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J. Frenkel

Citation: *J. Chem. Phys.* **7**, 538 (1939); doi: 10.1063/1.1750484

View online: <http://dx.doi.org/10.1063/1.1750484>

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troublesome. The emissions of these two substances appeared similar in all respects (see Fig. 2) and extended from 5460Å to beyond 4360Å. The strongest maximum appeared at about 5200Å. As in the case of compounds

yielding acetyl radicals, this fluorescence is probably due to the diketone bipropionyl.

The authors wish to express appreciation to Dr. Fred Perrin and the Eastman Kodak Company for making the densitometer tracings.

JULY, 1939

JOURNAL OF CHEMICAL PHYSICS

VOLUME 7

A General Theory of Heterophase Fluctuations and Pretransition Phenomena

J. FRENKEL

Physico-Technical Institute, Leningrad, U. S. S. R.

(Received May 1, 1939)

The present paper is a generalization of a preceding note on the statistical theory of condensation phenomena. It is based on the idea that the macroscopic transition of a substance from a phase *A* to a phase *B* is preceded by the formation of small nuclei of the *B* phase within *A*, these nuclei being treated as resulting from "heterophase" density fluctuations or as manifestations of a generalized statistical equilibrium in which they play the roles of dissolved particles, whereas the *A* phase can be considered as the solvent. The application of the general theory to pre-melting phenomena in crystals leads to a quantitative

explanation of the abnormal increase of the specific heat of the thermal expansion coefficient (and of the electric conductivity, in the case of ionic substances) in the close neighborhood of the conventional melting point, with the result that the surface tension between a crystal and its melt must be of the order of 1 dyne/cm. This result is checked by a calculation of the temperature corresponding to the highest crystallization rate of an overcooled liquid. Transitions of higher order and Curie points are also briefly discussed from the same point of view.

1. INTRODUCTION

THE ordinary density fluctuations in molecular systems can be denoted as "homogeneous" in the sense that they are associated with a definite state of aggregation or "phase" (gaseous, liquid or solid).

The object of this paper is to show that besides such "homophase" fluctuations it is necessary to consider fluctuations, consisting in local and transitory phase transitions.

Such *heterogeneous* or "heterophase" fluctuations must become especially important in the neighborhood of the corresponding transition points (temperatures or pressures) as determined by the condition of thermodynamic equilibrium between the respective phases and must give rise to a number of phenomena which we shall denote as "pretransition" phenomena. As an example we may cite the "premelting phenomena" in crystals recently discussed by Ubbelohde and consisting in an abnormally large increase of specific heats and thermal expansion coefficients of crystals in the vicinity

of the thermodynamic melting point.¹ These "anomalies" were formerly attributed to the influence of impurities (in conjunction with Raoult's law). Ubbelohde has disproved this interpretation without, however, advancing a fresh point of view. I believe that premelting consists in the actual *melting of the pure crystal in small regions of space and time*, that is in the formation of liquid droplets which can be considered as an example of heterophase fluctuations. I believe that similar fluctuations must take place in other phases near the transition point. Thus minute crystals must be found in liquids just above the crystallization point, minute vapor bubbles just below the boiling temperature, while minute liquid drops (or crystals) must exist in a vapor just above the condensation point.

The appearance of small nuclei of a new phase within a practically homogeneous substance (liquid or gaseous) has been admitted hitherto

¹ Ubbelohde, *Trans. Faraday Soc.* **34**, 292 (1938); also Strelkow, *Sov. Phys.* **12**, 23, 73 (1937); and Strelkow and Haschkovsky, *Physik. Zeits. de Sowjetunion* **12**, 45 (1937).

only in the case of undercooling or overheating, i.e., a thermodynamically unstable state. This limitation is however, utterly unwarranted. In a recent note on the statistical theory of condensation phenomena,² I have shown that liquid droplets must exist in a vapor not only below but also *above* the condensation point, the two cases being distinguished only by the statistical distribution of the droplets with regard to their size. In the case of a nonsaturated vapor their number rapidly decreases with increase of size while in an oversaturated vapor such a decrease has a preliminary character only, being due to the action of the surface tension and being finally replaced (theoretically) by a steady increase. In both cases the number of droplets consisting of g simple molecules (or atoms) is given by the same formula

$$N_g = C\xi^g e^{-\alpha g^{1/3}/kT}, \quad (1)$$

where the parameter ξ is smaller than unity for the nonsaturated vapor and larger than unity for the oversaturated one. The equation $\xi=1$ corresponds to the thermodynamic saturation point. It has been shown to yield the ordinary expression for the pressure of the saturated vapor (or more exactly its monomolecular fraction) as a function of the temperature.

