ACTA CHEMICA SCANDINAVICA 2 (1948) 53—62

On the Thermodynamics of 'λ-Transitions'

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The discovery by Keesom and his collaborators of what they named the λ-point of liquid helium, caused Ehrenfest[1] to put forward a thermodynamic theory of the transitions of the second order, characterized by discontinuity in the second derivatives of Gibbs' free energy, *viz.* in specific heat and coefficient of thermal expansion, but continuity in the first derivatives, S and V, the latter in contradistinction to the ordinary phase transitions, which are then called first order transitions.

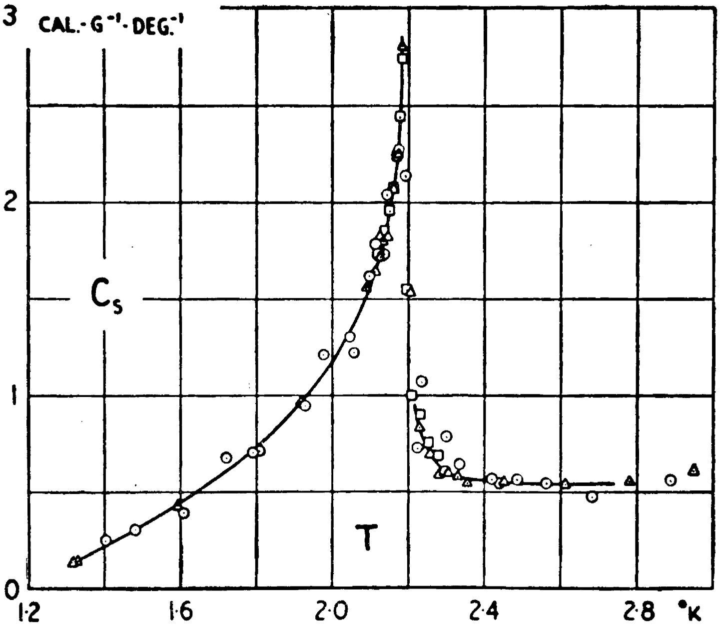

Fig. 1. The original measurements by Keesom and Keesom of the heat capacity of liquid He between 1.2° and 3° K. The heat capacity under the pressure of the saturated vapours, C_s, *is given in cal/g · deg.*

It is obvious that the second order transitions will show no phenomenon of two co-existing phases, and it was also pointed out at an early stage [2] that it was not permissible to regard them as occurring between two different phases each of which had fully continuous properties because an elementary calculation shows that the same phase would then be the more stable on both sides of the transition point. It is necessary, therefore, that this phase simply ceases to be physically defined, *i. e.* ceases to have even a theoretical possibility of existence when the transition point has been passed.

In his latest exposition of the theory,[3] Keesom seems to underestimate the rigour of this condition and tries to draw analogies to the possibility of experimental realization of unstable phases near ordinary transition points. The metastability of superheated or supercooled liquids, however, is easily explained by the fact that the liquid, though instable towards a macro-phase in a gaseous or solid state, respectively, is stable towards small germs of the same. Such 'germs' are therefore formed and dissolved continuously until one of them happens to grow beyond the critical size and becomes capable of forming a true germ for starting the growth of the stable macro-phase. The melting process, presumably, always finds imperfections on surfaces and interfaces where it can start without any such obstacle, and the only chance of establishing a superheated crystal is probably in working with perfect single-crystals, and no such work has hitherto been reported. But what is relevant in this connection is only that irrespective of its impracticability, the superheated crystal has perfectly well defined and continuous thermodynamic functions. The whole discussion is therefore entirely irrelevant to the problem of the second order transition.

Bridgman [4] has proposed a model of the thermodynamic discontinuity. He considers an order-disorder transition, and if the conventional conception of the same is used, his argument should read: At the transition point the disorder is complete, and the degree of order parameter equals zero. The disordering process cannot proceed further than to complete disorder, and the degree of order cannot be less than zero. Hence the prolongation of the free energy curve of the phase of progressive disorder does not correspond to any physically possible states. This pseudo-phase together with an always completely disordered phase, forms the two 'phases' between which a second order transition in Ehrenfest's sense can take place, although the free energy curve of the former may be the lower on both sides of the transition point.

