due to fact that the energy of this state is equal to nV; the factor $\binom{z}{n}$ in introduced to account for the number of arrangements of the n W atoms in the first shell.

Likewise the probability for a configuration in which n W atoms are in the first shell, and the central atom is W is equal to

$$w_n = \binom{z}{n} \varepsilon^n \, e(-(z-n)V/kT). \tag{10}$$

The relative probabilities that the central atom is right or wrong are given by:

$$r = \sum_0^z r_n = (1 + \varepsilon \, e(-V/kT))^z \tag{11}$$

and

$$w = \sum_0^z w_n = (\varepsilon + e(-V/kT))^z \, .$$

On the other hand the probabilities for a R or W atom in the first shell are respectively:

$$r_1 = \sum_0^z (z-n)(r_n + w_n) \tag{12}$$

and

$$w_1 = \sum_0^z n(r_n + w_n).$$

As the atoms in the first shell are not in a physical sense different from the central atom, we have:

$$\frac{r}{w} = \frac{r_1}{w_1}, \tag{13}$$

which equation reduces to:

$$\varepsilon = \left(\frac{\varepsilon + e(-V/kT)}{1 + \varepsilon \, e(-V/kT)}\right)^{z-1}. \tag{14}$$

It is now possible to calculate the „long range” order as a function of temperature. It turns out that this long range order is zero above a certain temperature determined by the equation:

$$(15) \qquad \frac{kT_c}{V} = 1/\log(z/z-2).$$

If the temperature is increased to T_c the short range order diminishes together with the long range order, and becomes equal to the short range order calculated without assuming long range order. Therefore a jump in the specific heat must be expected, as for $T = T_c$ the energies of both states (i.e. the states with and without long range order) become equal, but the specific heats remain different.

It might also be possible that, even at a lower temperature, the free energies of both states became equal. In fact this was found to be the case by Peierls for an alloy of the general composition $A_3 B$.

The specific heat curve is sufficiently close to the experimental curves, to permit the conclusion that the experiments do not contradict the basic assumptions.

A closer examination of Bethe's theory raises doubt as to its value in connection with the transition phenomena. We might ask, for instance, whether the method of successive consideration of more and more shells surrounding the central atom converges, and if it is convergent, what would be the result if the calculations were carried out in a high approximation.

This would mean that we should calculate the order of neighbours taking into account the influence of many shells, i.e. for a small crystal. As the order of neighbours is closely connected with the energy of the crystal, we might expect that in the same way as the energy the degree of order would decrease slowly at low temperatures, more rapidly in the neighbourhood of a „critical" temperature, and again slowly at high temperatures.

In fact Bethe's curve for the second approximation shows this character much better than the curve for the first approximation.

This means, however, that if we really calculated the order of nearest neighbours in a high approximation we should approach more and more the real curve and should not need the approximation including long range order.

The introduction of this calculation and more specially the introduction of the probality ε proves, therefore, to be a correction for the fact that the first calculation does not converge rapidly enough. Similarly we may expect that also in calculations with long range order the value of ε becomes unimportant if we carry out the calculation for many shells. For we may imagine that the surface of the crystal coïncides with a certain shell, and it is clear that at the surface ε may be chosen at will.

The „correction" caused by the introduction of the probability ε is the difference between the order of neighbours with and without long range order and is very important in the neighbourhood of the Curie point. If the curve for the short range order can be in error without the introduction of ε immediately below the Curie point, it will probably not be very reliable above the Curie point either. So the conclusions about the transition phenomena are very uncertain from a theoretical point of view.

It seems, therefore, that the method of Bethe is perhaps trustworthy below and above the transition point, but that it gives no reliable results in the immediate neighbourhood of this temperature; it does not convince us, for instance, that the model gives a possibility for a Curie point.

CHAPTER II.

The phase transition as an association.

§ 1. *The aim of a theory of transitions. The phase transition as a process of association.*

Thermodynamics does not predict anything about the form of the specific heat temperature curve except that the specific heat must be positive. So it is impossible to predict anything about the type of a transition by purely thermodynamical reasoning. Similarly thermodynamics allows every hysteresis effect except that it predicts in what direction a hysteresis loop must be traversed.

As thermodynamics and the general scheme of statistical mechanics are exactly equivalent the same can be said about general statistical considerations; there are no types of discontinuities in the partition function which can be excluded a priori, and if in the configuration space some parts of a surface of constant energy are separated from each other by regions of higher energy, all kinds of metastable states are possible.

It must be clear therefore that every prediction about the transition type of a substance must be based on the physical properties of the substance. If it were possible to evaluate the partition function for a certain case, all properties of the transition would be known at the same time. It is, however, very questionable wether this can be achieved. We must, therefore, find out some method which allows of detecting discontinuities in the partition function without exact calculation of this function.

As the different phase transitions have very different mechanisms, it may be difficult to find a physical description of the transition phenomena which will apply to all cases. It is, however, also of interest to posess a complete theory for a restricted class of transitions, especially if the transitions in this class are of different types. With this we have already the opportunity to investigate what are the physical conditions necessary for a transition of a certain type.

We will therefore discuss the transitions which can be described as a process of association. This process is such that at lower temperatures the molecules combine to groups of associated units, which become larger and larger until at very low temperatures one or a few macroscopically large associated group is formed. It is recommendable to speak here of association of units rather than of association of molecules, because this allows us to apply the concept of association in more cases; in the following we shall, however, often use the term „molecules" instead of „units".

A transition may be described as a process of association if it possible to define what the „units" are and if it is possible to give a definition of association which allows us to determine unambiguously whether or not a unit is associated with other units.

If this is possible we shall define a „group of associated units" by saying that a unit belongs to the same group as the units with which it is associated. Units which are not associated with others can be considered as forming groups by themselves.

As an example of how the conception of association may be used we shall indicate how the associated groups may be defined for the transition of the alloys discussed above.

For this purpose we imagine the crystal to be divided into unit cells. This can be done in four different ways (because there a four atoms in a unit cell) but we shall only consider one of these divisions. If a unit cell contains two *Au* atoms and two *Cu* atoms we shall call it associated with a neighbouring unit cell if this also contains two *Au* atoms and two

Cu atoms in the same configuration as in the first cell. For this it suffices that the direction of the „tetragonal axis" is the same for both unit cells.

If we consider only one division of the crystal into unit cells, this definition allows an unambiguous division of the unit cells into „associated groups". Moreover, an entirely ordered crystal is identical with an infinitely large group so that the transition from disorder to order can be described as an association of the unit cells into groups.

§ 2. *Qualitative discussion of the association process.*

The problem of association can be treated as that of the equilibrium of a chemical reaction, if the different kinds of associated groups are treated as different kinds of molecules. We must consider therefore the substance as a mixture and determine, which mixture is stable against all possible reactions:

$$(i) + (j) = (i + j). \tag{1}$$

(i) is in this equation the symbol for a group of i associatied units. The treatment of this problem must make use of the theory of mixtures. The application of the theory of mixtures to the theory of phase transitions is not new. Many examples have already been given by A. Smits and collaborators [1]. That it is possible to obtain some new points of view is due to the fact that we shall also consider here arbitrarely large groups, and therefore an arbitrarily large number of components.

Let the number of groups of i molecules in the substance be denoted by n_i ($i = 1, 2, 3$, etc.). The equilibrium values of these n_i are functions of temperature. Thermodynamics gives some very simple rules for the change of the n_i with temperature. If in the reaction (1) heat is developed when the process goes from left to right, for every i and j, the equilibrium constant of the reactions (1) will decrease with decreasing temperature. Therefore the equilibrium will shift to the right.

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[1] A. Smits, Die Theorie der Allotropie.

The larger is the heat, developed in one elementary process, the more rapid will be the change of the equilibrium constant K, for we have:

$$\frac{d \log K}{dT} = + \frac{Q}{kT^2} \tag{2}$$

where Q is the heat developed in one elementary process (1).

We will try to give a physical interpretation for this „heat of reaction" which will be restricted, however, to the larger groups. For the very large groups, the internal structure of the groups will be the same. A difference between groups of different size may be that they have a different ratio of „surface" molecules to „inner" molecules. If this difference between the surfaces exists it will in general also cause a difference between the energies per molecule of groups of different size. We may call this energy difference the difference in „surface energy" as it depends on the ratio of the number of surface molecules to the total number of molecules.

The heat developed if the reaction (1) proceeds from left to right is than the difference in surface energy between the two groups of i and j molecules and surface energy of one group of $i + j$ molecules. This difference will in many cases be positive, so that association will increase with decreasing temperature. Generally the heat of reaction will even increase together with i and j. If the number of surface molecules increases with some power of i, say with i^k, the heat of reaction in (1) is proportional to:

$$i^k + j^k - (i + j)^k$$

This expression is not only positive for $0 < k < 1$, but increases also if i and j increase.

The mean energy developed in the reaction (1) may therefore become larger if the substance is already partly associated, because the values of i and j become larger in all reactions. As a consequence Q in (2) will also increase and the equilibrium will go to the right, more and more rapidly. Therefore a possibility exists for cumulative processes. These processes may lead at a given temperature to a discontinuity in the association.

This short discussion may suffice to show the possibilities for understanding transition phenomena with the help of an association picture.

