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**Matter through the eye
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Matter through the eye of the association theory camera

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Association Theory is a conceptual scheme for picturing the activity of molecules that employs a kind of stop-motion mental photography. Its basic simplicity proves to be misleading in that Association Theory has already proven its capability in making precise and sophisticated quantitative predictions about a variety of phase transformations. This success lends substantial credence to the elegant insight it gives into molecular activity.

The equilibrium state is a convenient and useful concept because it eliminates time as an explicit variable. Hence, it has the capability of simplifying descriptions of a variety of natural phenomena. In the equilibrium state a substance has the same macro-properties (p , v , T , etc.) now as it had when it went into this state, and it continues to have these same properties as long as it is in this state. *The convenience of the equilibrium state is so great that we often invent hypothetical ones*, ones that are poised between what is possible and what is impossible, and which only approximate real conditions.

Here we shall introduce Association Theory as an equilibrium concept and with it develop a theory of the molecular structure of matter and the nature of the transitions between states of matter. We will talk about the gaseous, liquid, and solid states, include transitions among them, and even show how association theory deals with the critical state, super cooling, and nucleation. The reader is here not unduly burdened with underlying mathematical details; but is instead referred to original publications where such details are developed.



Robert Ginell's activities range through organic synthesis, conversion of nuclear energy, polymerization, and composition of thromboplastinase. He took his three degrees at the Polytechnic Institute of Brooklyn and held a postdoctoral appointment at the University of North Carolina, where he worked on shock waves and the theory of the burning. At Brooklyn College, where he is Professor of Chemistry, he was in charge of their Graduate Chemistry Division and in 1962 when the City University of New York was formed, he became Executive Officer of the joint Chemistry Ph.D. program. He is a member of the ACS, AIC, AAAS, and the New York Academy of Sciences, who awarded him the A. Cressy Morrison Prize in 1953.

Kinetic-molecular theory through conceptual stop-motion photography

The usual modern concept of the nature of matter starts with a time-dependent picture, the Kinetic-Molecular Theory. This familiar theory states that matter in the gaseous state consists of molecules that are in constant motion. They move in straight lines, collide with one another and the walls of the containing vessel. According to this theory, the heat contained in the substance is a function of the total energy of this system; the temperature, a function of the kinetic energy of the particles; and the pressure, a function of the momentum of the particles. The attempts to describe matter by using this picture are the province of Statistical Mechanics, which uses time as an explicit variable and considers equilibrium as a special case of a time-dependent phenomenon. While these attempts are undoubtedly true and useful, in many situations they yield cumbersome mathematics and necessitate assumptions that lead to little growth in understanding.

An alternative, and in many ways a simpler approach, follows from association theory. To justify this approach let us start with a thought experiment. Imagine that we had a motion picture camera of such speed and resolution that it could resolve and take pictures of molecular motion. With this camera let us then take a motion picture of a gas at equilibrium. The projected film would show us in slow motion, according to the Kinetic-Molecular Theory, particles (molecules) moving in straight lines, colliding with each other, colliding with the walls and rebounding. We would see a kaleidoscopic pattern of binary collisions, maybe some ternary collisions, perhaps quaternary collisions, etc. The collisions would not be instantaneous but would last a short interval of time, and the molecules would exhibit a volume. All this would be so if the Kinetic-Molecular Theory is a correct picture. In this work I do not dispute that it is and assume that this is what we would see. This is the picture that classical statistical mechanics describes in terms of momenta and position coordinates.

However, this is not the only way in which this film can be used (I). Rather than project it at normal speeds, let us stop the projector and examine a frame. On the first frame we, of course, see no motion; we see a number of single, isolated particles. We also see a number of double

particles, a number of triple particles and perhaps some larger aggregates. Whether the double, triple, etc., particles are molecules in the act of collision or whether they are groups of molecules that have been joined for a long period of time, we have no way of knowing from this frame. That is, we do not know the life-time of these pairs or triplets; time here is not a variable; a stationary frame has no time axis. Let us examine another frame further on in the film. Here the array of particles in the picture is different, but the frames bear quite a resemblance to each other; again, single molecules are present (1-mers), double molecules (2-mers), 3-mers, etc. The resemblance consists in not only the same species (1-mer, 2-mer, 3-mer, etc.) appearing; on counting we find (if enough molecules appear on a frame) that the number of each species on each frame is the same. This follows from the fact that we have taken a gas at equilibrium and each sample must have the same macro-properties as any other. Hence we have a gas at equilibrium that apparently consists of a mixture of 1-mers, 2-mers, 3-mers, etc. We say the gas is associated with a degree of association given by

$$Z_n = \frac{\sum_i i N_i}{\sum_i N_i} \quad (1)$$

where $\sum N_i$ is the number of individual particles, in units of moles per unit mass, while $\sum i N_i$ is the number of unimers in a given mass. (A particle or cluster of size j , a j -mer, contains j unimers; a 1-mer contains one unimer.)