Against this two arguments shall be given:

1. In many of the known order-disorder transitions there exists all through the transition interval a carrying lattice which makes it possible to distinguish unmistakably between 'right' and 'wrong' atoms. Negative degree of order then has the well defined physical meaning that more atoms are in wrong than in right places. Even in cases where a carrying lattice is not present, it is only a matter of convention to assign to a negative degree of order the same meaning as that of the numerically equal positive value.

2. The 'λ-curves' have tails. Above the transition point, the heat capacities in most of the investigated cases still have extraordinary high values, which are falling off with temperature. If we do not want to complicate our conceptions by assuming this to be some separate phenomenon, we must assume that the process, be it a disordering process or whatever else that goes on in the transition interval below the λ-point, does continue

also above the latter, though at a much smaller rate. Hence the internal parameter, be it the degree of local order or something else, cannot have reached its ultimate value at the λ-point proper.

It can be stated, therefore, that so far no satisfactory model of the pseudophases of Ehrenfest's theory has been given. But quite apart from that, it is important to bear in mind that the background for an introduction of pseudophases is in fact a dislike of discontinuities, which causes a search for an explanation of the λ-discontinuities by analogy to the theory of ordinary phase transitions in some transition between 'phases' which themselves have continuous properties. As this is impossible because, as we have seen, at least one of these pseudo-phases must possess some discontinuous properties, the whole introduction of such pseudophases, whether explicit or implicit, seems to have lost its point.

The same is true, of course, if, as is by far the most probable thing, the λ-curves of heat capacity *etc.* are not discontinuous in a strictly mathematical sense but only have an extremely steep peak. Then there is no discontinuity to explain away.

In the following treatment, therefore, we will approach the problem in a rather different way by considering the analogy to systems of two components and one phase, instead of to those of one component and two phases.

Discoveries in recent years have shown that very many pure substances are in fact equilibrium mixtures of isomeric or polymeric modifications[5]. It is possible to regard such substances as mixtures of pseudo-components and to treat them thermodynamically as such,* regardless of whether there is or is not any possibility of preventing the immediate attainment of equilibrium, and thus of experimental demonstration of the difference between the components. This in spite of the fact that in a phase-rule sense the systems are of one component only.

The partition function[6] of a mixture of the isomeric, chemically different compounds A, B, C .... in equilibrium with one another, is the sum of the partition functions of the components:

$$f = f_A + f_B + f_C + \dots$$

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* It is a matter of course that analogies to the theory of mixtures will be elucidating only if drawn to *correct* interpretations of the entities. A recent paper by Tisza (*Phys. Rev.* **72** (1947) 838) calls forth the following remark: The osmotic pressure of a solution is the pressure under which its solvent component would be in equilibrium with the pure solvent, and it has no simple kinetic interpretation. Unfortunately — from a pedagogical point of view — is it for ideal solutions numerically identical with the pressure which the solute molecules *would have exerted if* they had occupied the same volume in the ideal gas state, but they do not by any means actually exert it, neither on a wall nor on a semi-permeable membrane (added in proof).

and the partition function of a component is defined:

$$f_A = \sum_r \omega_r \cdot e^{-\varepsilon_r/kT}$$

molecules of the species A being able to exist in the degenerate quantum states r, each of the energy ε_r and with the weight factor ω_r.

Now, if for a compound A, in the pure state or in a mixture, we can divide the possible states into groups r', r'', r''' ... by some physical criteria, we can also split up the partition function accordingly:

$$f_A = f_A' + f_A'' + f_A''' + \ldots = \sum_{r'} + \sum_{r''} + \sum_{r'''} + \ldots = \sum_r$$

expressing it as the sum of the partition functions of the subspecies A', A'', A''' ... in exactly the same way as the partition function of all the interconvertible isomers is the sum of those of each of the components. As all the thermodynamic functions can be derived from the partition functions, we thus arrive at the conclusion that it is permissible to regard a chemically pure substance as a mixture of several components in equilibrium and to treat it as such according to the usual thermodynamic theory of mixtures, provided that the molecules of each of the pseudocomponents are unambiguously distinguishable from those of the other by some physical criterion.