§ 3. *The thermic potential of a mixture.*

In the previous paragraph it was already mentioned that in a theory of an associating substance the theory of chemical reactions in mixtures could be applied.

This theory is usually given in such a form that only thermodynamical symbols are used. This opens the possibility of following this example also here. Although the methods of statistical mechanics are more fundamental, they often lead to very complicated terminology and formulae. This is avoided if the thermodynamical notation is used, which is, moreover, in most cases merely a translation of the statistical notation. Instead of „Zustandssume" or „partition function" the free enery is used; the „number of states" corresponds to entropy, etc.

As the first problem in a statistical treatment of a system is to find an expression for the „Zustandssumme", our first problem must be to give a general expression for the thermic potential of a mixture.

We shall describe the mixture by the external variables p and T (or in some cases v and T) and by the numbers n_i of the different groups ($i = 1, 2, 3 \ldots . k$). The thermic potential ¹) is than a function of all these quantities:

$$P = P(p, T, n_1, n_2, \ldots \ldots n_k) \tag{3}$$

It is well known that it is possible to introduce the partial thermodynamic potentials for the molecules of different kinds. This follows immediately if we observe that the value of P increases proportional with the total mass of the system if the

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¹) The thermic potential used here will be the potential used by Planck:

$$P = S - \frac{U + pV}{T}$$

This potential is a maximum in the state of equilibrium.

composition is kept unchanged. We have, therefore, multiplying all n_i by $(1+\lambda)$:

$$(1+\lambda)\ P(n_i) \ = \ P(n_i(1+\lambda)).$$

Differentiation with respect to λ yelds for $\lambda = 0$:

$$P(n_i) \ = \ \Sigma\, n_i \frac{\partial P}{\partial n_i}.$$

We may write therefore:

(4*a*) $$P \ = \ \Sigma\, n_i p_i\,,$$

(4*b*) $$U \ = \ \Sigma\, n_i u_i\,, \qquad (U = \text{energy})$$

(4*c*) $$V \ = \ \Sigma\, n_i v_i\,, \qquad (V = \text{volume})$$

if we put:

(5*a*) $$p_i \ = \ \frac{\partial P}{\partial n_i},$$

(5*b*) $$u_i \ = \ \frac{\partial U}{\partial n_i},$$

(5*c*) $$v_i \ = \ \frac{\partial V}{\partial n_i}.$$

The physical meaning of the p_i, u_i and v_i becomes at once clear if we observe that for any change in the mixture at constant p and T the corresponding changes in P, U and V can be expressed as linear combinations of the p_i, u_i and v_i respectively.

We introduce the concentration of the molecules of the sort i by the definition:

(6) $$c_i \ = \ \frac{n_i}{\Sigma n_i},$$

so that

(7) $$\Sigma c_i \ = \ 1.$$

One of the most important properties of the p_i is that they can be written as

$$(8) \qquad p_i = f_i - R \log c_i,$$

in which the function f_i remains finite for every value of the c_i, while the p_i become infinite for $c_i \rightarrow 0$.

This property can be proved directly from the second law of thermodynamics in every case where it is actually possible to separate in a more or less direct way the different kinds of molecules. [1])

A general proof can be given on the basis of statistical mechanics, and we will give this proof in a simplified form.

The thermodynamic potential P is connected with the „Zustandssumme" or „partition function" Z by the relation:

$$P = k \log Z,$$

while the partition function Z is defined by:

$$Z = \sum_n e\left(-\frac{U_n}{kT}\right)$$

in which the summation has to be extented over all independent states of the system, and U_n is the energy of the state n. [2])

We now consider a species of molecules which is sufficiently rare, so that it is possible to divide the substance into a number of volume elements which contain many molecules but are still so small that the probability that one of them contains more than one molecule of the kind considered is very small.

If r molecules of the kind considered are present and the substance is divided into s volume elements or „cells", r cells contain a molecule, and $(s - r)$ do not.

The number of ways in which the molecules can be divided over the cells is equal to:

$$S = \frac{s!}{r!\,(s-r)!}$$

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[1]) Cf. A. **Rutgers**, Z. physik. Chem. A **173**, 73, 1935.

[2]) If the system is under constant pressure, the system must also include the piston, which causes the pressure p.

This number S is contained in the partition function as a factor, and the thermodynamic potential, therefore, contains the term $k \log S$. By Stirlings' theorem we have

$$k \log S = k \, [s \log s - r \log r - (s - r) \log (s - r)\,].$$

To the partial thermic potential p of the molecules considered this term gives the contribution:

$$R \frac{d \log S}{dr} = -R \log \frac{r}{s - r} \,.$$

If we use the fact that $r \ll s$, and introduce the concentration of the molecules considered

$$c = \frac{1}{N} \cdot \frac{r}{s},$$

(N is the mean number of molecules per cell), we obtain:

$$R \frac{d \log S}{dr} = -R \log c - R \log N.$$

So we have shown that the p contains a term which becomes infinite as $-R \log c$ for $c \rightarrow 0$.

Besides this term the logarithm of the partition function only contains terms which are, for small r, proportional to r. For if the partition function for a cell containing one molecule of the type considered is f_1 and the partition function for a cell containing no molecule of the type considered is f_0, the total partition function is approximately equal to:

$$Z = S \,.\, (f_1)^{r} \,.\, (f_0)^{s - r}.$$

From this expression it is easily derived that in $k \partial \log Z / \partial r$ the term $R \log c$ is the only one which does not remain finite for $c \rightarrow 0$.

These remarks are sufficient to show that even in cases where the formula (8) cannot be proved by purely thermodynamic reasoning it is still justified to accept it.

The f_i in formula (8) have a very simple meaning in the case of an ideal gas. Here they are independent of the composition of the mixture, and the expression:

$$e\,(f_i/kT)$$

represents the partition function for a molecule of the kind i. In general it is not possible to attribute an individual partition function to a certain kind of molecule. This is only possible in those cases where the „partial" energy and volume for the molecules considered [see eq. (3)] are independent of the composition of the substance.

For this indicates that for all physically important configurations of the system the influence of the other molecules on the molecules considered can be described by a constant factor.

§ 4. *Application to an associating mixture.*

In an associating mixture the possible reactions are indicated by:

$$(i) + (j) \leftrightarrows (i + j) \tag{1}$$

so we have to consider the groups as molecules of different kinds.

For a given substance we denote by n_1, $n_2, \ldots\ n_i$ the numbers of the different groups divided by Avogadro's number.

If N is the total number of grammols we have evidently:

$$\Sigma\, i n_i = N$$

The concentrations of the groups are defined by:

$$c_i = \frac{n_i}{\Sigma\, n_i} \tag{6a}$$

For the partial potential, energy, etc. we use the notations: $i\mu_i$, $i\varepsilon_i$, etc.:

$$i\mu_i = \frac{\partial P}{\partial n_i} \tag{9}$$

so that the μ_i etc. refer to a single molecule and can be compared for different groups.

We will introduce the quantities φ_i by the equations:

(10) $$i\varphi_i = i\mu_i + R \log c_i.$$

The conditions for the equilibrium are very simple. They express the fact that the function

(11) $$P = \Sigma\, i n_i \mu_i$$

is a maximum at constant values of p and T. So we obtain:

(12) $$\mu_i = \mu,$$

for all i. This is most easily verified by calculating the change in P caused by a transition of some groups of k molecules into groups of i molecules.

As a direct consequence wo obtain by (7)

(13) $$P_{max.} = N\mu,$$

while equation (10) can now be given in the form:

(14) $$c_i = e\left(i \frac{\varphi_i - \mu}{R}\right).$$

As the sum of the concentrations must equal unity, we have the additional equation:

(15) $$1 = \sum_i e\left(i \frac{\varphi_i - \mu}{R}\right).$$

If the φ_i are supposed to be known, μ is determined as a function of temperature from this equation.

§ 5. *The energy and specific heat for an associating substance.*

The thermic functions for the associating substance may now be obtained by the usual methods. The energy and the specific heat are of special importance.

The energy is given by:

(16) $$U = T^2 \frac{\partial P}{\partial T}.$$

If we use the formula (11) for the thermic potential we obtain:

$$U = T^2 \sum_i i n_i \frac{\partial \mu_i}{\partial T} + T^2 \sum_i i \mu_i \frac{dn_i}{dT}.$$

The second term in this expression is zero for the state of equilibrium because all μ_i are equal and $\Sigma i\, dn_i/dT$ is zero. Introducing the φ_i from (10) the energy can be expressed as:

$$U = \sum_i i n_i \frac{\partial \varphi_i}{\partial T}, \text{ or,}$$

$$U = \sum_i i n_i u_i \tag{17}$$

where u_i is the energy per molecule of a group i molecules as defined in (5*b*).

The specific heat is obtained by differentiation of (17):

$$c = \sum_i i n_i \frac{\partial u_i}{\partial T} + \Sigma i u_i \frac{dn_i}{dT}. \tag{18}$$

The first term is the „normal" specific heat, the second term is due to the „transition energy". We shall show that this part of the specific heat is always positive.