Since the particles present are in equilibrium, this means that the species are individually in equilibrium with each other. The number of each species present at equilibrium is regulated by the value of the equilibrium constants of the system. The reactions can be written as



with an equilibrium constant of $K_{r,s}$ for all values of r and s . Actually, we do not have to consider all these equilibrium constants, but can restrict ourselves to a single set containing $j-1$ constants that refer to the reactions with the 1-mer, namely



whose equilibrium constant is $K_{1,r}$, r having any value. The rest of the equilibrium constants can be formed as

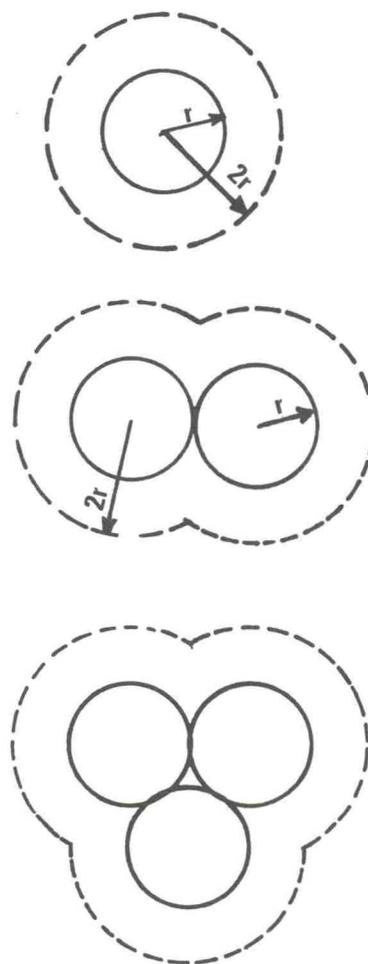


Figure 1. The covolumes of the lower j -mers. The dotted line encloses the covolume or excluded volume. It can be seen that the covolume of a 2-mer is not twice that of a 1-mer.

combinations of this set. The relationship between the numbers of each species is quite simple, namely

$$C_j = K_j C_1^j \quad (2)$$

where

$$K_j = \frac{1}{2} \prod_{x=1}^{j-1} K_{1,x}; j \geq 2 \quad (2a)$$

$$K_1 = 1 \quad (2b)$$

$$C_j = N_j/v$$

and where v = total volume and C_j is the concentration of the species of size j . K_j is the concentration equilibrium constant and is independent of the size of the sample. This follows from the fact that changing the size of the sample in Equation 2 does not change the value of C_j or C_1 . These relationships can be derived both by a kinetic process and an equilibrium process.

Equation of state

To connect these equations with the external variables P , v , and T , we carry out a classical derivation of particles moving in a box and rebounding from the walls, except that for the number of particles in the classical derivation we substitute the number of particles in the mixture of species we have described above. Actually we consider the various sized particles to have no attraction to each other but to have a volume. The attractive forces in the gas are considered to yield the various species. Thus we think of the gas as a mixture of species, each behaving ideally except that each has a volume. The derivation is quite straightforward and the equation of state derived is

$$P \left(1 - \frac{\bar{v}}{v} \right) = RT \sum_i C_i \quad (3)$$

In this equation of state, which is quite simple, there are two more variables than in the simple gas equation, but there are *no arbitrary constants*. The two new variables are $\sum C_i$, which comes from association theory, and \bar{v} , the covolume of the particles, which comes from this derivation. It must be recognized that the covolume, or excluded volume as it is sometimes called, of a 2-mer cannot be twice that of a 1-mer. This can readily be seen from Figure 1. Hence it follows that the total covolume should be defined as

$$\bar{v} = \bar{v}_1 N_1 + \bar{v}_2 N_2 + \bar{v}_3 N_3 + \dots = \sum \bar{v}_j N_j \quad (4)$$

It can be shown that this equation of state is the closed form of the virial equation of state, which is

$$\frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \dots \quad (5)$$

by inserting the definitions of \bar{v} and $\sum C_j$ into Equation 3 and expanding. Since it has been shown empirically that the virial equation of state represents quite exactly the P - v - T properties of real gases, this derivation puts a theoretical foundation under the virial equation of state and simultaneously confirms the validity of this equation of

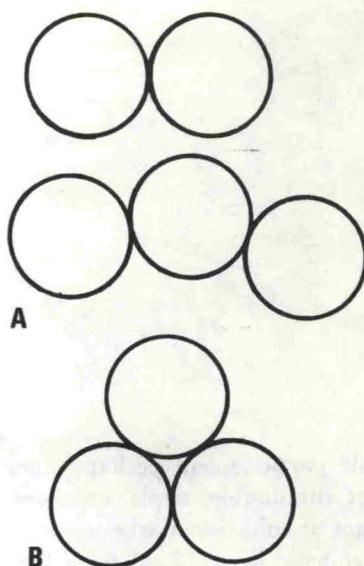


Figure 2. The 2-mer and the 3-mers
A, linear form; B, closely packed form

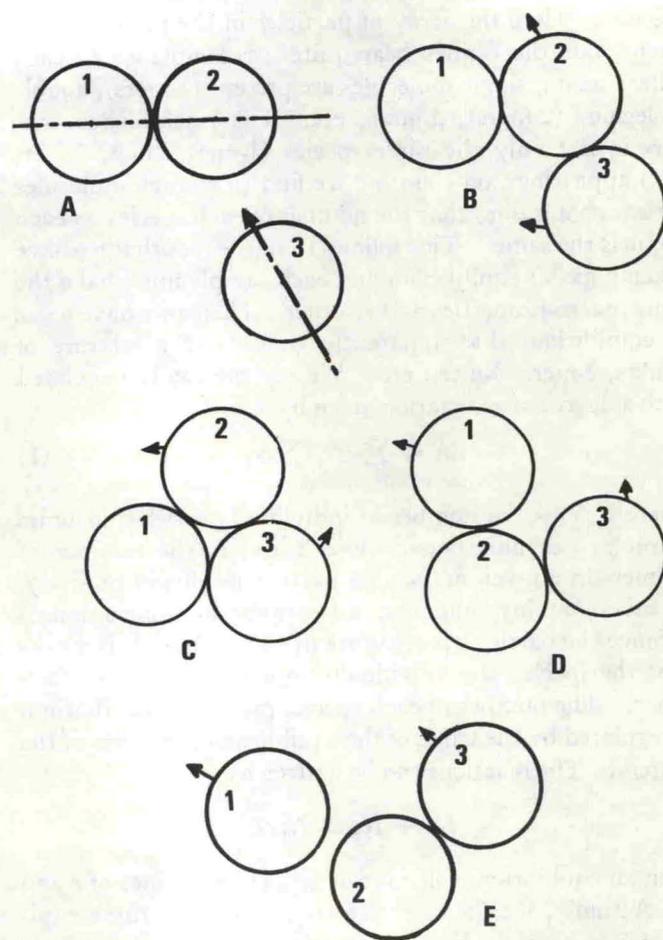


Figure 3. Formation and degradation of a 3-mer
A, just before collision; B, Moment of collision. First bond forms. Unimer #3 imparts momentum to unimer #2. #3 has component of momentum which carries it toward unimer #1; C, Second bond forms. If energy of collision is small, all the kinetic momentum is converted to rotational momentum. If energy of collision is large, goes to D; D, If momentum is great, first bond breaks. If momentum is not too great, goes to C and then back to D and repeats; E, Great momentum, second bond breaks