In some way this result is quite obvious as the statistical and thermodynamic treatment cannot depend on whether the physical difference between two sorts of molecules is of such a kind that it is macroscopically recognizable, *e. g.* by different optical rotatory power, or whether it is only a difference in quantum state.

What makes it somewhat obscure at first sight, however, is the well known »Gibbs' paradox». But the pertinent offence against the laws of thermodynamics is committed only if the difference between molecules belonging to different components is not unambiguously defined because then the enumeration of states goes wrong.

On this basis it is now remarkably easy to describe the λ-transition and several related phenomena in such a way that analogies and contrasts are very clearly visualized.

Consider some compound or element which can have its atoms arranged in say two different ways. We may think of para-orto hydrogen, monocline-rhombic sulphur, monomer and trimer sulphurdioxide, solid nitrogen with rotating and non-rotating molecules, alloys with ordered unit cells and cells with some of the atoms inversed, or whatever we like, if only the difference can be unambiguously defined.

In principle we shall be able to put down a partition function for each of the two different components in pure state and to draw curves of their free energies as functions *e. g.* of temperature. The interesting part of these curves will be where the distance between them is near to or smaller than RT. If the two components are unable to mix in that interval, we observe the familiar phenomenon of a transition point where the free energy curves intersect, and

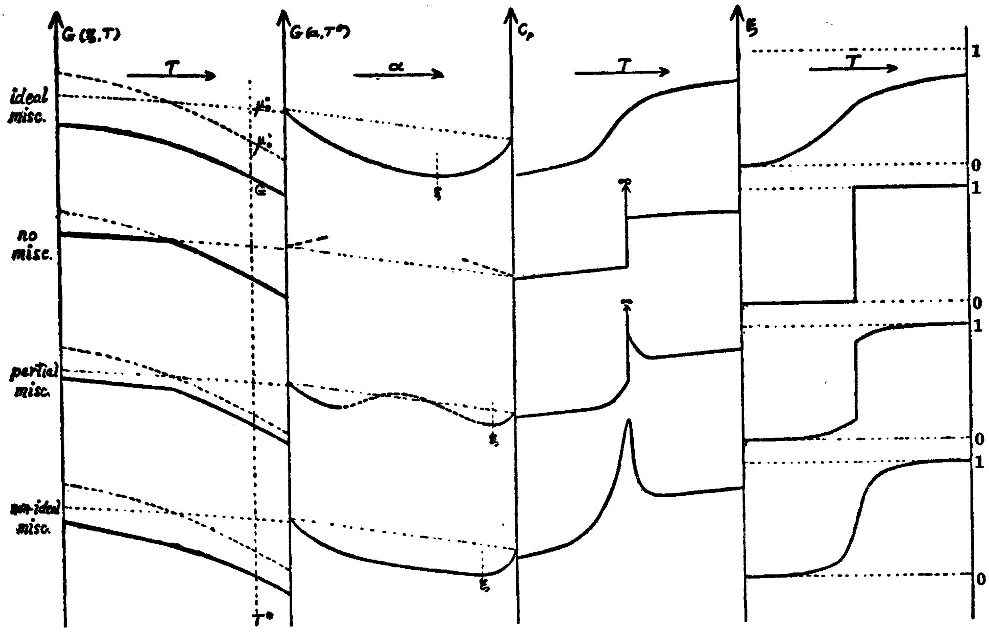

Fig. 2 shows the rough shape of the curves in four cases with different kinds of miscibility of two pseudo-components: 1) Free energy as function of temperature and compared with the free energies of the 'pure components'. 2) For a chosen temperature T^*: the free energy with varying mole fraction a. 3) C_p versus T. 4) The equilibrium mole fraction, ξ, versus T.

where two phases, each consisting of a pure component, are in equilibrium. All thermodynamic functions except G change discontinuously here, while in all other points they vary quite smoothly.