An expression for dn_i/dT may be obtained from (6*a*):

$$\frac{dn_i}{dT} = \frac{dc_i}{dT} \Sigma n_i + c_i \frac{d\Sigma n_i}{dT}. \tag{19}$$

$\frac{dc_i}{dT}$ is found from (14):

$$\frac{dc_i}{dT} = \frac{ic_i}{RT^2}(u_i - u), \quad \text{where } u = U/N. \tag{20}$$

If we write the second term of (18) in the form:

$$\sum_i i(u_i - u) \frac{dn_i}{dT}$$

it appears that the second term of dn_i/dT gives zero after summation over i. The specific heat is finally equal to:

$$c = \Sigma\, i\, n_i \frac{\partial u_i}{\partial T} + \Sigma\, i^2\, n_i\, (u_i - u)^2. \tag{21}$$

The „anomalous" part of the specific heat is therefore closely related to the fluctuations in the „energy density" of the substance.

The only thing we have so far assumed is that all the differential coëfficients of the φ_i exist. This is not always certain, especially for the second derivative. We can only hope that the definition of the association is given in such a way that such inconveniences do not occur.

Apart from this difficulty it seems that the description of the association phenomena fits well the qualitative description in § 2, and is not essentialy different from the usual association theory with a finite number of components.

CHAPTER III.

The possibility of discontinuities in the energy and specific heat.

§ 1. *The limits of the association model at low temperatures.*

A closer examination of the formulae obtained in the previous chapter raises the question whether the method used is always correct.

Thermodynamics can only be applied if the number of similar objects is very large, and in the method used even the number of possible different groups is already of the same order as the total number of molecules. It is therefore impossible that all n_i are large compared with one.

There are two ways in which this difficulty can be overcome. Firstly it may be remarked that the summation over all values of i is purely formal, because the values of c_i for larger i are very small, so that the existence of these groups may be neglected. So we shall obtain a fairly accurate picture if we limit the values of i by some maximum value.

On the other hand, we may suppose that if the total number of molecules is increased the c_i remain constant. For every given value of i we can make the number of groups of i molecules arbitrarily large by increasing the total number of molecules sufficiently.

From this point of view all φ_i have a meaning, although the value of φ_i can only be found by statistical calculations. It is therefore not only permissable to speak of φ_i as a well-defined quantity but even of the limit of the sequence

$$\varphi_1, \varphi_2, \varphi_3, \ldots\ldots \varphi_k, \ldots.$$

This limit we will call φ_∞, the thermic potential of an infinite group.

The second argument can only be used if the φ_i and the c_i do not depend on the total numbers of molecules. It may happen, however, that there exist groups so large that they contain a number of molecules comparable with the total number of molecules. In this case, the number of these groups cannot be made arbitrarily large by simply increasing the total number of molecules. Therefore the picture of an associating substance can no longer be applied.

The necessary and sufficient condition for the correctness of the formulae is therefore that the expressions for the c_i decrease sufficiently rapidly with i. When this condition is satisfied, the sum:

$$(1) \qquad Q = \sum_1^\infty e \left(i \frac{\varphi_i - \mu}{R}\right)$$

is convergent.

By applying Cauchy's theorem for convergence, viz.

$$\lim \sqrt[n]{u_n} < 1,$$

we find as a condition for convergence:

$$(2) \qquad \lim_{i \to \infty} \varphi_i = \varphi_\infty < \mu.$$

Now the equilibrium conditions express already for all i:

$$\mu_i = \mu$$

and therefore, by ommision of the term $-R \log c_i$ from μ_i:

$$\varphi_i < \mu$$

We shall therefore always have:

$$\varphi_\infty \leqslant \mu$$

i.e. the thermic potential per molecule is always larger or equal to the thermic potential of the infinite group.

Only in the case that $\varphi_\infty = \mu$ it may happen that the association picture can no longer be applied. If a temperature T_0 exists where $\varphi_\infty = \mu$, we have from (II, 15).

$$(3) \qquad 1 = \sum_1^\infty e \left(i \frac{\varphi_i - \varphi_\infty}{R}\right)$$

At temperatures higher that T_0, μ is always larger than φ_∞. This can be easily shown, if we write (II, 15) in the form

$$1 = \sum_i e \left(i \frac{\varphi_i - \varphi_\infty}{R}\right) e \left(i \frac{\varphi_\infty - \mu}{R}\right)$$

By differentiation with respect to T we obtain:

$$T^2 \frac{d(\varphi_\infty - \mu)}{dT} = - \frac{\Sigma\, i\, c_i\, (u_i - u_\infty)}{\Sigma\, i\, c_i}$$

If we may admit $u_i > u_\infty$ this left hand side is certainly negative.

The results is therefore that at temperatures higher than T_0 the association model is correct.

At the temperature T_0, however, μ is equel to φ_∞. The meaning of this equality is that the thermic potential of the substance is equal to that of an „infinite" group and that therefore in the substance very large groups may be formed. We shall therefore consider in more detail the properties of the very large groups.

§ 2. *The infinite groups and the low temperature phase.*

The fact that at temperatures below T_0 infinite groups may exist in the substance leads to the supposition that the temperature T_0 is a „transition temperature". The first question is, therefore, whether there are similarities between an „infinite" group and a „low temperature phase".

The characteristic features of the phases in a two phase system are, firstly, that the different phases are separated by a boundary, and, secondly, that this boundary has some simple geometrical form. Therefore only a small fraction of the molecules contained in one phase is within molecular distances of the surface.

If we envelop the molecules belonging to an „infinite" group in a boundary, this boundary will in general consist of many non-connected parts. The infinite group will inclose some molecules which are not associated with it, but which are surrounded on all sides by associated molecules.

If we want to define the „low temperature phase" it is of course necessary to count also these molecules as belonging to the phase; for if we did not the word „phase" would no longer have a purely macroscopic meaning.

After the elimination of all the inner surfaces of the infinite group the remaining surfaces must show some simple geometrical form if we wish to call it the boundary of the „low temperature phase". This condition will not always be fulfilled and we must distinguish two kinds of states of the infinite group:

a) the „open" states, where the number of surface molecules is comparable with the total number of molecules, and

b) the „closed" states, where the number of surface molecules is very small compared with the total number.

Only if the infinite group is formed in a „closed" state we shall call its boundary the boundary of the „low temperature phase".

Even with this restriction the definition of phase is not yet entirely equivalent to the thermodynamical concept.

It is now possible to reduce the difference of the phases to a difference in the geometric connections between the associated molecules. In the low temperature phase it is always possible to find a chain of associated molecules connecting two associated molecules, while it is not possible to connect two unassociated molecules belonging to the phase by a line which does not pass trough an associated region.

In the high temperature phase it is always possible to connect two unassociated molecules by a line which does not pass through an associated region, and it is in general not possible to connect two molecules by a chain of associated molecules.

If together with the infinite group no low temperature phase is definable, there may be different geometric relations. The relative position of associated and unassociated regions may, for instance, be like the pores and the body respectively of a sponge. It is even conceivable that the infinite group is flat in one direction or forms a chain; this may happen, for instance, in crystalline liquids.

§ 3. *The existence of a transition temperature.*

We shall now discuss the question whether there is a temperature T_0 for wich the relation (3) is satisfied.

This will certainly not be the case, if the series:

$$S = \sum_1^\infty e\left(i \frac{\varphi_i - \varphi_\infty}{R}\right) \tag{4}$$

is *di*vergent for all temperatures. It is therefore of interest first to show, that the series S is *con*vergent if the infinite group is one such that a „low temperature phase" may be defined.

The expression $i\varphi_i$ measures, according to its definition, the increase of the thermic potential of the system by addition of a group of i molecules, apart from the term $R \log c_i$. The expression $i(\varphi_i - \varphi_\infty)$ measures therefore the difference between this increase and the increase obtained if we add i molecules to an „infinite" group, i.e. to a group containing many particles compared with i.

For the convergence of the sum S only the assymptotic value of $i(\varphi_i - \varphi_\infty)$ is important. As now the structures of all large groups are equal, the difference $i(\varphi_i - \varphi_\infty)$ is only caused by the different number of surface molecules in both cases. The number of surface molecules for a group of n molecules is proportional to $n^{2/3}$. The increase of the total number of surface molecules of all groups after addition of a group of i molecules to the system is therefore proportional to $i^{2/3}$, while the increase in the number of surface molecules if the molecules are added to a very large group is negligible. The expression $i(\varphi_i - \varphi_\infty)$ is therefore equal to $\alpha i^{2/3}$.

This difference may be called: the thermic potential of the surface of the group. From the fact that the group has a simple external form we may conclude that this surface potential is negative, because otherwise the group would spontaneously increase its external surface.

The general term of the series S approaches therefore $e(\alpha i^{2/3})$, where α is negative. S is thus certainly convergent.

Next we shall show that if the series S is convergent there will also be a temperature at which its sum is unity.