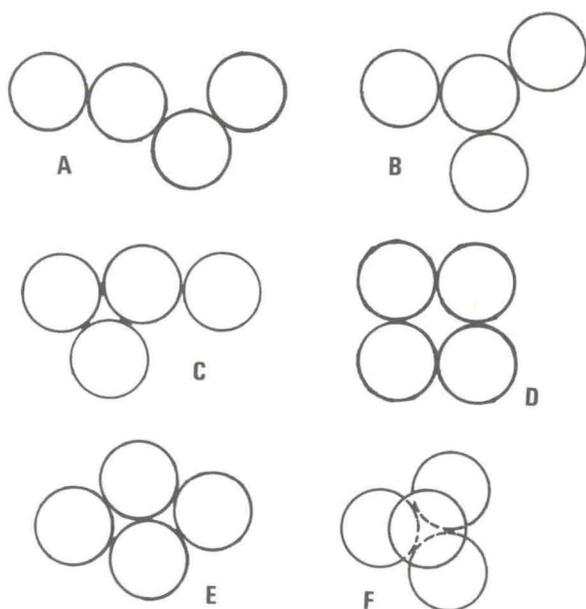


Figure 4. Forms of the 4-mer
A and B, strictly linear forms (3 bonds); C and D, 4 bonds form. C is formed by the collision of a 1-mer and a close-packed 3-mer. D is an unstable transition form; E, 5 bonds; from C by making one additional bond; F, 6-bond tetrahedral form. All four unimers are in 3-holes. Degradation takes 3 steps

state as it applies to gases. In the development (of this derivation) the virial coefficients are given explicitly in terms of the equilibrium constants and the covolumes. The general form of the virial coefficients is,

$$G_m = \bar{v}_{m-1} - (m-1)K_{1,m-1} \quad (6)$$

The first few virial coefficients are

$$G_2 = B = \bar{v}_1 - K_2$$

$$G_3 = \{[C - 4K_2 + 3\bar{v}_1K_2 + \bar{v}_1^2]/K_2\} = \bar{v}_2 - 2K_{1,2}$$

$$G_4 = \frac{[D + 20K_2^3 - 18K_2K_3 - K_2^2(14\bar{v}_1 - 5\bar{v}_2) - K_2(2\bar{v}_1\bar{v}_2 - 5\bar{v}_1^2) + 5\bar{v}_1K_3 - \bar{v}_1^3]}{K_3}$$

$$G_4 = \bar{v}_3 - 3K_{1,3}$$

etc. B, C, D , etc. are the virial coefficient from Equation 5.

The fact that the successive \bar{v}_x and $K_{1,x}$ enter linearly with each additional virial coefficient means that if the virial coefficients of a gas are known, the values of \bar{v}_x and $K_{1,x}$ can be determined for each step successively and in principle, the total \bar{v} and ΣC_j can also be determined.

The gas

Thus far we have derived an equation of state that is shown to be the closed form of the virial equation of state. Since the virial equation of state is the equation which best describes a gas, we feel that we know what a gas is. To recapitulate: a gas is a substance that consists of a mixture of species: 1-mers, 2-mers, 3-mers, etc. in equilibrium with one another. This definition, which seems satisfactory, nevertheless presents us with some

implicit questions. The first is: What does the "etc." in the definition stand for? In other words, how large a species can exist in the gas? And related to this question is another question: from the point of view of association theory what is a liquid and how is it related to a gas? A concurrent question is what is a solid? How can you, by this theory, explain the sharply distinct states of gas on one hand, and liquid and solid on the other? These questions demand an answer, and to be able to answer them systematically we must first inquire into the nature of the larger species of clusters (j -mers), (larger than the 4-mer).

The larger clusters (2)

The simplest forms of j -mers, not considering the 1-mers, are the 2-mers and the 3-mers as shown in Figure 2. As can be seen from the figure, there are two forms of the 3-mer and only one of the 2-mer. The question immediately arises: Do both forms of the 3-mer exist side by side in equal quantities or does one predominate? To answer this question we take two principles as axiomatic. The first is: events that can happen sequentially, rarely, if ever, happen simultaneously. By simultaneous we mean mathematically instantaneously. If the smallest interval of time elapses between the events, they are sequential. Hence *events happen simultaneously only when they can occur no other way*. The events we are discussing in this section are bond formation. According to this principle only one "bond" forms at a time, although succeeding bonds may form after a short interval. Two bonds form simultaneously only when it is impossible to form them sequentially. The second principle is: the more bonds a unit of a particle has with another part of the particle ("atom" can be read for unit of a particle), the more difficult it is to dissociate or remove it from the particle. In other words, the more bonds there are in a particle, the more stable the particle. The principle implies that the more bonds a particle has, the more events (bond breaking) are necessary to break it apart and hence the longer its lifetime.