If the two components are partially miscible, we shall get the same kind of transition point, but in its neighbourhood we shall observe an abnormally great heat capacity and perhaps other signs of a pre-melting like behaviour. The greater the mutual solubilities are, the more pronounced is the effect, and the less is the relative magnitude of the heat of transition proper. The miscibility may of course be one-sided, so that only one of the components is detectably soluble in the other.

If, on the other hand, the two components form ideal or nearly ideal mixtures, the equilibrium state will contain a smoothly increasing fraction of the high energy component, and the specific heat curve will show the sort of rise that is characteristic of intervals where molecules take up energy corresponding to a hitherto unexcited degree of freedom.

But if, eventually, the components are completely miscible, though with great deviations from ideality, then we can get the 'λ-transitions'. The activity coefficient of the solute component rises steeply with concentration, so that this component only appears in any appreciable fraction quite near to the temperature at which the G-curves intersect. Within a narrow range of temperature then, the two components will change their rôles as solvent and solute. The heat of transition from the one nearly pure component to the other is smeared out over the same interval and appears as the abnormal specific heat. If the great deviations from ideality do not extend to the whole range of concentrations but only to a certain interval, the above considerations will apply to the transition through this interval.

To investigate what kind of singularity we may expect to find in the thermodynamic functions, we will briefly consider a few of the relevant equations.

One mole of A consists of α moles of A' and $(1-\alpha)$ moles of A''. Gibbs' free energy is:

$$G = \alpha\mu' + (1-\alpha)\mu''$$

and the condition of internal equilibrium is:

$$\left(\frac{\partial G}{\partial \alpha}\right)_{p,T} = \mu' - \mu'' = 0 \qquad \text{or} \qquad \mu' = \mu'' \text{ for } \alpha = \xi$$

$$C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,eq} = T\left\{\left(\frac{\partial S}{\partial T}\right)_{p,\xi} + \left(\frac{\partial S}{\partial \alpha}\right)_{p,T}\left(\frac{\partial \xi}{\partial T}\right)_{p,eq}\right\}$$

and the only term that may be expected to cause singularity is $\delta\xi/\delta T$. To derive an equation for this we write:

$$d\left(\frac{\partial G}{\partial \alpha}\right) = \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial \alpha}\right)dp + \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \alpha}\right)dT + \frac{\partial}{\partial \alpha}\left(\frac{\partial G}{\partial \alpha}\right)d\alpha$$

and obtain:

$$\left(\frac{\partial \xi}{\partial T}\right)_{p,eq} = -\frac{\partial^2 G/\partial\alpha\partial T}{\partial^2 G/\partial\alpha^2} = \frac{(\partial S/\partial\alpha)_{p,T}}{(\partial^2 G/\partial\alpha^2)_{p,T}} = \frac{S'-S''}{(\partial^2 G/\partial\alpha^2)_{p,T}}$$

A singularity, therefore, will occur if $\partial^2 G/\partial\alpha^2$ equals zero, which condition means that the two components form a critical mixture, as is easily verified by a glance at Fig. 3. In this particular problem $\partial G/\partial\alpha$ equals zero as stated