From (4) follows:

$$\frac{dS}{dT} = \Sigma \frac{i}{R} \frac{\partial(\varphi_i - \varphi_\infty)}{\partial T} e\left(i \frac{\varphi_i - \varphi_\infty}{R}\right), \text{ or:}$$

$$\frac{dS}{dT} = \Sigma \frac{i}{RT^2} (u_i - u_\infty)\, e\left(i \frac{\varphi_i - \varphi_\infty}{R}\right) \tag{5}$$

If δ is the smallest value which the smallest of the expressions $i(u_i - u_\infty)/R$ takes on in a certain temperature region, we have:

$$\frac{dS}{dT} > \frac{\delta}{T^2} S, \text{ or:}$$

$$\frac{d\log S}{dT} > \frac{\delta}{T^2}$$

If S at the temperature T_1 has the value S_1 we obtain by integration between T and T_1 $(T < T_1)$:

$$\log S_1/S > \delta\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

The right hand side can be made arbitrarily large (provided δ always remains positive and does not tend to zero) and there will certainly be a temperature at which

$$\log S_1/S = \log S_1, \quad \text{or} \quad S = 1.$$

For those cases where the infinite groups are formed in open states nothing can be predicted. If the number of the surface molecules is proportional to the total number of molecules in the group the surface effects do not cancel in the value of φ_∞ and so the value of $i(\varphi_i - \varphi_\infty)$ cannot be reduced to surface effects.

§ 4. *Discontinuities at the transition temperature.*

Although it is not exclused that the equation (3) is satisfied in those cases where the infinite groups are formed in open states we shall restrict the following discussion to those cases where these groups are formed in closed states, and a low temperature phase exists.

At the transition temperature T_0 the thermic potential of the substance is equal to that of the infinite group, and part of the substance will therefore combine to form an infinite group at that temperature.

We have not assumed that the φ_i are independent of the „composition" of the substance, i.e. of the variables c_i; so we must admit that φ_∞ also depends on the composition of the substance. We must therefore consider the interaction between the infinite group and the rest of the substance.

The simplest possibility is that the interaction between the „low temperature phase" and the rest of the substance is confined to the surface molecules. An increase of the number of molecules in the infinite group will cause a corresponding increase of the „low temperature phase" and will not cause any specific change in the interaction between the two „phases".

Therefore the value of φ_∞ is in this case independent of the mass ratio of the two phases.

It is now highly probable that at the temperature T_0 the energy of the substance will show a discontinuity. For the energy of the substance above and at T_0 we may write (see II, 17):

$$(6) \qquad U_2 = N\left(u_\infty + \frac{\Sigma\, i c_i\,(u_i - u_\infty)}{\Sigma\, i c_i}\right)$$

The energy of the low temperature phase is not equal to that of the infinite group, u_∞. We must also account for the energy due to the included groups of unassociated particles, and write therefore:

$$(7) \qquad U_1 = N\left(u_\infty + \frac{\Sigma\, i c'_i\,(u'_i - u_\infty)}{\Sigma\, i c'_i}\right)$$

For most cases it is clear that $U_1 < U_2$, although this cannot be proved generally. Of course, it is impossible that $U_1 > U_2$, but we cannot exclude a priori the possibility that $U_1 = U_2$. In general we must assume that, although the energy of a group inclosed in the low temperature phase is larger than the energy of the similar group in the high temperature phase, i.e.

$$(u'_i - u_\infty) > (u_i - u_\infty),$$

there are much less of such groups in the first case, so that $U_2 > U_1$. If this is the case, at temperatures below T_0 the low temperature phase is stable and is therefore also a „phase" according to the thermodynamic definition.

The description given here may be applied to practically all transitions under constant pressure, as the interaction between the two phases may be neglected in all these cases.

§ 5. *Monomorphic transitions.*

The interaction between the low temperature phase and the rest of the substance cannot always be neglected. A trivial example of such an interaction is provided by the transitions at constant volume. Here the mass-ratio of the two phases determines the pressure in the system, and a change in the pressure influences of course all the φ_i as well as φ_∞.

Another example of a specific interaction between the two phases is given by the monomorphic transitions. These are transitions which occur in crystals without breaking up and rebuilding of the crystal-lattice.In these cases the lattice parameters depend on the mass-ratio of the two phases and the ratio will thereby also influence the different φ_i and φ_∞.

Finally we must mention the case in which the molecules have fields of force which are not „convergent", i.e. fields of force which may be perceptible even at large distances (compared with molecular dimensions) with a suitable arrangement of the molecules. As examples we may mention the fields of electric and magnetic dipoles and the Coulomb fields of charged particles.

All these cases may be treated in a formal way by assuming that the thermic potential both of the low temperature phase and of the high temperature phase depends on their mass-ratio.

Let us, therefore, consider a state of the substance in which an infinite group is formed, and also a „low temperature phase". Calling n_1 the number of molecules in the low temperature phase, and n_2 the number of molecules in the high temperature phase, we may speak of the thermic potentials of these phases p_1 and p_2:

$$p_1 = \frac{\partial P}{\partial n_1} \text{ and } p_2 = \frac{\partial P}{\partial n_2} \tag{8}$$

The meaning of a differentation with respect to n_1 or n_2 must be defined exactly. If we add ν_1' molecules as a part of the infinite group the low temperature phase increases with, say, $\nu_1' + \nu_1''$ molecules, because also unassociated molecules inclosed by the infinite group belong to it.

We must, therefore, add at the same time unassociated molecules to the system in such a way that the total number of molecules in the high temperature phase, n_2, remains constant.

We have, of course:

$$P = n_1 p_1 + n_2 p_2$$

The „equilibrium" between the phases is determined by:

$$p_1 = p_2 \tag{9}$$

If we assume p_1 and p_2 to be functions of $c_1 = n_1/(n_1 + n_2)$, the change of c_1 with temperature is given by differentiating (9):

$$\frac{dc_1}{dT} = -\frac{\dfrac{\partial p_1}{\partial T} - \dfrac{\partial p_2}{\partial T}}{\dfrac{\partial p_1}{\partial c_1} - \dfrac{\partial p_2}{\partial c_1}}, \quad \text{or:}$$

$$\frac{dc_1}{dT} = -\frac{1}{T^2}\,\frac{u_1 - u_2}{\dfrac{\partial p_1}{\partial c_1} - \dfrac{\partial p_2}{\partial c_1}} \tag{10}$$

The numerator of the fraction may be assumed to be negative ($u_1 < u_2$); the sign of the denominator is related to the stability of the equilibrium. The denominator can be written:

$$(11) \qquad \frac{\partial p_1}{\partial c_1} - \frac{\partial p_2}{\partial c_1} = \frac{1}{n_1 + n_2} \frac{\partial^2 P}{\partial {c_1}^2}$$

because:

$$\frac{\partial P}{\partial c_1} = (n_1 + n_2)(p_1 - p_2).$$

If the equilibrium is stable, P is a maximum, the denominator is negative, and c_1 decreases with increasing temperature.

Let us first consider the case that the equilibrium is not stable. It must be expected that than either the substance will be in a state for which $c_1 = 1$, or for which $c_1 = 0$.

If T_1 is the temperature where the low temperature phase appears for the first time with decreasing temperature, we have at $T = T_1$:

$$(12a) \qquad p_1\,(c_1 = 0) = p_2\,(c_1 = 0).$$

For $T > T_1$, and $c_1 = 0$, $p_1 < p_2$. Similarly, if at T_2 the high temperature phase appears for the first time with increasing temperature, we have at $T = T_2$:

$$(12b) \qquad p_1\,(c_1 = 1) = p_2\,(c_1 = 1).$$

If the equilibrium between the „phases" is not stable,

$$\frac{\partial p_1}{\partial c_1} > \frac{\partial p_2}{\partial c_2},$$

and at $T = T_2$:

$$p_1\,(c_1 = 0) < p_2\,(c_1 = 0). \qquad \text{(compare (12}b\text{).}$$

This is only the case for temperatures higher than T_1, and thus T_2 will be higher than T_1.

The phase transition will therefore show a hysterisis effect. When cooling down, the low temperature phase will only be formed at $T = T_1$; when warming up the high temperature phase will be formed at $T = T_2$. Between T_1 and T_2 a real equilibrium temperature T_e exists where:

$$p_1\,(c_1 = 1) \;=\; p_2\,(c_1 = 0).$$

but at this temperature the two phases will not change over because the intermediate states where c_1 is between 0 and 1 have a higher thermic potential.

These considerations can be applied to the monomorphic transitions. If in a crystal a transition occurs without formation of a new lattice, both phases must have about the same lattice parameters. This will be true in particular at the temperature where one of the phases begins to exist.

The thermic potentials of both phases are, of course, dependent on the lattice parameters, and in the pure phase these lattice parameters are so adjusted as to make the thermic potential a maximum.

So we have:

$$p_1\,(c_1 = 1) > p_1\,(c_1 = 0), \quad \text{and}$$

$$p_2\,(c_1 = 0) > p_2\,(c_1 = 1).$$

As a consequence both terms of the sum

$$\frac{\partial p_1}{\partial c_1} - \frac{\partial p_2}{\partial c_1}$$

are positive, and any equilibrium between the two phases will be unstable. So the hysteresis effects mentioned above must be expected.

This seems to give a satisfactory explanation of the hysteresis effects observed in the transitions of $Cu\,Au_3$ [1]) and NH_4Cl [2]).

In these transitions two transition temperatures T_1 and T_2 exist; between T_1 and T_2 there is no transition from the high

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[1]) G. Borelius, C. H. Johansson und J. O. Linde. Ann. Physik, **86,** 291, 1928.