From the point of view of these two principles, the 3-mer with three bonds is more stable than the 3-mer with two bonds and the 3-mer with two bonds is more stable than the 2-mer with one bond. Opposing this tendency of the most stable form to persist is the effect of the amount of kinetic energy inherent in the collisions that form these species. The more violent such motion, the shorter the lifetime of a particular species. If the energy of the collision is too great, some relatively stable species may not form at all. The sequence of events that result in the three-bonded 3-mer is shown in Figure 3.

When we come to the 4-mer, we have a larger number of species possible than in the 3-mer (see Figure 4). The most stable of these species is the tetrahedral one. Here each unimer is in a 3-hole (a unimer bound to three other unimers is described as being in a 3-hole). Three bonds must be broken to dissociate a unimer from this aggregate. The whole particle is, of course, symmetrical. This is the

simplest type of dissociation of the tetrahedral 4-mer. If one wishes to remove a 2-mer (that is, two joined unimers simultaneously), one must break four bonds. Energetically this is more difficult than breaking three bonds and hence unimer break-off is the preferred type of dissociation.

With the 5-mer, the various species of which are shown in Figure 5, complications ensue and a new phenomenon manifests itself (3). Most of the forms of the 5-mer are very like those of the 4-mer, the unimers being bonded to one or two other unimers, or being in a 3-hole. We call these forms linear forms or simply-bonded forms. On the other hand, one of these forms is quite different, being multiply-bonded (the nine bond form). By multiply-bonded particles, I mean particles in which there are unimers that are held by four or more bonds. Such multiply-bonded unimers require either an extra step for their dissociation (this is possible in the simpler clusters) or more important, require the breaking of two bonds *simultaneously* as the first step in the dissociation. This mode of aggregation and degradation is illustrated in Figure 6. The first conclusion that we must draw from this type of degradation is that unimers in a 4-hole (or 5-hole) are more stably held than unimers in a 3-hole. But the stability is not equal to the stability resulting from an extra step of one more bond to be broken, the particle has enhanced stability because the first step requires the breaking of two bonds simultaneously. This observation provides us with the clues necessary to explain the formation of the liquid state, and its distinctness from the gas. It also offers us an explanation of the critical state.

The phase transition of the gas to the liquid state (3)

Lowering the temperature of a gas has several consequences. First, the average kinetic energy of the particles in the gas is lowered. This results in a lengthening of the average lifetime of each particle cluster since collisions of the required energy for the simultaneous dissociation of two bonds do not occur as frequently as the energy required for single bond dissociation. The increased lifetime or residence time of particles yields the greater amount of time necessary for more complexly bonded clusters to form. This means that, whereas a gas at higher temperatures consists in the main of 1-mers, 2-mers, and a sprinkling of 3-mers, as the temperature decreases the proportion of 3-mers increases, and 4-mers and perhaps linear 5-mers appear. The substance still remains a gas. As the temperature is further decreased, a point is reached where the closely packed 5-mer appears. *This point is exceptional.* It is the condensation point. Here the closely packed multiply-bonded 5-mers appear. Since they have enhanced stability vis-a-vis the 2-mers, 3-mers, 4-mers, and linear 5-mers, and hence have longer lifetimes, the equilibrium is shifted and further collisions result in the formation of large clusters rather than dissociation. The gas is rapidly drained of 2-mers, 3-mers, and 4-mers. The process produces a halt in the temperature drop. Up

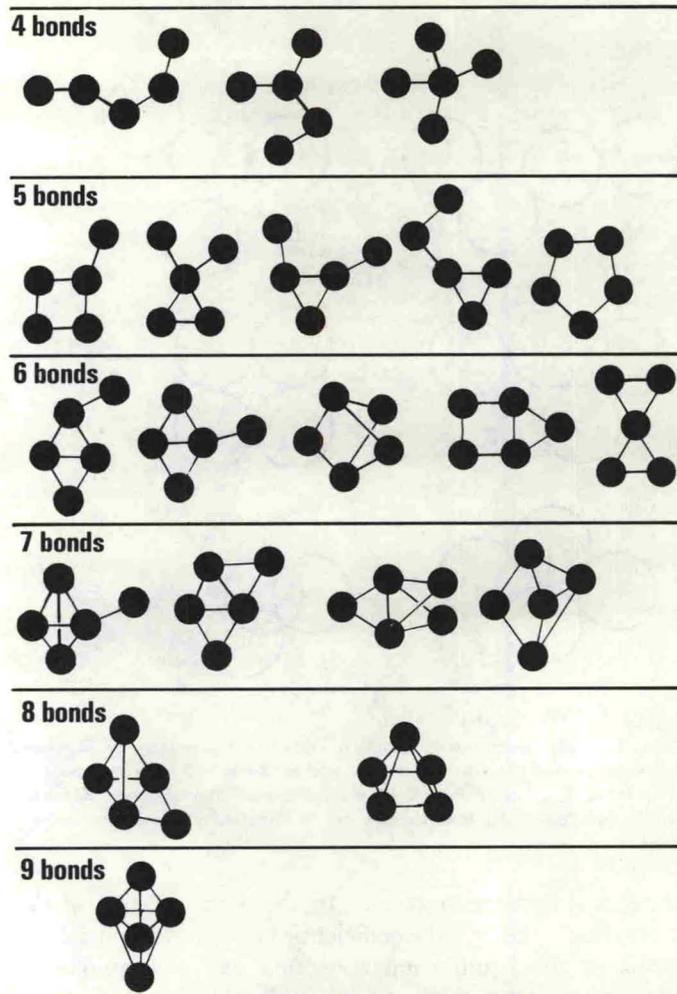


Figure 5. Forms of the 5-mers
Some of these forms are drawn in 3-dimensional projection. Although all the connected unimers really touch, they are shown with bonds joining them to make the spatial relationship clearer

to this point in the gas, the rate of heat loss had been constant and the temperature drop rate was uniform since the processes producing the heat were the formation of the simply bonded unimers. At this point there is a new type of process occurring. The formation of multiply-bonded unimers releases more energy than the formation of simply bonded unimers. The result is a halt in the cooling curve.