The term "fluctuation" does not convey the correct picture of the origin and destruction of the droplets we are considering. It can lead to the idea that a drop of a given size (g) arises as a result of a single big fluctuation leading to the condensation of g atoms of the gas phase. In reality the drops are gradually growing or decaying by the capture or evaporation of single molecules, the whole system of drops of various size (up to $g=1$) being in a state of statistical equilibrium (so long as $\xi < 1$) in the same sense as a gaseous mixture of chemically reacting molecules. This picture of chemical equilibrium has been used by the author in the derivation of Eq. (1), the "drops" being treated as multiply associated molecules.

This method can be extended to other cases, such as the formation of gas bubbles in a liquid or liquid droplets in a crystal and a number of other heterophase fluctuations, associated with

order-disorder phenomena in solid solutions both above and below the Curie point, or with ferromagnetic phenomena in the same region, etc.

It should be mentioned in conclusion that the introduction of heterophase fluctuations and the corresponding "pretransition" phenomena is just as necessary, as a complement to the ordinary thermodynamic treatment of heterogeneous equilibria, as the introduction of homophase fluctuations in the case of thermodynamic equilibrium in homogeneous substances.

2. GENERAL THERMODYNAMIC THEORY OF HETEROPHASE FLUCTUATIONS AND OF PHASE TRANSITIONS

Let us consider a substance which can exist in two different states (phases) A and B in the neighborhood of the transition point $A \rightarrow B$. Contrary to the crude thermodynamic treatment we shall assume that before the transition starts as an ordinary discontinuous transformation of A into B , the system usually denoted as A is not exactly homogeneous, but contains "nuclei" of the B phase (in the shape of gas bubbles, liquid droplets, crystal grains and so on). This "real" heterogeneous system corresponding to the pretransition conditions of the idealized system A will be denoted with Ab .

Our problem will consist in the determination of the statistical distribution of the b nuclei within A under given external conditions as specified by the temperature T , pressure p and other parameters (such as magnetic or electric fields, etc.) which may influence the equilibrium conditions. For the sake of simplicity we shall take into account the temperature and pressure only and the conjugated "extensive" parameters—the entropy and volume. Under such conditions a b nucleus can be specified by its volume v (which of course must be very small compared with the total volume V of the system under consideration) or by the number g of molecules constituting it. The statistical distribution of the nuclei must be described by a certain function f_g equal to the number of nuclei containing g molecules.

This description is of course incomplete. Nuclei of the same size can have different shapes; we shall however limit ourselves to that shape

² J. Frenkel, J. Chem. Phys. 7, 200 (1939).

which corresponds to the smallest possible value of the surface free energy (in case of liquid drops or gas bubbles—to a spherical shape). The results of the simple theory are not substantially modified by an allowance for other shapes besides the most advantageous one. It would be necessary likewise to take account of the fact that the formation of b nuclei inside the A phase can be accompanied by a local fluctuation of the pressure within a small region of space which encloses the nucleus and its immediate surroundings. Thus, for example, the formation of a liquid drop in a crystal must be accompanied by a more or less local increase of pressure associated with an extension of the crystal in the adjacent region. This pressure or elasticity factor can sometimes be more important than the shape-factor. Yet we shall likewise leave it out of account.

Under such simplified conditions our problem which consists in the determination of the distribution functions f_σ can be solved as follows. Let $\varphi_A(p, T)$ and $\varphi_B(p, T)$ denote the thermodynamic potentials of the corresponding phases referred to 1 molecule. The transition point or rather curve (p, T) is defined by the equation $\varphi_A = \varphi_B$. Assuming p to have a given constant value p_0 , this corresponds to a definite transition temperature T_0 . We shall assume the actual temperature T to be different from T_0 in the sense of making φ_A smaller than the value of φ_B , which corresponds, on the rough thermodynamic theory, to the pressure P_0 of the A phase. In the corrected thermodynamical theory, which takes into account the heterophase fluctuations we must find within A a number of b nuclei with a potential $\varphi_B(p_0, T)$. The transition of g molecules of the A phase into a b nucleus corresponds to a change of the potential of the whole system by the amount $g[\varphi_B(p_0, T) - \varphi_A(p_0, T)]$, increased by the surface potential between the nucleus and the surrounding A phase. This surface potential can be written in the form $\alpha g^{\frac{1}{3}}$, where $g^{\frac{1}{3}}$ is proportional to the surface while α is a measure of the surface tension. The total increase of thermodynamic potential is thus equal to

$$\Delta\Phi = (\varphi_B - \varphi_A)g + \alpha g^{\frac{1}{3}}. \quad (2)$$

This corresponds to a probability proportional

to $e^{-\Delta\Phi/kT}$, that is to an expression

$$f_\sigma = C \cdot e^{-\Delta\Phi/kT} \quad (3)$$

for the distribution function. The coefficient C need not be exactly constant; as a matter of fact it must be considered as a relatively slowly variable function of g .

The preceding method of deriving f_σ from the point of view of the thermodynamic theory of fluctuations does not permit one to determine exactly the coefficient C and hence the actual number of b nuclei. A more satisfactory treatment of the whole question is obtained from another point of view, which is a generalization of that used in our condensation theory. According to this view, the presence of b nuclei in the A phase with a certain distribution, given by the function f_σ , must be considered not as a result of "fluctuations" but as the manifestation of a statistical equilibrium of a somewhat unusual type.