[2]) A. Smits und C. H. Mac Gillavry. Z. phys. Chemie, **A 166,** 97, 1933.

temperature phase to the low temperature phase nor a transition in the reverse direction. Especially for NH_4Cl has this been determined with much care.

If we take experiments with powder, instead of with large crystals, the temperatures T_1 and T_2 may be somewhat different for different grains, and this might cause a deviation of the hysteresis from the simple NH_4Cl type.

Although this cause of hysteresis exists for all discontinuous monomorphic transitions, it must be stressed that even in pure substances still other causes may exist giving rise to more complicated hysteresis phenomena. This will probably the case for $Cu\,Au$ [1]) and CH_4. [2])

§ 6. *Long range forces and discontinuities in the specific heat.*

The argument used in the preceding paragraph, which showed that a coëxistence of two phases in a monomorphic transition is unstable, is quite general and there are not many possibilities for interactions between two phases to which a similar argument cannot be applied.

As a first possibility may be mentioned the phase transitions at constant volume. Here the thermic potential of both phases is influenced by the pressure, and the pressure is again determined by the mass-ratio of the phases. The coexistence of the two phases is stable. If the pressure is indicated by π, we have:

$$\frac{\partial p_1}{\partial \pi} = -\frac{v_1}{T} \quad \text{and} \quad \frac{\partial p_2}{\partial T} = -\frac{v_2}{T} \tag{13}$$

and, therefore

$$\frac{\partial (p_1 - p_2)}{\partial \pi} = \frac{v_2 - v_1}{T}.$$

Now an increase of c_1 means a decrease of π if only the specific volume of the first (or low temperature) phase is smaller than the specific volume of the second.

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[1]) C. H. Johansson und J. O. Linde, Ann. Phys. **25**, 1, 1936.

[2]) A. Eucken, E. Bartholomé, Nachr. Ges. Wiss. Göttingen **2**, 51, 1936.

So we have:

$$(15) \qquad \frac{\partial (p_1 - p_2)}{\partial c_1} = \frac{v_2 - v_1}{T} \cdot \frac{\partial \pi}{\partial c_1}$$

and this is negative.

So the denominator in (10) is negative, $\partial^2 P / \partial c_1{}^2$ is also negative, and the equilibrium is stable.

Instead of a discontinuity in the energy we must observe in these cases a discontinuity in the specific heat of the system.

The energy above the transition temperature T_0 is given by U_2 and below T_0 it is equal to:

$$(16) \qquad U = U_1 + (1 - c_1)(U_2 - U_1).$$

The specific heat is obtained by differentiation:

$$(17) \quad c = \frac{\partial U_1}{\partial T} + (1 - c_1) \frac{\partial (U_2 - U_1)}{\partial T} - \frac{1}{T^2} \frac{(U_2 - U_1)^2}{\dfrac{\partial p_1}{\partial c_1} - \dfrac{\partial p_2}{\partial c_1}}$$

The last term is obtained by insertion of the expression for dc_1/dT from (10). According to this formula the specific heat must be discontinuous at the temperature T_0; below T_0 it will be larger than above T_0. It must be assumed that neither $U_1 = U_2$ nor $\partial (p_1 - p_2) / \partial c_1$ is infinite.

In most observed cases the specific heat is very large near the transition point, and decreases rapidly at lower temperatures. If we only observe one discontinuity in the specific heat this must be explained by assuming that the expression $\partial (p_1 - p_2) / \partial c_1$ increases with increasing temperature from negative infinite to a small negative value.

This is actually the case in the transition liquid gas at constant volume. Here the expression

$$\frac{\partial \, (p_1 - p_2)}{\partial c_1}$$

reduces by applying the ideal gas law to the vapour and neglecting the volume of the liquid to:

$$\frac{\partial \log \pi}{\partial c_1}.$$

It is of course possible that two discontinuities exist. If we cool down a liquid in a suitable volume, we may observe a discontinuity at the temperature where the solid phase begins to exist and also at the temperature where the last drop of the liquid is frozen.

A second possibility for a specific interaction between the two phases leading to a stable equilibrium is provided by those transitions in which long range forces play a part. Such transitions are, for instance, the ferromagnetic transitions and the transitions of Seignette salt.

One of the properties of the „low temperature phase" in these transitions is that many dipoles are directed parallel. The combined field of these oriented dipoles will not be restricted to the volume occupied by the low temperature phase, but will also be of importance outside this volume and there it will tend to orient the dipoles in the direction of the field. At those places where the direction of the external field is not the same as that of the dipoles which are already oriented, it will act against the increase of the low temperature phase.

It seems hardly possible to apply here too the formal calculation of the equilibrium between the two phases as given in the previous paragraph. Bloch[1]) could show, however, that the most stable state of a ferromagnetic body is not one single group of parallel magnetic dipoles, but a combination of differently oriented regions. This effect is also a consequence of the magnetic interaction between the dipoles. If we want to have a more detailed picture about what happens at the Curie-point, we may therefore assume that the low temperature phase is formed in different regions in the crystal with differently directed magnetisation.

Between these regions there must be, of course, disordered regions, which in our picture we must call the „high temperature phase". Very near to the Curie temperature these disordered regions will practically contain all molecules of the

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[1]) F. Bloch, Zs. Phys. **47**, 295, 1932.

crystal, but at lower temperatures the ordered regions increase.

This suggests that the transition will not be a sharp transition of the kind first, but a transition of the second kind. The arguments given do no permit a more rigourous proof.

It is of interest to remark that many transitions which were formerly believed to be transitions of the second kind are at present known to be transitions with latent heats. At this time the only transitions for which the experimental evidence indicates a transition of the second order are the ferromagnetic transitions, the transition of Seignette salt, the superconductors and liquid helium. One might therefore be inclined to accept the hypothesis that all jumps in the specific heat are due to some non converging interaction. In the first three cases it is not difficult to convince oneself that an interaction of the „non convergent" type is possible.

For liquid helium this is not obvious, and it is therefore of interest to remark that a wave mechanical treatment of the interaction between hard spheres contains in fact a possibility for a long range interaction. This will be shown presently but only in a very crude way, so that it is not possible to decide the question whether or not this effect has anything to do with the mechanism of the transition point of liquid helium.

If we consider one impenetrable molecule of diameter ϱ inclosed in a sphere of radius $R + \varrho/2$ the Schrödinger eigenfunctions are the well-known expressions:

$$\psi_{n,k} = \frac{1}{\sqrt{r}} I_{k+\frac{1}{2}} (\lambda_n r) \, Y_k (\vartheta, \varphi), \tag{18}$$

where Y_k is a spherical harmonic of degree k, $I_{k+\frac{1}{2}}$ is the Bessel function of degree $k + {}^1/_2$ (k integer) and λ_n is the n'th root of the equation

$$I_{k+\frac{1}{2}} (\lambda_n R) = 0, \tag{19}$$

which expresses the boundary condition that the wave function must be zero at the wall of the vessel.

If we want to study the interaction between two hard spheres we may do this in a provisional way by assuming the second molecule to be fixed in the center of the enclosing sphere.

The boundary conditions for the wavefunction of the „free" molecule now become:

$$\begin{aligned} &(20) & \psi'_{n,k}(\lambda R) &= 0 \quad \text{and} \\ & & \psi'_{n,k}(\lambda \varsigma) &= 0. \end{aligned}$$

The eigenfunctions are now combinations of Bessel functions of degree $k+\frac{1}{2}$ and $-k-\frac{1}{2}$; the first function contains the factor $r^{k+\frac{1}{2}}$ and the second one the factor $r^{-k-\frac{1}{2}}$, so that is infinite at the origin.

We put therefore:

$$(21) \qquad \psi'_{n,k} = \frac{Y_k(\vartheta,\varphi)}{\sqrt{r}} \left[a\, I_{k+\frac{1}{2}}(\lambda_n r) + b\, I_{-k-\frac{1}{2}}(\lambda_n r)\right]$$

and can choose a, b and λ_n is such a way that the boundary conditions (20) satisfied.

This leads to the equation for λ_n:

$$(22) \qquad \frac{I_{k+\frac{1}{2}}(\lambda_n \varsigma)}{I_{-k-\frac{1}{2}}(\lambda_n \varsigma)} = \frac{I_{k+\frac{1}{2}}(\lambda_n R)}{I_{-k-\frac{1}{2}}(\lambda_n R)}$$

We assume that $\varsigma \ll R$. Near the origin the Bessel function $I_k(r)$ can be approximated by $c_k r^k$, so that the left hand side of (22) is approximately equal to $\alpha \lambda_n^{2k+1} \varsigma^{2k+1}$, where α is a constant.

The right hand side may also be approximated if we restrict ourselves to the first power of the change in λ_n. If the solution obtained from (19) is called $(\lambda_n)_0$ we may write:

$$\alpha \lambda_n^{2k+1} \varsigma^{2k+1} = R \Delta \lambda \cdot \frac{\partial}{\partial r} \left(\frac{I_{k+\frac{1}{2}}(r)}{I_{-k-\frac{1}{2}}(r)}\right)_{r=(\lambda_n)_0/R}$$

We shall fix our attention on the change in the energy value in its dependence on R. The energy of the „free" molecule is equal to $h^2 \lambda_n^2 / 8\pi^2 m$, and λ_n is, by (20), inversely proportional to R.