At this condensation point the gas is rapidly emptied of 2-mers, 3-mers, and 4-mers and large clusters (the liquid phase) form. Somewhat below this temperature the system contains a liquid phase consisting of large clusters in equilibrium with 1-mers, and a vapor phase consisting of 1-mers and perhaps some 2-mers. The 1-mers in the liquid phase are in equilibrium with the 1-mers in the vapor phase. The large clusters in the liquid phase we shall call α -mers where $\alpha \geq 5$.

Mathematical development at the condensation point (4)

Interestingly enough the previous mathematical equations, which were derived for the gas, break down at the condensation point and we cannot go smoothly and

continuously from the gas to the liquid. In particular, Equation 2a no longer holds and we must redefine certain quantities. In the liquid we make the following definitions:

$$\begin{aligned} C_1 &= C_1 \\ C_x &= 0; 2 \leq x < \alpha \\ &= C_x; \alpha \leq x \leq m \\ &= 0; m < x \end{aligned} \quad (7)$$

hence m is the largest species. Further

$$\begin{aligned} K_{1,x} &= \frac{C_{x+1}}{C_1 C_x}; x \geq \alpha \\ K_1 &= 1 \\ K_x &= 0; 2 \leq x < \alpha \end{aligned} \quad (7a)$$

$$\begin{aligned} K_\alpha &= \frac{C_\alpha}{C_1^\alpha}; \alpha > 2 \\ K_x &= K_\alpha \prod_{y=\alpha}^{x-1} K_{1,y}; \alpha < x \leq m \\ K_x &= 0; x > m \end{aligned} \quad (7b)$$

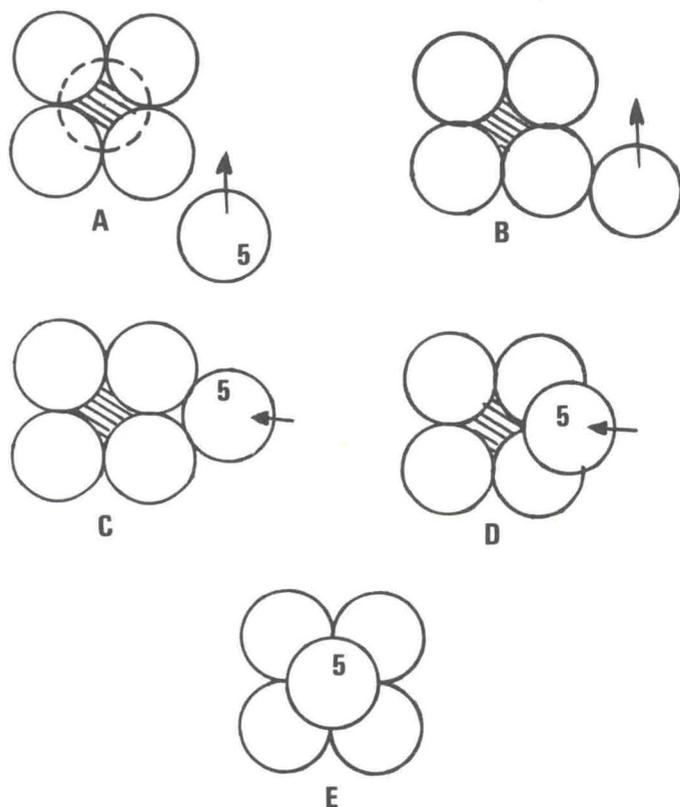


Figure 6. Formation of bonds in a 4-hole

A, Approach (the dotted atom is below the plane of the 4 atoms and fixes these 4 in position. It is only partially shown in the other views); B, First bond forms between atom #5 and one unimer of the 4-hole; C, Second bond forms between #5 and the adjoining unimer; D, Movement of unimer #5 on surface of plane of 4; E, Simultaneous formation of bonds 3 and 4 between unimer #5 and 4-hole. These two bonds must be formed simultaneously

Degradation of unimer #5 in a 4-hole: The first step is the reverse of step E; the simultaneous breaking of 2 bonds. The next two steps are the reverse of steps C and B

Equation 7b is the redefined Equation 2a. With these redefinitions, the equation of state, Equation 3, remains unchanged.

The solid and the liquid states (2)

The remaining questions propounded previously are still to be answered. To be able to do this we must first investigate some of the still larger clusters (larger than the 5-mer). We shall neglect the simply bonded clusters and only examine the closely packed (multiply-bonded) species since at this point we realize that the multiply-bonded clusters are those that comprise the liquid and solid.

The closely packed forms of the 6-mers are shown in Figure 7. There are two of these, both of which have the same number of bonds. While the 6a-mer can be formed directly from the closely packed 5-mer, the 6t-mer can only be formed from the closely packed 5-mer by first forming the 6a-mer and then going through an isomeric transition where one bond is broken and another formed. These forms are interesting only because of this isomeric transition and because they are a step toward the closely packed 7-mers, which are shown in Figure 8. With the closely packed 7-mers an important phenomenon appears, namely, the closely packed forms do not have the same number of bonds. One of the forms, the 7a-mer, differs from the other forms in that it has an extra bond. This extra bond is slightly weaker than the other bonds in the 7-mers. By weaker I mean that whereas all previous bonds are considered to be at places where the atoms touch, in the 7a-mer there is one stable position where, while the atoms do not touch, they are uniquely close together. This is shown in Figure 9. Further the 7a-mer is degenerate, since this weak bond can appear in 6 different positions (5 identical) by an isomeric shift that should require very little activation energy. The result of this extra bond and degeneracy is that this form has added stability. As we go from the 7-mers to the 8-mers, then the 9-mers and up, this a structure persists in having more bonds than the structures built up from the other forms (the t structure). A graph showing the results obtained by model building with spherical unimers is shown in Figure 10. Figure 11 is a photograph of models of the 19a-mer and the 19t-mer. The 19a-mer resembles our mental image of a liquid while the 19t-mer has a regular shape corresponding to our mental image of a crystal.