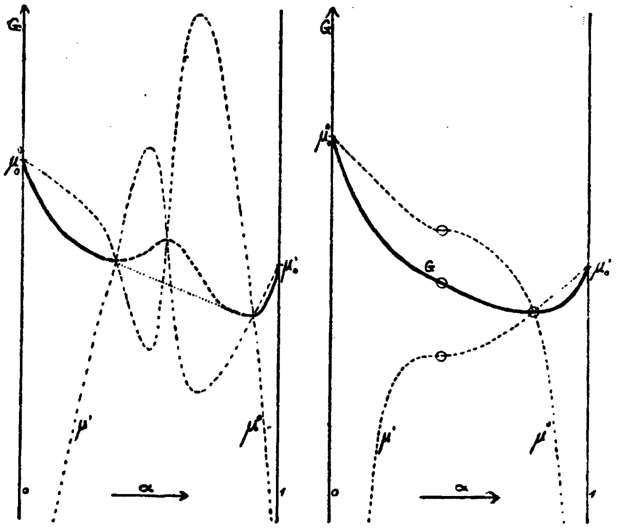

Fig. 3. The molar free energy, G, of a binary mixture and the chemical potentials of the components versus mole fraction, a, in case of 1) partial miscibility and 2) critical miscibility. In our particular case of chemical equilibrium between the 'components' the four circled points will fall in one, in which all the three curves will have horizontal tangents.

above, and for critical mixtures in general $\partial^2 G/\partial\alpha^2 = \partial^3 G/\partial\alpha^3 = 0$ if α is taken to mean the mole fraction of a component in general.

A similar singularity will then occur also in the expansion coefficient:

$$\left(\frac{\partial V}{\partial T}\right)_{p,eq} = \left(\frac{\partial V}{\partial T}\right)_{p,\xi} + \left(\frac{\partial V}{\partial \alpha}\right)_{p,T} \left(\frac{\partial \xi}{\partial T}\right)_{p,eq}$$

and in the compressibility:

$$\left(\frac{\partial V}{\partial p}\right)_{T,eq} = \left(\frac{\partial V}{\partial p}\right)_{T,\xi} + \left(\frac{\partial V}{\partial \alpha}\right)_{T,p} \left(\frac{\partial \xi}{\partial p}\right)_{T,eq}$$

where

$$\left(\frac{\partial \xi}{\partial p}\right)_{T,eq} = -\frac{\partial^2 G/\partial p \partial \alpha}{\partial^2 G/\partial \alpha^2} = -\frac{(\partial V/\partial \alpha)_{T,p}}{(\partial^2 G/\partial \alpha^2)_{T,p}}$$

If we have an example of a phase transition with a very high degree of pre-melting and pre-crystallization, as, according to the work of Ubbelohde[7], we may expect to find for the melting of pure high paraffins, and if we imagine this degeneration of the melting point to proceed still further by increase either in pressure or in chain length, the partial miscibility of the components may reach the critical mixing point at a certain stage, and we shall see no more separation into two phases. The heat of transition will have degenerated to a singularity in the C_p-curve, which according to the above derivation will show a steep peak rising sharply to infinity from both sides. But as soon as the degeneration proceeds further, and the miscibility, though still far from ideal, is no longer critical, then the C_p-curve will become continuous, although preserving a possibly very steep peak.

The possibility of a critical point for the solid-liquid phase equilibrium was much discussed in classical thermodynamics [8], and it seems likely that under favourable conditions it may be realised in a manner like this. But so far we do not know the true characteristic difference between the molecular states in the liquid and in the solid states, and therefore we cannot say whether phenomena like those described by Ubbelohde [7] do correspond to a real 'miscibility of states' or whether the molecules can acquire only some and not all of the characteristics of the states of the other phase.

It is clear, however, that it calls for rather special assumptions for a transition of this kind to be realised in more than a point, *viz.* for instance that in a pressure interval $\partial^3 G/\partial p \partial \alpha^2 = (\partial^2 V/\partial \alpha^2)_{p,T} = 0$. The C_p-curve for the λ-transition of liquid helium as it is known to occur in the interval 0—25 ats. therefore must be supposed to be continuous however steeply it rises.

On the whole, it can be said that when we cannot observe the degeneration from two phase transition through critical transition to λ-transition, it will practically never be possible to decide definitely that a true discontinuity does occur. And anyway, in circumstances differing only infinitesimally, the discontinuity will no longer occur in a strictly mathematical sense, although the physical appearance will be practically indistinguishable. It seems the most reasonable thing, therefore, to give up the concept of second order transitions and to speak only of λ-transitions and critical λ-transition.