From this point of view the function f_σ can be determined by a method, which is a generalization of the method used in the thermodynamic theory of chemical equilibrium in a gas mixture or in a dilute solution.

The total potential of Ab can be represented by the formula

$$\Phi = N_A \varphi_A + \sum_\sigma f_\sigma (\varphi_B g + \alpha g^{\frac{1}{3}}) + kT \left(N_A \ln \frac{N_A}{F} + \sum_\sigma f_\sigma \ln \frac{f_\sigma}{F} \right), \quad (4)$$

where

$$F = N_A + \sum_\sigma f_\sigma \quad (4a)$$

is the total number of "molecules" in the general sense of the term, nuclei of different size being treated as molecules of different kind in a chemically heterogeneous mixture or "solution" (gaseous, liquid or solid), the A phase playing the role of the solvent. The last term in (4) corresponds to the entropy increase characteristic of such a mixture. If it were neglected the equilibrium condition $\delta\Phi = 0$ with the additional condition

$$N_A + \sum g f_\sigma = N = \text{const.} \quad (5)$$

(N being the total number of simple molecules) would lead to the equations

$$\varphi_B - \varphi_A = \alpha g^{-1},$$

which are incompatible with each other for different values of g . It should be remarked that an equation of a similar type can be used to determine the "critical" value $g = g^*$ for such a nucleus of the B phase which is in an *unstable* equilibrium with the A phase in the "super-transition" state (i.e., in a state beyond the transition point $A \rightarrow B$).

This equation is derived from the condition $\delta\phi = 0$ if ϕ is defined by the formula

$$\phi = N_A \varphi_A + g \varphi_B + \alpha g^{\frac{1}{2}}$$

corresponding to a single value of g , under the condition $N_A + g = N = \text{const.}$ (instead of the condition (4a)). In the case of liquid drops in an oversaturated vapor or vapor-bubbles in an overheated liquid this leads to Thomson's well-known formula for the change of pressure corresponding to a given temperature.

Coming back to Eq. (4) we must add to the general condition (5) a number of conditions of the type

$$\delta N_A : \delta f_{g-1} : \delta f_g = 1 : 1 : -1, \quad (5a)$$

which correspond to a transition of one molecule from a g nucleus to the A phase, the number f_g of g nuclei decreasing by unity, while that of $(g-1)$ nuclei increases by the same amount.

Taking the variation of Φ under the condition (5a) we get

$$\begin{aligned} \varphi_A - [(\varphi_B g + \alpha g^{\frac{1}{2}}) - (\varphi_B (g-1) + \alpha (g-1)^{\frac{1}{2}})] \\ + kT \left(\ln \frac{f_{g-1}}{f_g} + \ln \frac{N_A}{F} \right), \end{aligned}$$

that is

$$\begin{aligned} \frac{f_g}{f_{g-1}} = \frac{N_A}{F} \exp \{ -[(\varphi_B - \varphi_A) + \alpha(g^{\frac{1}{2}} - (g-1)^{\frac{1}{2}})]/kT \} \\ \cong \frac{N_A}{F} \exp \{ -[(\varphi_B - \varphi_A) + \frac{2}{3}\alpha g^{-\frac{1}{2}}]/kT \}. \quad (6) \end{aligned}$$

Replacing g by $g-1$, $g-2 \dots$, g_0 and multi-

plying the resulting expressions we get:

$$f_g = \left(\frac{N_A}{F} \right)^{g-g_0} f_{g_0} \exp \{ -[(g-g_0)(\varphi_B - \varphi_A) + \alpha(g^{\frac{1}{2}} - g_0^{\frac{1}{2}})]/kT \}. \quad (6a)$$

Here g_0 denotes the smallest value of g for which the notion of b nucleus preserves a physical meaning. In the case of liquid drops in a vapor one can put $g_0 = 2$; in the case of liquid drops in a crystal g_0 must be much larger. The exact value of g_0 , as will be seen, is immaterial for the theory. The important point consists in the necessity of modifying the condition (5a) for $g = g_0$ in the sense that the destruction of one g_0 nucleus can take place only by a simultaneous transition of all the g_0 simple molecules constituting it into the A -phase. This process is characterized accordingly by the equation

$$\delta N_A : \delta f_{g_0} = g_0 : -1,$$

which gives

$$\varphi_A g_0 - (\varphi_B g_0 + \alpha g_0^{\frac{1}{2}}) + kT \left(g_0 \ln \frac{N_A}{F} - \ln \frac{f_{g_0}}{F} \right) = 0,$$

that is

$$f_{g_0} = F \left(\frac{N_A}{F} \right)^{g_0} \exp \left\{ -\frac{g[(\varphi_B - \varphi_A) + \alpha g_0^{-\frac{1}{2}}]}{kT} \right\}. \quad (6b)$$