The models were built with beads of uniform size. Each successive bead was placed in the most highly bonded position possible with the results shown in Figure 11. In the 19t-mer each bead is firmly fixed into position, that is, it fitted exactly into a 3- or 4-hole. Within the 19a-mer, very often there were positions in which a bead could be placed in two closely spaced alternate spots, which were, however, not close enough to be called an extra weak bond, but close enough so that another bead would not fit. The bead could then move between these two positions with little activation energy. By this I mean that the center of gravity of the bead would not need

to be "raised very high" to go to the adjoining position. (A bead in a 3-hole has to be raised to a considerable height to move from one 3-hole to the adjoining 3-hole. One bond is broken and then one is formed in this process. A still more difficult process is the case of the 4-hole). The symmetry of the 19 a -mer is approximate 5-symmetry, that is, it is built around the pentagon. A single bead lies in the center of five beads in a 5-hole, above and below the plane of the pentagon, while over this central bead is another pentagon. The planes of the pentagons are generally not parallel. This type of arrangement is not efficient in filling space and the 19 a -mer is full of voids that are less in volume than a whole bead. On the other hand the 19 t -mer is built around 6-symmetry and such a structure fills space efficiently. Bernal (5) has noticed the same phenomenon when he wrapped "Plasticene" spheres in film and dropped them into a large container in a random fashion. The impressions of the surrounding spheres on any sphere were in groups of 5. Apparently approximate-5-symmetry is the result of random packing. From this approximate-5-symmetry packing stem many of the characteristic properties of liquids; their fluidity and flow properties and their increased specific volume. This behavior is in contrast to that of the solid where rigid 6-symmetry (or 3- or 4-symmetry) is the rule. Unimers in this latter type of symmetry fill space efficiently. The unimers in the liquid can move from position to position with little or no activation energy and no elastic restoring force, while in the solid clusters, since the space is filled efficiently, movement is very difficult and there are large restoring forces.

Hence a liquid consists of large clusters in approximate 5-symmetry while a solid consists of still larger particles in 6-symmetry (or 3- or 4-symmetry). From Figure 10 we see that the 19 a -mer has more bonds than the 19 t -mer counting the weak bonds. At some size greater than 19 (the models were only built up to this size) these curves must cross, because as the sizes become larger two things happen: in the t -structures more positions consisting of 5- and 6-holes appear, while in the a -structure very few of such positions are apparent. However, the large clusters are formed systematically from small clusters in the natural process of condensation. Hence it is obvious why liquids usually form preferentially in condensation. The smaller clusters that form first are the more stable liquid clusters and they give rise to clusters that have the a -structure, which is the liquid structure. In the larger size clusters the most stable clusters (those having more bonds) are the solid clusters. The question now arises what is the process by which liquids change to solids. We know that this change is a difficult one, often very difficult.

Nucleation and the conversion of liquids to solids (2)

Experiment shows that conversion of liquids to solids is difficult: the formation of supercooled liquids is common. The postulation has been that nuclei are necessary for such a conversion process. The question is: what are these nuclei and how are they formed?

The structure of the liquid is based on 5-symmetry while the structure of the solid is based on 6-symmetry (or

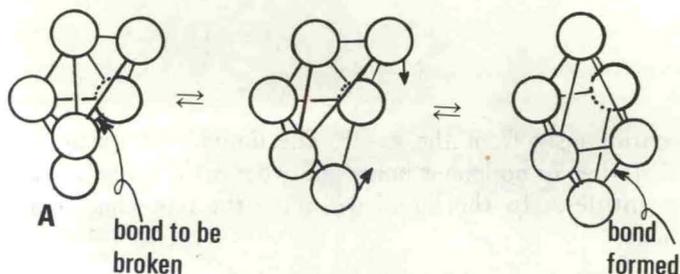


Figure 7. The 6-mer transition
A, the 6 a -mer formed from a nine-bonded 5-mer and a 1-mer (12 bonds); B, the transition form: one bond broken; C, the 6 t -mer (12 bonds); bond remade

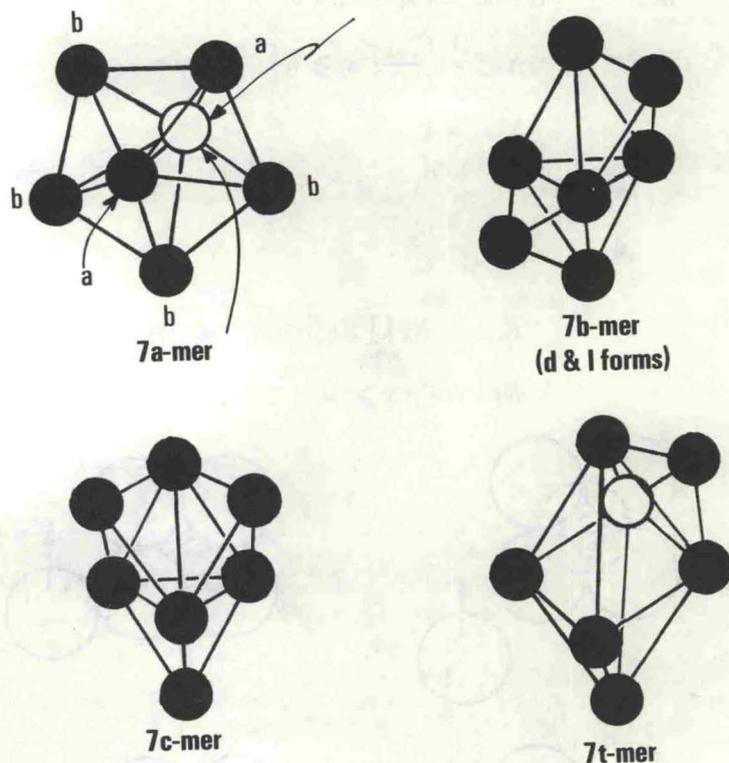


Figure 8. Closely packed forms of the 7-mers
The weak bond in the 7 a -mer appears either as a b-b bond or an a-a bond. Probably the whole structure adjusts so that all the bonds are equivalent. The 7 a , 7 b , and 7 c are formed from the 6 a -mer while the 7 t -mer comes from the 6 t -mer