So we obtain, if we put $\lambda_n = s_n / R$:

$$(23) \qquad \alpha \frac{h^2}{4\pi^2 m} \cdot \frac{s^{2k+2}}{R^{2k+3}} \cdot \varsigma^{2k+1} = \Delta U \cdot \frac{\partial}{\partial r} \left(\frac{I_{k+\frac{1}{2}}(r)}{I_{-k-\frac{1}{2}}(r)}\right)_{r=(s_n)_0}$$

The coëfficient of ΔU is written in such a form that it is independent of R. The change in the energy value is therefore proportional to R^{-2k-3}, and is rapidly decreasing with indreasing R for every value of $k \geqslant 1$. For $k = 0$, however, it decreases only as R^{-3} and corresponds therefore to a „non converging repulsion" between the particles.

This result does not allow of a direct application to a „gas" or „liquid" of hard spheres. Nevertheless it suffices to show that the influence of quantum mechanics may lead to unexpected consequences and that it may be responsible for some interaction of a non convergent type not existing in classical mechanics.

§ 7. *The configuration of the associated units.*

Hitherto we have limited ourselves to those cases where the infinite group is formed in closed states. In this paragraph we shall discuss the question whether the picture of association can be applied, and, if so, whether the infinite groups will be formed in open states or closed states.

As a first example we shall apply the association picture to the so-called „Schottky transitions". It is assumed that in these transitions the molecules of a substance have some discrete energy levels such that the interaction between the molecules is independent of the energy level occupied by the molecules.

It is very easy to determine the partition function which describes the specific heat etc. due to this transition. It is known that no discontinuity can be expected.

If we would define in this case an „association" between molecules, this could be done in a formal way by saying that two molecules are associated if they are nearest neighbours (in a crystal) and both in the lowest energy state.

The „infinite group" would than have a very irregular form and it would not be possible to speak about the „surface" of this group or to define a low temperature phase (comp. § 2).

With decreasing temperature the mean size of the group increases and we may expect that at some temperature the dimensions of some groups will become comparable with those of the crystal; at this temperature it is no longer correct to apply the usual formulae for association.

We may now introduce in the system a small coupling between nearest neighbours so that they tend to be in the same energy state. This will, of course, not prevent the formation of the infinite group in „open states". Only if the coupling is sufficiently large, will the associated molecules group themselves together in closed states.

From this example we see that in some cases we must distinguish between the transition energy, which is here the energy necessary for the molecule to pass into an excited state, and the correlation energy, which is the energy gained if two molecules which are in the lowest energy state are placed so that they are nearest neighbours. If this correlation energy is not sufficiently large it is useless to apply the picture of association.

A similar situation is met with in the so-called „rotation-transitions". It is generally accepted, though not always with proof, that many transitions in salts with complex ions are due to a transition of these ions from a vibratory motion to a rotary one. It is assumed that a transition of some ions from, say, vibration to rotation induces the other ions to do the same, because it reduces the energy difference between the „vibration" and „rotation" levels. Very little is as yet known about the real mechanism of this interaction. We may consider two limiting cases:

Firstly, we may think that the field of force in which the ions move is practically independent of the state of motion of these ions themselves. In this case the transition is exactly analogous to the Schottky transitions.

Secondly we could imagine that the field of force changes so that at low temperatures the ions would not rotate unless their kinetic energy should be very high compared with kT and at higher temperatures they would rotate unless their energy were extremely small.

An argument in favour of the second assumption is provided by Bijvoet and Ketelaar's X-ray investigation ¹) of $NaNO_3$.

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¹) J. M. Bijvoet and J. A. A. Ketelaar, J. am. chem. Soc. **54**, 625, 1932.

They could show that at low temperatures the distance between a *Na* ion and a NO_3 ion is too small to allow a rotation of the nitrate ion (which is considered as a rigid body) and at high temperatures the distance is sufficiently large for rotation.

Even if the second assumption is made, and the transition to a rotatory motion of some ions makes it easier for other ions to do the same, it is not yet necessary that the rotating ions (and similary the vibrating ones) combine into groups; it is equally possible that they tend to the largest possible distance apart. Every rotating ion in a „vibrating" phase is equivalent to a local expansion of the lattice. The combined effect of these disturbances is certainly to increase the mean lattice distance and to facilitate rotation for other ions. But nevertheless it may happen, that the local disturbances of the lattice are such that the probality that a rotating ion is found in the immediate neighbourhood of another rotating ion is smaller than on the average.

The real mechanism of the interaction between the complex ions will often be of another kind. This is most clearly demonstrated by the fact that some salts even decrease their volume when passing from a vibratory to a rotatory state. The aim of the preceding remarks was, however, to show that even details of the transition mechanism may be very important, not only for the question whether or not it is possible to treat the transition as an association process, but also for the question whether or not the transition will be discontinuous.

A very remarkable experimental case is that of the transitions of NH_4Cl ¹) and of ND_4Cl ²) of which transitions the first shows a discontinuity in the energy (with hysteresis) and the second a continuous one (without hysteresis).

To understand qualitatively which factors are important in determining whether an infinite group is formed in an open state or a closed one the transition gas-liquid may be taken as an example.

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¹) A. Smits und C. H. Mc Gillavry, Z. phys. Chem. A **166**, 97, 1933.

²) A. Smits and G. J. Muller, Nature **139**, 804, 1937.

Let us call two molecules associated if they are less than a certain distance apart (this distance must be chosen in relation to the dimensions of the molecular field). In a dilute gas the only reason why associated groups are formed is that their energy is low; their a-priori probability is in fact very small. The larger associated groups will therefore be formed in closed states. In a compressed gas, however, there would be a larger a-priori probability for the formation of associated groups even if these groups should not have a small energy, because the molecules are on the average much nearer to each other. Therefore the structure of the infinite group is at higher pressure not only determined by the condition that its energy is small, but the configuration will also be such that it has a larger a-priori probability.

With increasing density we may therefore expect that the configuration of the infinite group approaches more and more and more a random arrangement. Therefore more and more inclusions of unassociated molecules will occur, and finally the most frequent arrangement will be in open states.

Parallel with this change the energy of the low temperature phase increases and it is therefore possible that the low temperature phase shows an anomalous specific heat. If we cool down a gas at higher and higher pressures a density will be reached at which the infinite groups are no longer formed in closed states, so that no low temperature phase can be defined as in § 2. The corresponding pressure might be identified with the critical pressure. It is not yet possible to prove this supposition.

§ 8. *The order-disorder transitions.*

Similar considerations give also a provisional answer to the question why in so many transitions in which a latent heat is observed this latent heat is so small compared with the total energy change during the transition. In most cases the specific heat anomaly is very important, specially on the low temperature side of the transition. As an example we shall take the order-disorder transitions discussed in I. At the same time we shall add some remarks to this discussion in order to facilitate a comparison between these theories and the present treatment.

The association may be defined as indicated in II, § 2. For every unit cell 16 different arrangements exist (each of the 4 lattice points can be occupied in two different ways). If one unit cell is ordered (i.e. if it contains two *Au* atoms and two *Cu* atoms) there is a probability of $[1 - (15/16)^6]$, or 0,33, that it is associated with one of the six neighbouring cells. And if already more than 1/16th part of the cells are ordered, this probability is correspondingly larger. Therefore even at elevated temperatures there will exist ordered groups of considerable size, but in „open" states. At lower temperatures these groups will combine by additional association of some cells and form either open groups, or closed groups with many inclusions of disordered regions. So there is a perfect analogy with the gas in the critical region and similar effects in the specific heat may be expected.

The arguments given do not provide a basis for a qualitative calculation of these anomalies. For such calculations the theories discussed in I are useful.

The theory of Bragg and Williams considers mainly those states of the alloy where the „right" and „wrong" atoms are present in unequal amounts. For, if the alloy is considered as an agglomerate of groups, the ratio between the numbers of „right" and „wrong" atoms must very nearly equal unity. Only if an „infinite" group is present, or a low temperature phase is formed, may the numbers of the two kinds of atoms be different from each other.

The „degree of order" defined by B. and W. is also closely related to the number of particles in the infinite group. This degree of order is the difference between the numbers of „right" and „wrong" atoms, divided by the total number of atoms. If we assume that the „finite" associated groups contain as many „right" as „wrong" atoms, these groups give no contribution to the degree of order. This degree of order is then equal to the number of atoms contained in the infinite group (supposed to contain „right" atoms) divided by the total number of atoms. This is not entirely correct, because the groups inclosed by the infinite group will consist mainly of „wrong" atoms. So the degree of order will become somewhat smaller.

It is also possible to give the analogue of Bethe's short range order. A very good measure for this order is the total number of groups, divided by the number of groups which would exist in a perfectly random arrangement.

We have shown that it is very well conceivable that the transition from a state in which only finite groups exist to a state in which infinite groups are present, passes without any discontinuity in energy or specific heat. It seems therefore that this possibility cannot be excluded at present also for the order-disorder transitions. Peierls [1]) and Landau [2]) seem to regard it as obvious that some discontinuity must occur. This can only be proved, however, if it is assumed that the free energy as a function of the degree of long range order satisfies some conditions, such as that it can be developed as a power series in this degree of order, etc. These assumptions are not necessary, and therefore the proof of the existence of a discontinuity has not yet been given.