Combining (6b) and (6) we get:

$$f_g = F \exp \left\{ -\frac{g(\varphi_B - \varphi_A) + \alpha g^{\frac{1}{2}}}{kT} \right\} \quad (7)$$

or

$$f_g = F \xi^g \exp \left(-\frac{\alpha g^{\frac{1}{2}}}{kT} \right) \quad (7a)$$

with

$$\xi = \exp \left(-\frac{\varphi_B - \varphi_A}{kT} \right) \equiv e^{-\beta}. \quad (7b)$$

This result is equivalent to (3) or to Eq. (1) which was obtained by a somewhat different (and more special) argument for the case of a vapor near the condensation point. The advantage of the present theory over the previous

one (which treated the b nuclei as resulting from spontaneous fluctuations) consists in the fact that it replaces the undetermined constant C in (3) by a perfectly definite factor F , defined by (4a).

So long as $\sum f_b \ll N_A$, in practice this factor can be identified with N .

3. THEORY OF PREMELTING PHENOMENA

If the temperature T lies sufficiently close to T_0 , the potential difference $\varphi_B - \varphi_A$, or

$$[\varphi_B(p_0, T) - \varphi_B(p_0, T_0)] - [\varphi_A(p_0, T) - \varphi_A(p_0, T_0)]$$

reduces approximately to

$$\left[\left(\frac{\partial \varphi_B}{\partial T} \right)_0 - \left(\frac{\partial \varphi_A}{\partial T} \right)_0 \right] (T - T_0) = (S_A^0 - S_B^0) (T - T_0),$$

where S_A^0 and S_B^0 denote the entropies of the respective phases per molecule at the thermodynamic transition point $T = T_0$. Introducing the latent heat of the transition

$$\lambda = T_0 (S_B^0 - S_A^0)$$

we thus have

$$\varphi_B - \varphi_A = - \frac{\lambda (T - T_0)}{T_0}. \quad (8)$$

If λ is positive T must obviously be smaller than T_0 and vice versa. Substituting this expression into (7b) and replacing T in the denominator by T_0 we get finally:

$$\beta = \frac{|\lambda_0 (T - T_0)|}{k T_0^2}. \quad (8a)$$

The increase of the number of b nuclei with an approach towards T_0 must be manifested by a number of different "pretransition" phenomena such as an anomalously large scattering of light and of ultrasonic rays. Leaving the discussion of these questions to a subsequent paper we shall consider here the abnormally large increase of the specific heat and of the thermal expansion coefficient which forms the essence of premelting phenomena in crystals (cf. Introduction).

The additional value of the specific heat due to premelting ΔC can be calculated as follows.

The latent heat of fusion per molecule at $T \cong T_0$ being λ , the heat necessary for the formation of a liquid drop consisting of g simple molecules must be equal to $g\lambda$ (if capillary effects are neglected). We thus get

$$\Delta C = \sum \lambda g \frac{df_g}{dT} = N \lambda \frac{dJ}{dT} \quad (9)$$

with the abbreviation

$$J = \frac{1}{N} \sum g f_g = \int_{g_0}^{\infty} e^{-\beta g - \gamma g^3} g dg, \quad (9a)$$

where

$$\gamma = \frac{\alpha}{kT}.$$

So far as we are interested in the behavior of ΔC near the melting point, γ can be treated as a constant ($= \alpha/kT_0$) independent of the temperature, while β is a linear function of T vanishing at $T = T_0$. Hence it is clear that both J and

$$\begin{aligned} \frac{dJ}{dT} &= - \frac{d\beta}{dT} \int_{g_0}^{\infty} e^{-\beta g - \gamma g^3} g^2 dg \\ &= \frac{\lambda}{k T_0^2} \int_{g_0}^{\infty} e^{-\beta g - \gamma g^3} g^2 dg \end{aligned} \quad (9b)$$

are functions of T which steadily increase as T approaches T_0 .

Multiplying the expression (9b) with $N(v_B - v_A)$ and dividing it by the volume of the crystal Nv_A we obtain the additional value of the thermal expansion coefficient due to premelting:

$$\Delta \kappa = \left(\frac{v_B}{v_A} - 1 \right) \frac{dJ}{dT}. \quad (10)$$

A comparison between (10) and (9) yields

$$\frac{\Delta \kappa}{\Delta C} = \frac{(v_B/v_A) - 1}{L}, \quad (10a)$$

where $L = \lambda N$ is the latent heat, corresponding to the fusion of the whole crystal.