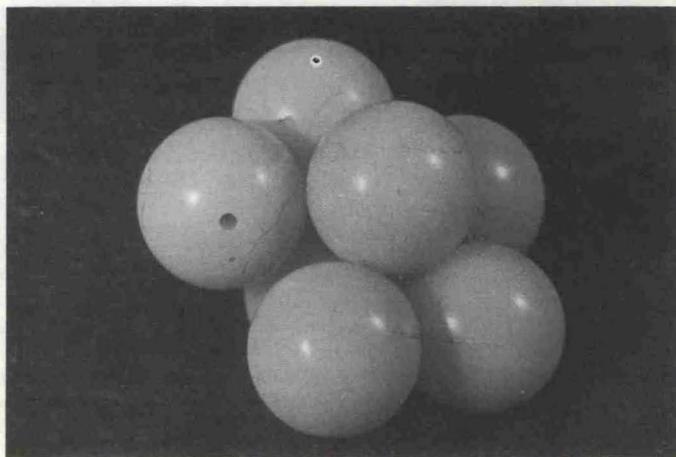


Figure 9. Photo of bead model of the 7 a -mer
The weak bond is shown. All the beads touch at the other bonds

3- or 4-symmetry). The problem then of crystallization is the conversion of a system in 5-symmetry to one in 6-symmetry. This is difficult since it demands the cooperative breaking of many bonds in liquid clusters and subsequent movement to preferred positions in 6-symmetry. However, events take place one at a time and unimers move so that the largest number of bonds are formed. The unimers cannot foresee that later they will be more stable in 6-symmetry. Hence spontaneous or homogeneous nucleation occurs rarely. On the other hand, heterogeneous nucleation is simple, rapid, and predictable. In heterogeneous nucleation a seed crystal, which is a small crystal of solid, is introduced. *The seed crystal is in 6-symmetry and is of a size that is stable.* This seed can grow by utilizing the 1-mers that are in equilibrium with the liquid clusters because the stability of the unimer in the solid cluster is greater than that in the liquid cluster. The solid cluster then grows at the expense of the liquid clusters surrounding it. As the liquid clusters become smaller, it becomes easier for them to go into the form of the *t*-structure (6-symmetry) and hence more nuclei are formed. Thus the process is an accelerating one and the liquid rapidly changes from an *a*-structure (5-symmetry) to a *t*-structure.

Methods of inducing nucleation and subsequent crystallization are known other than introducing a seed. One such method is violent, prolonged agitation followed by a period of rest. It seems likely that in this method the mechanical agitation physically breaks up the large liquid clusters into smaller ones. Since the external conditions (P , T) are such that solids are stable, the smaller liquid clusters have a chance to convert into *t*-clusters, these being the nuclei around which further growth and crystallization occur. Another method of inducing nucleation is to store the liquid sample at very low temperatures (dry ice temperatures) for a long period of time and subsequently warm them up to allow for subsequent growth. Here storing the liquid clusters at very low temperature increases the lifetime of all clusters. Some small *t*-clusters may form and if warmed up slightly will persist long enough to allow them to grow to a stable size. After the clusters are large enough and hence stable enough, considerable warming is possible and growth continues by the unimer addition process. Such forms of homogeneous nucleation are not predictably certain and are difficult to achieve.

Melting

The reverse of crystallization, melting, is by comparison a simple problem. As the solid cluster in 6-symmetry is warmed, the clusters get smaller because of kinetic motion, that is, α decreases in value. Also, because of the amplitude of the vibration of the unimers, the specific volume increases. The unimers can migrate to other positions and small aggregates can form with 5-symmetry, which are more stable than the small aggregates in 6-symmetry. Hence the substance melts. In observing the melting process in crystals one can see that the corners melt first, then the edges, and finally the bulk. This happens because the unimers at the corners and edges are the least bound and hence can more easily rearrange to the stable 5-symmetry. The melting point is not absolutely sharp, the melting of the

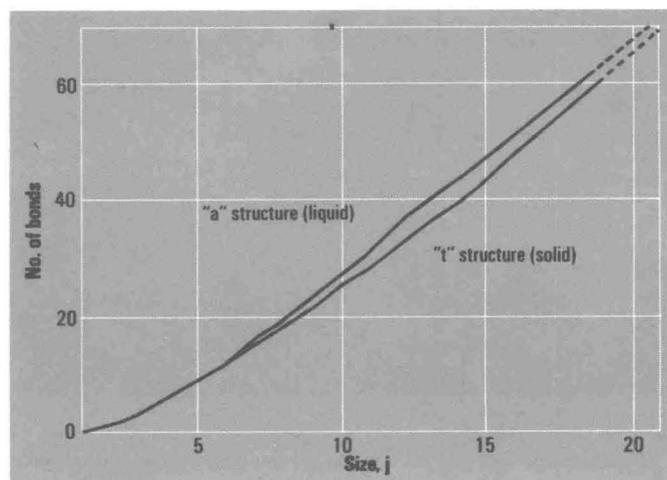


Figure 10. J vs. number of bonds

Contact points are considered bonds. Note that the 5-symmetry α -structure has more bonds than the 6-symmetry t -structure. The lines must cross at much larger sizes, the number of bonds in the t -structure then being more than in the α -structure

corners occurring at a slightly lower temperature. No nuclei are necessary in the process in contrast to crystallization.