Although the present treatment may be of use for the purpose of localising the uncertainties left in the existing theories, it cannot replace them. So far it has not been possible to base on it some quantitative calculation of the specific heat anomalies or of the latent heat.

§ 9. *Phase transitions in linear and two dimensional systems.*

An interesting application of the calculations in § 1 and § 3 is possible in the problem of the phase transitions in linear and two dimensional systems.

For a linear system it can be shown that no discontinuity in the energy or specific heat is possible. This has been proved

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[1]) R. Peierls, Helv. phys. Acta, suppl. II, 81, 1934.

[2]) L. Landau, Phys. Z. Sow. Union, 1937.

already several times [1] but for completeness' sake it will be repeated here. Strictly speaking we must limit ourselves to the statement that the existence of a discontinuity can never be proved with the help of an association theory.

The proof is as follows: For the existence of a discontinuity it was necessary that a temperature should exist where the expression (3) was equal to unity:

$$S = \Sigma\, e\left(i\,\frac{\varphi^{i} - \varphi_{\infty}}{R}\right) = 1.$$

From the properties of the expressions $i\,(\varphi_i - \varphi_\infty)$ it must now be shown that for a linear system this equation is not satisfied at any temperature. There are two causes for a difference between the thermic potential of a group i molecules and that of i molecules as a part of a very large group. In the first place the surface effect; because the „surface" of a group consists of the two end molecules, independent of the size of the group, this will give a term in $i\,(\varphi_i - \varphi_\infty)$ which approaches a constant value for high values of i. Secondly the group of i molecules has a degree of freedom which the i molecules associated with a very large group have not got, viz. the coordinate of the center of gravity of the group. This adds also a constant term in the $i\,(\varphi_i - \varphi_\infty)$.

So the general term of the series S does not tend to zero, but to a constant value; S diverges and its sum can therefore never be unity. If we wanted to prove in general that no discontinuity is possible in a linear system, we should still have to prove that all φ_i are continuous functions of temperature. This proof will however not be attempted here.

In a two dimensional system the absolute value of expressions $i\,(\varphi_i - \varphi_\infty)$ may increase with $i^{1/2}$, if the groups are formed in closed states. Therefore phase transitions are possible and this is what we also observe in the study of surface films.

The same is true if in a three dimensional system the mole-

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[1] K. F. Herzfeld and G. M. Goeppert Mayer, J. chem. Phys. **2**, 38, 1934.
G. Heller and H. A. Kramers, Proc. roy. Acad. Amsterdam, **37**, 378, 1934.
R. Peierls, Helv. phys. Acta, suppl. 2, 82, 1934.

cules form plane arrangements. We may even call this ordered configuration of the molecules „low temperature phases". If a transition temperature should exist, there would be a strong interaction between the high temperature phase and the low temperature phase. We must therefore expect either a discontinuity in the specific heat or hysteresis effects, but never a normal phase transition.

It is an interesting problem whether such cases are realized in some crystalline liquids. Unfortunately not many accurate determinations of the specific heats of these liquids exist.

§ 10. *Recapitulation.*

Finally we shall briefly repeat the most essential points from the preceding discussion.

A substance in which a transition takes place may sometimes be described as a mixture of groups of associated units. The concentration of the groups containing i associated units is given by

$$c_i = e\,(i\,\frac{\varphi_i - \mu}{R}),$$

where the φ_i are functions of temperature and concentrations, and are always finite.

This description of the substance is only possible at temperatures above the transition temperature T_0, which is determined by:

$$\Sigma\, e\,(i\,\frac{\varphi_i - \varphi_\infty}{R}) = 1.$$

A transition temperature is not possible in a linear system, but in a two dimensional and in a three dimensional one it may exist.

Its existence can only be proved if the „infinite groups" are formed in „closed states", i.e. in states where the number of surface molecules increases relatively more slowly than the total number of molecules in the group. If this is the case, the expressions $i(\varphi_i - \varphi_\infty)$ depend for large i on surface effects.

If the groups are formed in closed states, it is also possible to define a „low temperature phase" below the temperature T_0.

At the temperature T_0 there will be a discontinuity whose character depends on the interaction between the high temperature phase and the low temperature one. The possibilities are:

a. a normal phase transition, if the interaction between the two phases can be described as a surface effect;
b. a phase transition with hysteresis, if the equilibrium between the phases is not stable. This is proved to be the case in most monomorphic transitions.
c. a jump in the specific heat if a stable equilibrium between the phases is possible. It is suggested that a necessary condition for this equilibrium should be the existence of a „long range" interaction between the molecules.

It is useful to add here some points which could not be solved with the method proposed.

It is never possible to exclude the existence of a discontinuity, because the φ_i may prove to be discontinuous functions of temperature. The reason why this can never be excluded is that the definition of the associated units is in general rather arbitrary.

The method also fails to give a general method which allows a reduction of the partition function in such a way that discontinuities may be detected more easily.

Finally some suggestions may be made to which the preceding discussion gives rise.

It does not seem to be impossible to treat the low temperature phase and the high temperature phase symmetrically. We may, for instance, describe the liquid-gas transition as a gradual formation of „gas bubbles" in the liquid, just as we have described the reverse transition as a gradual formation of liquid drops in the gas phase. Similarly these gas bubbles may combine at a transition temperature to macroscopically large vapour bubbles, and cause a phase transition.

A final point is, that the most important question in the problem of phase transitions is how to determine the properties of the infinite group. It seems therefore probable that in a consistent statistical theory a division of the configuration space into a number of „phase cells" will be made. Every cell will be different from another cell in that a relation which exists in the configurations of one cell between practically all the particles at the same time, exists in the other cells only between a limited number of particles simultaneously. It seems at present impossible to indicate such a relation without ambiguity.

SAMENVATTING.

Men kan de veranderingen die bij een omzettingspunt in een stof worden waargenomen dikwijls beschrijven als een proces dat in principe continu gedacht kan worden, ook in die gevallen waarin in werkelijkheid een discontinuïteit optreedt.

Bij de overgang damp-vloeistof kan dit het meest aanschouwelijk gebeuren door deze overgang op te vatten als een associatie. Door deze beschrijvingswijze ook op andere gevallen toe te passen, komt men tot eenige nieuwe gezichtspunten.

Onder invloed der wederzijdsche aantrekking worden de moleculen in een damp geassocieerd tot groepen van twee, drie of meer moleculen. Deze associatie zal bij lagere temperatuur steeds voortschrijden, totdat de vloeistoftoestand is bereikt, waarin bijna alle moleculen tot een groote geassocieerde groep zijn vereenigd. Men moet hierbij b.v. twee bolvormige moleculen als geassocieerd beschouwen als hun middelpunten minder dan een gegeven afstand van elkaar zijn verwijderd.

Voor een meer exacte beschouwing van dit proces kan men gebruik maken van de theorie der chemische evenwichten. De toestand van de damp wordt aangegeven door de aantallen (n_i) of de concentraties (c_i) van de groepen van i geassocieerde moleculen; de thermische potentiaal is te schrijven als een som over deze groepen:

$$P = \sum_i i\, n_i\, \mu_i,$$

waarin $i\mu_i$ de thermische potentiaal van een i-voudige groep is. Schrijft men de Gibbsche mengentropie expliciet op, dan heeft men

$$i\mu = i\varphi_i - R \log c_i$$

waarna men uit de evenwichtsvoorwaarde (P maximaal) vindt:

$$c_i = e\,(i\,\frac{\mu - \varphi_i}{RT})$$

Hierin is μ de thermische potentiaal van de stof per mol. De overige thermodynamische grootheden kunnen hieruit worden afgeleid en als sommen over i opgeschreven worden.

Het proces van het vloeibaar worden verloopt nu volgens de experimenten met een discontinuïteit, en het is de vraag of in de boven gegeven beschrijving deze discontinuïteit ook te voorschijn komt. Dit blijkt inderdaad het geval te zijn.

Hierbij is de grootheid φ_∞, de limiet van φ_i voor groote i, van veel belang; deze grootheid bepaalt b.v. het voorkomen van zeer groote dichtheidsfluctuaties in de damp. Het blijkt n.l. dat er geen discontinuïteit mogelijk is, tenzij er een temperatuur bestaat, waarbij de thermische potentaal van de damp gelijk is aan deze „thermische potentiaal van de oneindig groote groep". De voorwaarde daarvoor luidt dat een temperatuur moet bestaan, waarbij:

$$\sum_i e\,(i\,\frac{\varphi_i - \varphi_\infty}{RT}) = 1 \tag{1}$$

(Deze vergelijking volgt door in de identiteit $\Sigma c_i = 1$ te sulstitueeren $\mu = \varphi_\infty$). Om deze vergelijking te bespreken moet er iets bekend zijn omtrent de verschillen $\varphi_i - \varphi_\infty$. Dit is in 't algemeen slechts mogelijk, indien de geassocieerde groepen als „kleine druppels" zijn te beschouwen, d.w.z. als zij bij toenemend molecuulgetal een relatief kleiner aantal oppervakte moleculen hebben. Men kan dan inzien dat de veranderingen in de energie, entropie, enz. die plaatsvinden bij combinatie van grootere groepen alleen bepaald worden door oppervlakte effecten, en dat dus in 't bijzonder de verschillen $i\,(\varphi_i - \varphi_\infty)$ evenredig zijn met het oppervlak van de groep van i moleculen, dus met $i^{2/3}$. (Bij zeer groote groepen vallen de oppervlakte effecten, per molecuul berekend, weg; het verschil $i\,(\varphi_i - \varphi_\infty)$ bevat dus juist de bijdrage van het oppervlak van de groep van i moleculen).