The calculation of the absolute value of ΔC (or $\Delta \kappa$) depends essentially upon the choice of the number g_0 , i.e., the smallest number of molecules which can form a liquid drop in a

crystalline medium. It is clear that this number must be large compared with unity. The important point however is to see whether it is large or small compared with that value $g \equiv \bar{g}$ which corresponds to the maximum of the integrand in (9a) or (9b). In the case of (9b) g is determined by the equation

$$2/g = \beta + \frac{2}{3}\gamma g^{-1},$$

which reduces to $\bar{g} = (3/\gamma)^{1/2}$ if $\beta = 0$, i.e., $T = T_0$. Now since $\alpha g^{1/2} = 4\pi\sigma r_0^2$ where σ is the surface tension between the liquid and the crystalline phase, we have

$$\alpha = 4\pi\sigma \left(\frac{r_0^3}{g}\right)^{1/2} \cong \sigma v_B^{1/2},$$

$v_B^{1/2}$ being the area occupied by one molecule on the surface of the liquid phase. If the latter were free, $\sigma v_B^{1/2}$ would be of the same order of magnitude as the latent heat of *evaporation* of the liquid (per molecule), that is about 10 times larger than the latent heat of fusion λ and consequently about 20 times larger than kT_0 , since according to Trouton's rule, $\lambda \cong 2.5kT_0$. The surface tension at the boundary between the liquid and the corresponding crystal must however be much smaller than that of the free surface of the liquid. We are thus entitled to expect that in our case $\alpha = \sigma v_B^{1/2}$ is of the same order of magnitude as kT_0 or perhaps even smaller (see below). If it assumed that $\gamma \cong kT$, \bar{g} turns out to be of the order of a few units. Taking $\gamma = \frac{1}{10}$ we get $\bar{g} = 160$ which is probably of the same order of magnitude as g_0 .

The value of g_0 as well as that of γ (i.e., σ) can be ascertained by comparing with the experimental data the maximum value of ΔC (at $T = T_0$) on the one hand, and the rate of increase of ΔC (in the neighborhood of T_0) on the other.

It is known that the increase of ΔC becomes appreciable at a temperature lying a few degrees below the melting point, while the maximum value of ΔC in the case of relatively simple substances can be of the order of 100 cal./mole and more.

We thus see that the factor $e^{-\beta g_0}$ in the integrand of (9b) must reduce ΔC (compared with its maximum value) in the ratio 100 : 1, when

$T_0 - T = 5$, say. Putting $T_0 = 500$ we have

$$\beta = \frac{\lambda}{kT_0} \frac{T_0 - T}{T_0} \cong 3 \cdot 10^{-2}.$$

Hence it follows that g_0 must be of the order of 150. Assuming that \bar{g} at $T - T_0$ is not larger than this we can calculate $(\Delta C)_{\max}$ with the help of the approximate formula

$$(\Delta C)_{\max} = \frac{N\lambda^2}{kT_0^2} \frac{3}{2} g_0^{7/3} \int_{g_0}^{\infty} e^{-\gamma g^{1/2}} d(g^{1/2}),$$

which is obtained from (9) and (9b) if the factor $g^{7/3}$ is replaced by its maximum value in the integration range. We thus get

$$(\Delta C)_{\max} = \frac{3}{2} Nk \left(\frac{\lambda}{kT_0}\right)^2 \frac{g_0^{7/3}}{\gamma} e^{-\gamma g_0^{1/2}}.$$

The product Nk referred to one mole and expressed in calories is equal to 2; $(\lambda/kT_0)^2$ is approximately equal to 6. Hence it follows that the factor $g_0^{7/3}/\gamma e^{-\gamma g_0^{1/2}}$ must be of the order of 10. With $g_0 = 150$ this gives $\gamma = \frac{1}{3}$, which corresponds to a surface tension of the order of 1 dyne/cm.

This figure seems to be of the correct order of magnitude. It can be checked in a quite independent way from a consideration of the speed of crystallization of a supercooled liquid (see §4). Unfortunately the surface tension between a crystal and its melt has not yet been measured directly. In the case of ionic crystals the approach to the melting point is characterized not only by an anomalous increase of C and κ , but also, as a rule, by a similar increase of the electric conductivity. It is clear without calculation that the increase of conductivity due to the premelting must be proportional to $\sum g f_g = J$ and can thus be represented by the expression (12). A more exact theory of this effect is obtained as follows. If E_A is the average value of the electric field in the A phase (crystal) then its value within a drop of the liquid phase B is equal to³

$$E_B = \frac{3}{(\sigma_B/\sigma_A) + 2} E_A, \quad (11)$$

where σ_A and σ_B are the respective values of the

³ Cf. J. Frenkel, *Lehrbuch der Elektrodynamik*, II (J. Springer, Berlin, 1928), pp. 432-433.

electric conductivity (not to be confused with the surface tension!). Owing to the surface charges each drop has an electric moment $p_0 = P_B v_0 = P_B v_B g$, where

$$P_B = \frac{3 (\sigma_B/\sigma_A) - 1}{4\pi (\sigma_B/\sigma_A) + 2} E_A.$$

This corresponds to an average polarization of the system Ab

$$P = \sum p_0 f_0 / V,$$

where V denotes its volume $\cong v_A N$ or

$$P = P_B \frac{v_B \sum g f_0}{v_A N} \cong P_B \frac{J}{N}.$$

In the absence of liquid drops E_A would be identical with E_0 —the applied potential gradient. In the presence of such drops we must have

$$E_0 = E_A + 4\pi P = \epsilon E_A,$$

where

$$\epsilon = 1 + 3 \frac{(\sigma_B/\sigma_A) - 1}{(\sigma_B/\sigma_A) + 2} \frac{J}{N}$$

can be denoted as the additional dielectric constant of the medium due to its inhomogeneity. Since the second term is very small compared with unity, we can put $E_A = E_0$.