This whole treatment is of course of a very formal and descriptive character, as is the thermodynamic treatment of mixtures to which it relates. Only in combination with statistical mechanics under the assumption of some physical model will it attain any explanatory value, and only then will it be of interest to evaluate further the given formulae. But as pointed out by Keesom [3] himself, Keesom-Ehrenfest's equation $\frac{dp}{dT} = \frac{\triangle C_p}{TV \triangle \alpha_p}$ will preserve its validity regardless of the kind of the singularity, if only $\triangle C_p$ and $\triangle \alpha_p$ are taken as the increments in the same small temperature interval.

As regards the order-disorder transitions the very difference between Bragg-Williams' treatment and that of Bethe is in the different interaction between cells of the two different kinds. This, in connection with the present treatment, stresses the fact that what does determine the kind of a transition is the mutual interaction between molecules or cells of different kinds. The relative energy and free energy of each kind in the 'pure state' will determine only the range of temperature where it occurs. Hence it is a pronounced cooperative phenomenon.

The nature of the known λ-transitions in crystals being fairly well accounted for by the order-disorder description, the only known λ-transition in liquid phase attracts the greater interest at present. Several models of the helium transition have also been proposed, but we will reserve the discussion thereof for a separate paper.

Only as an illustration to this treatment, however, we shall briefly describe in the language used here one model which is compatible with the *thermodynamic* properties of He II, though not directly with the kinetic ones.

We assume for ordinary liquid He a structure corresponding to a coordination number 12 and with a number of nearest neighbours $z \simeq 11$. Ordinary liquids would at some sufficiently low temperature pass over in a crystalline state of the same coordination number, but for He at not too high pressures another structure of some lower coordination number, say 8 (or 6), must be assumed for some reason or other to be more stable, *i. e.* to be of a lower free energy. How the transition between this last mentioned state and the liquid will take place now depends not on the energies of a He-atom in the two states, but on the energy of an atom with a number of nearest neighbours in between, say 9 or 10. We may consider the two states as pseudo-components distinguished *e. g.* by the He-atoms having numbers of nearest neighbours z, a) equal to and b) greater than 8 (or 6) respectively. If now the energy of an atom varies linearly with z, the two components, if obeying Boltzman statistics, will be ideally miscible, and even in the case that quantum statistics must be applied, the deviations from ideality will not be large enough for a transition point to be detectable.

But it may be that for any such intermediate value of z the energy is much higher than that corresponding to the two states, *e. g.* if an interaction peculiar to the state of low coordination number is responsible for its stability. That will cause a clustering of the atoms of low coordination number into some kind of crystallites, and any degree of deviation from ideality may arise therefrom.

The model very much recalls Bernal and Fowler's model of liquid water and on further consideration of it, it becomes easy to understand how a model as that by Keesom and Gorter[3] of the two-phase system in an opaque vessel of constant volume may well picture the crude features of a λ-transition. When the deviations from ideal miscibility are *almost* large enough to cause a phase separation, the transfer of atoms from the crystallites to the 'serum' takes place *almost* as the transfer between two defined phases. But just in the interesting point of 'transition' that important difference appears, that the crystallites will disappear continuously though perhaps rather quickly with rising temperature, while the discontinuity is characteristic of the model system because it is *really* of two phases and hence can be realised in a temperature interval only because the volume is kept constant. Gorter and Keesom's model, therefore, does not really bridge, as it is meant to, the gap between continuity and discontinuity.

This result does not depend upon the details of the model here assumed, but it will undoubtedly come true by any model which duly takes into account that there is always only one real phase.

SUMMARY

The degeneration of ordinary phase transition is exposed by close analogy to the theory of mixtures. Ordinary phase transition corresponds to no miscibility of molecules in the two states characteristic of each of the phases; pre-melting and analogous phenomena mean partial miscibility, and to full but non-ideal miscibility, anomalies which appear as humps on the heat capacity curve *etc.* correspond, in pronounced cases giving rise to 'λ-transitions'. Only in case of critical miscibility the transition becomes a true second order transition in Ehrenfest's sense.

It is shown by statistical arguments that such a splitting up into two pseudo-components and treatment of these as components in a mixture can be effected without inconsistencies.

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Received December 11, 1947.