Indien de „oneindig groote groep" werkelijk deze eenvoudige vorm heeft, blijkt, dat men in een toestand van de stof waarin zoo een groep aanwezig is, ook een „lage temperatuurphase" kan definieeren. Deze „phase" bevat alle moleculen, die door het uitwendig oppervlak van de groep worden omsloten. Zou het aantal oppervlakte moleculen niet relatief klein blijven, dan zou weliswaar een „oneindig groote groep" kunnen ontstaan, doch het zou niet mogelijk zijn, een „lage temperatuurphase" als macroscopisch begrip te definieeren.

Bij de temperatuur T_0, waarbij aan (1) is voldaan, zal nu de damp, bestaande uit min of meer geassocieerde moleculen, in evenwicht zijn met de „lage temperatuur phase", en er zal een normale phase overgang plaats vinden.

De boven gegeven beschrijving kan nu formeel worden uitgebreid op andere gevalien, waarin het mogelijk is bij de overgang het begrip „associatie" te definieeren. Dit is b.v. mogelijk bij de ordeningsovergangen in legeeringen.

Bij deze uitbreiding zijn eenige complicaties mogelijk. Men overziet de mogelijkheid daarvan, indien men zich een toestand van de stof voorstelt, waarin de „lage temperatuur phase" (l.t. phase) en hooge temperatuur phase (h.t. phase) gelijktijdig aanwezig zijn. Terwijl bij de overgang damp-vloeistof onder constante druk het evenwicht tusschen de afzonderlijke phasen niet wordt beinvloed door de massaverhouding van de twee phasen, behoeft dit niet altijd zoo te zijn.

Men kan hier twee mogelijkheden onderscheiden. Ten eerste kan het evenwicht van de phasen labiel zijn, zoodat bij elke temperatuur hetzij de h.t. phase, hetzij de l.t. phase stabiel is en er geen coëxistentie der phasen kan optreden. Ten tweede kan een stabiel evenwicht mogelijk zijn. Men moet dan een sprong in de soortelijke warmte verwachten bij de temperatuur, waarbij de l.t. phase het eerst optreedt, terwijl bij dalende temperatuur deze phase aangroeit.

Het eerste geval doet zich voor bij de z.g. monomorphe overgangen in kristallen. Hierbij wordt het kristalrooster bij de overgang niet verbroken. De l.t.-phase moet dan ontstaan in een rooster, waarvan de roosterafstanden die zijn van de h.t.-

phase. De zuivere l.t.-phase zal echter andere roosterafstanden hebben, en daar deze afstanden overeenkomen met de meest stabiele toestand van deze phase, zal de l.t.-phase, die coëxisteert met de h.t.-phase, steeds minder stabiel zijn dan de zuivere l.t.-phase. Hetzelfde geldt voor de h.t.-phase.

Zoo zal dus, bij de temperatuur T_c waar de zuivere phasen dezelfde thermische potentiaal hebben, geen overgang plaats vinden. Daarvoor zou immers noodig zijn dat een tusschentoestand werd overschreden, waarin zeer veel moleculen tot een l.t.-phase zouden zijn aangesloten, doch de roosterafstanden die van de h.t.-phase zouden zijn. Deze toestand zal minder stabiel zijn dan de uitgangstoestand en dus niet spontaan optreden. De overgang zal eerst bij een lagere temperatuur optreden. Eveneens zal bij verhooging der temperatuur het punt T_c zonder overgang gepasseerd worden en de h.t.-phase bij hooger temperatuur optreden.

De hysteresis-verschijnselen die men op deze wijze kan verwachten, komen overeen met wat men bij monomorphe overgangen waarneemt, in het bijzonder bij NH_4Cl en Cu_3Au. Sommige van dergelijke overgangen vertoonen meer gecompliceerde hysteresis verschijnselen die vermoedelijk slechts door een nadere beschouwing van het mechanisme te verklaren zijn.

De mogelijkheid van een stabiel evenwicht tusschen twee phasen is gegeven in een systeem dat onder constante druk afkoelt. Minder triviaal is het geval dat er krachten zijn tusschen de moleculen die slechts langzaam op grootere afstand afnemen, b.v. dipoolkrachten. Als de werking van deze krachten door een geschikte plaatsing der moleculen versterkt wordt, kan het krachtveld van een geordend gebied tot ver buiten dat gebied merkbaar zijn. Op deze wijze is ook evt. een wisselwerking tusschen twee phasen mogelijk.

Bij de vorming van een ferromagnetische phase geven de gelijkgerichte elementairmagneetjes aanleiding tot een magnetisch veld, dat op sommige plaatsen de overige magneetjes parallel richt aan de reeds bestaande ordening, op andere plaatsen daartegen in. Dit kan aanleiding geven tot het naast elkaar bestaan van verschillend georiënteerde gebieden, gescheiden door ongeordende gebieden. Deze laatsten (de h.t.

phase) zullen beneden het Curiepunt afnemen ten koste van de eersten (de l.t. phase). Er is dus aanleiding tot de hypothese, dat het ontstaan van een Curiepunt samenhangt met het bestaan van directe langeafstandswerking tusschen de moleculen.

De bovengenoemde noodzakelijke voorwaarde (1) voor het bestaan van een „overgangstemperatuur" geeft aanleiding tot een nieuw bewijs dat in een lineair systeem geen phaseovergangen mogelijk zijn. Dit bewijs berust op het feit, dat de „oppervlaktewerking" uitgedrukt in $i(\varphi_i - \varphi_\infty)$ voor een lineaire groep steeds de werking is van twee moleculen en dus voor grootere i constant wordt. De reeks divergeert dan en er is geen temperatuur, waarbij aan (1) voldaan is.

Men kan inzien dat voor een tweedimensionaal systeem een phaseovergang wel mogelijk is, omdat daar het aantal randatomen met i toeneemt, en (1) convergeeren kan.

Op grond van de in het begin van deze samenvatting genoemde beschouwingen kan men ook een analogie vinden tusschen het verschijnsel van de kleine verdampingswarmte van een gas in de nabijheid van de kritische temperatuur en de kleine latente warmte waargenomen bij veel monomorphe overgangen. Deze overwegingen voeren echter niet tot concrete resultaten en leenen zich niet goed voor een verkorte weergave.

STELLINGEN.

I.

De gangbare theorieën van het electrisch geleidingsvermogen geven geen verklaring van het feit dat de electronen in een metaal beweeglijk zijn.

II.

Het is van belang om, in verband met de resultaten van de metingen omtrent de thermo-electrische kracht van supergeleiders in een magneetveld boven de sprongtemperatuur, de susceptibiliteit van supergeleiders in dit temperatuurgebied bij dezelfde veldsterkten te bepalen.

W. H. Keesom and C. J. Matthijs, Physica **5**, 1, 1938.

III.

De verschillen in de R/R_0 curven welke voor weerstandsthermometers in het temperatuurgebied van 14°—80° K. zijn gevonden, kan men qualitatief op bevredigende wijze verklaren door aan te nemen dat niet slechts de restweerstand, maar ook de Debye θ voor de verschillende draden verschillend is.

IV.

De door Bohr gegeven theorie omtrent de absorptie van γ-quanta door kernen vertoont veel analogieën met de absorptie van licht door ionenkristallen.

N. Bohr, Nature **141**, 326, 1938.

V.

De onzekerheid die bestaat bij de quantitatieve berekening van de levensduur van α-stralers is veel grooter dan Bethe aangeeft.

H. A. Bethe, Rev. Modern Phys. **9**, 164, 1937.

VI.

De stelling dat de totale verandering van de raaklijnrichting bij het eenmaal doorloopen van een gesloten continue kromme zonder singuliere punten gelijk is aan 2π, kan worden uitgebreid tot eenige gevallen waarin de raaklijnrichting discontinu is, mits men de „richting van de raaklijn" in een punt van de kromme op geschikte wijze defineert.

H. Hopf, Compositio Math. **2**, 50, 1935.

VII.

De werkloosheid in Nederland kan op technisch eenvoudige wijze bestreden worden door het restitueeren van een matig gedeelte van de loonen aan de ondernemers.

A. Bijl, Tijdschr. Nederl. Werkloosheidsraad, Nov. 1933;
de Economist, Maart 1938.
N. Kaldor, J. of Political Economy, Dec. 1936.

VIII.

De gebruikelijke definities van het begrip „hoeveelheid circuleerend geld" zijn niet exact. Men moet betwijfelen of dit begrip in de quantitatieve economie bruikbaar zal zijn.

De [illegible]

[illegible]

VI.

De stelling dat [illegible]

[illegible]

VII.

[illegible] in Nederland [illegible]

[illegible]

[illegible]

VIII.

De [illegible] van het [illegible]