The average strength of the electric current flowing in the system Ab per unit area is defined by the formula

$$i = \frac{\sigma_A E_A V_A + \sigma_B E_B V_B}{V} = \sigma_A E_A + \left(\frac{\sigma_B E_B}{\sigma_A E_A} - 1 \right) \frac{V_B}{V} E_A$$

where

$$V_B = v_B \sum g f_0 = v_B J$$

is the total volume occupied by the liquid drops. Putting $V = v_A N$ and neglecting the difference between v_A and v_B we see that the effective increase of electrical conductivity due to pre-melting is given by the expression

$$\Delta\sigma = \left(\frac{\sigma_B E_B}{\sigma_A E_A} - 1 \right) \sigma_A \frac{J}{N}$$

or according to (11)

$$\Delta\sigma = \left[\frac{3\sigma_B/\sigma_A}{\sigma_B/\sigma_A + 2} - 1 \right] \sigma_A \frac{J}{N}. \quad (12)$$

If σ_B is very large compared with σ_A —which is the case with practically all ionic substances—the preceding expression reduces to

$$\frac{\Delta\sigma}{\sigma_A} = 2 \frac{J}{N}. \quad (12a)$$

I have not made any quantitative comparisons of this formula (in conjunction with the expressions (9) and (9a)) with the experimental data. The theory seems, however, to be in a satisfactory qualitative agreement with experiment.

We have limited ourselves in this section to the discussion of premelting phenomena for the reason only that they are relatively better studied than pretransition phenomena of other kinds. There is no doubt however that in all cases we must expect a perfectly similar behavior. Thus, for example, precrystallization phenomena must be observed in a liquid in the vicinity of its thermodynamic crystallization point due to the formation of small crystalline nuclei. It seems possible to detect the latter by a study of the scattering of light or of x-rays in the close vicinity of the crystallization point, and also in a somewhat indirect way by the measurement of the specific heat and of the thermal expansion coefficient which are known to have abnormally large values on *both sides of the crystallization point*. Similar effects should be expected in the case of allotropic transformations of various types within the crystalline state, and also in the case of the so-called transitions of the second and higher order, which are characterized by a discontinuity of the specific heat and of the thermal expansion coefficient, in the absence of a latent heat, and finally in the case of transitions associated with “ λ -points” or Curie points, such as the transitions from an ordered arrangement of the atoms of a binary solid solution to a disordered one, or transitions from the ferromagnetic to the paramagnetic state. Thus, for example, in the case of ferromagnetism small domains with parallel orientations of the electron spins must persist above the Curie

point. Contrary to the usually accepted picture, these domains become smaller and less numerous as the temperature is raised. This is probably the cause of the gradual drop of the specific heat of ferromagnetic bodies, which reaches its highest value at the Curie-point, above the latter. On the other hand, below the Curie-point small domains must appear without a resulting spin, the number and size of these domains declining as the temperature is lowered. It would be interesting to study all these effects in more detail than has been done up to the present time.

4. "SUPER-TRANSITION" STATES AND CRYSTALLIZATION OF AN OVERCOOLED LIQUID

In the preceding sections we have limited ourselves to the consideration of pretransition phenomena, which correspond to a stable statistical equilibrium. It is well known, however, that the thermodynamic transition point T_0 can often be transgressed without any noticeable traces of a macroscopic transition $A \rightarrow B$ (overcooled or overheated liquid, overcooled vapor and so on). The resulting statistically unstable states will be denoted as "super-transition" states. Their existence is explained by the fact the transition from A to B , so long as it is going on by the way of B nuclei arising in the A phase, is a very slow process, which can practically remain unnoticeable. Volmer was the first to give an estimate of the velocity of this process in the case of the condensation of an oversaturated vapor, as a function of the degree of over-saturation (or over cooling, if the pressure is kept constant). In an earlier paper² we have given a somewhat simpler derivation of Volmer's result.

The theory developed in §2 opens the way to a perfectly general formulation and solution of the problem of supertransition phenomena. They are distinguished from pretransition phenomena by the fact that the potential difference $\varphi_B - \varphi_A = \beta kT$ in the Eqs. (7) and (7b) becomes *negative* yielding a value of ξ which is larger than unity. Hence it follows that the distribution function f_θ does not decrease steadily with increase of g as before, but decreases until a

certain value

$$g^* = \left(\frac{2}{3} \frac{\gamma}{|\beta|} \right)^3 = \frac{8}{27} \left(\frac{\alpha T}{\lambda |T - T_0|} \right)^3 \quad (13)$$

is reached, whereafter it begins to increase approximately as $e^{|\beta|g}$. Here $|\beta|$ denotes the absolute value of β .

The maximum value of f_θ

$$f_{\theta^*} = N e^{-\frac{1}{2} \gamma \theta^{*2}} \quad (13a)$$

defines the rate of the process $A \rightarrow B$ in the supertransition state, since b nuclei in their gradual growth must necessarily pass through the critical size g^* . It should be mentioned that the critical size can be defined as corresponding to an unstable equilibrium between the A -phase and one b nucleus in the sense of the condition $\phi = \max.$, where $\phi = (N - g)\varphi_A + g\varphi_B + g^3\alpha$. In the case of liquid drops in an oversaturated vapor the critical size corresponds to Thomson's formula for the vapor pressure about a small drop of a given size. A similar interpretation is possible in all other cases.

Equation (13a) in conjunction with (13) enables one to calculate the value of the difference $(T - T_0)$ for which the process $A \rightarrow B$ acquires a marked velocity (this corresponds to a value of the exponent of the order of unity). In reality a number of supertransition states are known to exist which cannot be accelerated by any increase of $(T - T_0)$. The simplest of them is the cooling down of a liquid into a glassy solid without crystallization. This anomaly can be explained by the existence of a certain *activation energy* U , which is necessary for the transition AB . It has been shown by the writer in 1932 that U can be identified with the activation energy which determines the temperature dependence of the viscosity coefficient in the expression $\eta = \text{const. } e^{U/kT}$ or of the diffusion coefficient $D = \text{const. } e^{-U/kT}$ of the corresponding liquid.⁴ The same idea was applied later by Becker for the explanation of the existence of an optimal temperature for phase-transitions in supersaturated solid solutions.⁵ Hence we see

⁴ This coincidence follows from the fact that the viscous flow of a liquid and its crystallization both take place by the same diffusion mechanism (cf. J. Frenkel, *Sov. Phys.* **1**, 498 (1932)).

⁵ R. Becker, *Ann. d. Physik* **32**, 128-140 (1938).

that the velocity of the transition process $A \rightarrow B$, insofar as it takes place through the growth of b nuclei within the A phase, is proportional to the expression

$$\exp \left[-U/kT - \frac{1}{3} \gamma g^{*4} \right]$$

or according to (13)

$$\exp \left\{ -\frac{1}{kT} \left[U + \frac{1}{3} \alpha \left(\frac{2}{3} \frac{\alpha}{\lambda} \frac{T}{|T_0 - T|} \right)^3 \right] \right\}, \quad (14)$$

where we have assumed $T < T_0$ in the case of the crystallization of an undercooled liquid.

The preceding expression has a more or less sharp maximum at a temperature

$$T_1 = T_0/x,$$

where x is defined by the equation

$$\frac{3(x-1)^4}{2x+1} = \frac{\alpha}{U} \left(\frac{2}{3} \frac{\alpha}{\lambda} \right)^3, \quad (14a)$$

the maximum value of (14) being equal to

$$\exp \left[-\frac{3x}{2x+1} \frac{U}{kT} \right]. \quad (14b)$$

A numerical calculation of this "optimal" (i.e., highest crystallization rate) temperature is hampered by the absence of experimental data on the surface tension between the liquid and the crystalline phase.

Taking $\alpha/\lambda = 2.10^{-2}$, as required by the consideration of premelting phenomena, and assuming U to be of the same order of magnitude as λ (which is actually the case with relatively simple substances) we get approximately

$$\frac{3(x-1)^4}{2x+1} = 10^{-8},$$

that is

$$x-1 = 10^{-2},$$

which with $T_0 = 300$, say, gives

$$T_0 - T_1 = 3^\circ\text{C}.$$

This figure is quite reasonable, although it seems to be somewhat too small, especially in the case of liquids which show a tendency to solidify without crystallization. According to

Eq. (14a) such substances must be characterized by a relatively high value of the surface tension σ between the liquid and the crystalline phase. Under such conditions one should expect the corresponding substances in the crystalline state to develop premelting phenomena on a higher and broader scale than ordinary substances, characterized by a small value of σ . It seems very probable that the so called "amorphous" substances, i.e. substances which do not crystallize on cooling, can be specified by an abnormally large value of the crystal-liquid surface tension coefficient in conjunction with a large value of the activation energy for diffusion U . The latter condition follows from the expression (16b) for the maximum velocity of crystallization.

The preceding theory can be applied without substantial modifications to supratransition phenomena connected with transition of higher orders and with "Curie points" of different kinds. The latter case can be illustrated by the treatment of the transition of an undercooled binary solid solution from an disordered arrangement of the atoms to an arrangement with a degree of order corresponding to the temperature under consideration. This question has been recently treated by the author in a special paper.⁶

5. CONCLUDING REMARKS

The theory of pretransition phenomena developed in this paper takes into account only effects which are connected with a sharp change of the aggregation state and which can be attributed to "premature microtransitions." In reality, besides such discontinuous or qualitative changes arising in the phase A near its transition point T_0 into the phase B , a continuous "quantitative" modification of the structure and properties of A takes place, such as dilation and dissociation of the crystal lattice, or a gradual decrease of the degree of distant order in the alternation of the different atoms in a binary solid solution and so on. The abnormal increase of the specific heat C and of the thermal expansion coefficient κ near the transition point can partially be attributed to these *continuous* changes. The latter cannot explain, however, the sharp increase of C and κ in the close neighbor-

⁶ In conjunction with W. Anastasevich, J. Exp. and Theor. Physics, in press (Russian).

hood of the transition point. It seems that for the explanation of these phenomena appeal must be made to the discontinuous pretransition mechanism discussed in the present paper. This mechanism can be likened to that which is advocated in the case of electrolytic dissociation, say, by the old chemical theories of Arrhenius, Van't Hoff and Ostwald, whereas the quantitative mechanism corresponds to the Debye-Hückel theory of complete dissociation and co-operative interaction. In the case of concentrated electrolytic solutions both mechanisms must be taken into account a part of the dissolved molecules dissociating into ions according to Ostwald's theory, and these ions acting on each other according to the Debye-Hückel

theory. A similar condition is found in the study of the premelting phenomena. It is clear that the gradual dilatation and dissociation of the crystal lattice must speed up the beginning of the premelting process, and that, on the other hand, this premelting must accelerate the dissociation of the remaining portion of the crystal lattice, which is seriously disturbed by the appearance of liquid droplets within it.

It would be possible to improve our theory by taking into account the internal pressures produced by these drops because of their larger molecular volume. The scarcity of the available experimental data does not warrant, however, a more detailed treatment of these secondary effects.

JULY, 1939

JOURNAL OF CHEMICAL PHYSICS

VOLUME 7

An Elementary Theory of Condensation

F. CERNUSCHI* AND H. EYRING

Princeton University, Princeton, New Jersey

(Received February 28, 1939)

A theory of liquids is presented based on the assumption of the presence of holes in a lattice-like structure and using a method analogous to that used in treating order and disorder in alloys. This treatment provides an elementary theory of condensation and a clear and simple treatment of the critical phenomena of liquids and also yields a theoretical curve for the density of vapor and liquid as a function of temperature in agreement with the experimental curve. The existence of more than one phase arises as a consequence of the theory.

INTRODUCTION

WE shall develop an elementary theory of the critical phenomena in liquids. For that purpose we shall assume the simplest possible model which can give us a clear interpretation of that phenomena. We believe that our model may be considered as a good first approximation and that the theory developed in this paper can be further developed on the basis of these assumptions.†

* On a fellowship from the Argentine Association for the Progress of Science.

† *Historical Note.*—As far as we are aware Ising (*Zeits. f. Physik* **31**, 253 (1925)) was the first to apply a statistical method of order and disorder. He applied it to the one-dimensional theory of ferromagnetism. Some clear ideas about the subject are found in the paper by Gorsky (*Zeits. f. Physik* **50**, 64 (1928)). Later came the papers by Bragg and Williams about order and disorder for long range interactions (*Proc. Roy. Soc. A145*, 699 (1934); *A151*, 540 (1935)). Bethe (*Proc. Roy. Soc. A150*, 553 (1935)) gives a

Let us assume: (1) that the particles (atoms or molecules) are moving in a regular array of holes,

modified method applicable to short range interactions. For the one-dimensional case Ising's method is more rigorous. More recently the methods of order and disorder have been applied by many writers to a great variety of problems involving critical conditions. Fowler has applied a somewhat modified method to critical conditions on a surface (*Fowler's Statistical Mechanics* (1936), pp. 832–839). Peierls (*Proc. Camb. Phil. Soc.* **32**, 477 (1936)) has applied Bethe's method to analyze the critical conditions of the adsorbed particles on a surface. Cernuschi (*Proc. Camb. Phil. Soc.* **34**, 392 (1938)), using the quantum analog of Gibbs's canonical equations (Fowler, *Proc. Camb. Phil. Soc.* **34**, 282 (1938)) and two layers of adsorbed particles, discusses the critical conditions of the adsorption isotherm. It would require too much space to give a complete list of the papers dealing with critical conditions. We shall only mention two of the most recent papers because they deal with similar problems; a paper by Kirkwood (*J. Phys. Chem.* **43**, 97 (1939)) in which order and disorder is applied to the problem of liquid solutions; and the paper by Lennard-Jones (*Proc. Roy. Soc. A169*, 317 (1939)), in which a theory of melting is developed using order and disorder. Critical phenomena for a single liquid,