The critical state and fluids (3)

An explanation of the curious phenomena which occur in this interesting state remains to be discussed. When an equilibrium system of a liquid and a vapor is heated, usually under pressures, the phase boundary is visible as the temperature increases. When, however, the critical temperature is reached it suddenly disappears. However, if the tube containing the mixture is not agitated during the process, density differences between the former liquid and former vapor regions persist for some time, if the temperature is kept close to the critical temperature. Gentle inversion of the tube does not destroy the density difference, although vigorous agitation and/or large temperature rises do. These phenomena are amenable to explanation by association theory.

At temperatures well below T_c , the liquid-vapor equilibrium system consists of a liquid phase containing 1-mers and large α -mers, where α is much greater than 5, and a vapor phase in equilibrium with the liquid phase containing 1-mers and 2-mers. The 1-mers of the liquid phase are in equilibrium with the 1-mers in the vapor phase. The gap consisting of species in zero concentration in the liquid phase is extremely large. The refractive index of the two phases is vastly different because differing species in the two phases and the phase boundary are distinct.

As the temperature is increased the gap becomes smaller, that is, α decreases in value and the number of 1-mers in the liquid increases. At the same time in the vapor, the number of 1-mers increases because they are in equilibrium with the 1-mers in the liquid phase. Because of the temperature rise and the increase in the number of 1-mers in the vapor phase, the number of collisions in the vapor phase increases. This means that as the temperature increases the number of 2-mers, 3-mers and 4-mers and linear 5-mers in the vapor increases. The phase boundary becomes more indistinct although still visible. At the

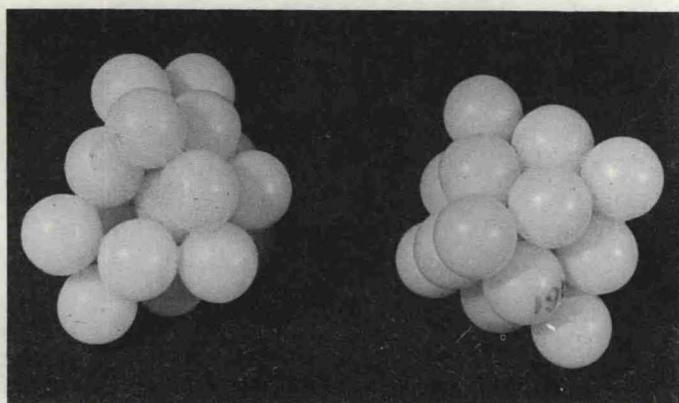


Figure 11. The 19-mers
The 19 α -mer on the left and the 19 β -mer on the right. Notice the compact regular array of the 19 β -mer. This is typical of crystalline solids. On the other hand the 19 α -mer looks random and has a number of small gaps in the structure. Some are shown. This is typically the liquid structure

critical point, α in the liquid phase becomes five. This means that the smallest species in the liquid is the 5-mer, while the largest species in the vapor is also the 5-mer. Hence at this point the distribution in species becomes continuous between the two phases. Since the composition is continuous, the refractive index is the same and the phase boundary disappears. In this same process the densities of the two phases have been approaching one another (Law of rectilinear diameters). However, in an undisturbed tube the densities do not become equal at this point. At the temperature, T_c , where the refractive index disappears, the former vapor phase region consists of species of sizes from 1 to linear 5, while the former liquid

phase region consists of clusters from 5 up. Hence there is a density difference. This difference disappears on mixing by violent agitation, although gentle inversion of the tube does not destroy it. Thermal currents owing to temperature differences will also destroy the density gradient as will kinetic motion owing to a temperature rise.

Above the critical temperature, the distribution of species is continuous, no gap is present. This fluid state resembles a gas in that a continuous distribution of species is present and a liquid in that large multiply-bonded species exist. The high temperature ensures that no gap forms in the fluid state that exists above the critical temperature.

Quantitative experimental tests

The argument thus far has been theoretical and descriptive, and, we feel, plausible. The test of a theory is however its quantitative agreement with experiments. In this section we will set forth the points where we can contact numbers.

First: If we calculate α for the substances (6), argon, oxygen, nitrogen, and water from the triple point to the critical point from the known values of the vapor pressure P the liquid volume V and T , we obtain Table 1. As can be seen from the table the value of α at the critical point is approximately 5 for all these substances, even for one as complex as water. The theory does not predict that α will be exactly 5 at the critical point but approximately so. While the values of α , the smallest size of liquid cluster in the various liquids, varies enormously at the triple point, they approximate 5 at the critical point. The principal

Table 1. Average degree of association of the α -mer from the triple point (T_{tp}) to the critical point (T_c)

T(°K)	$P_{\text{sat}}(\text{exp})$ (atm)	$P_{\text{sat}}(\text{calc})^d$ (atm)	α^e	T(°K)	$P_{\text{sat}}(\text{exp})$ (atm)	$P_{\text{sat}}(\text{calc})^d$ (atm)	α^e
Argon^a				Nitrogen^a			
83.8(T_{tp})	0.6798	0.6813	4000	63.15(T_{tp})	0.1230	0.1268	14000
90	1.321	1.314	1700	70	0.3800	0.3774	3600
100	3.210	3.194	550	80	1.349	1.323	820
110	6.591	6.606	220	90	3.551	3.527	250
120	12.00	12.10	97	100	7.676	7.710	96
130	20.00	20.20	47	110	14.48	14.62	40
140	31.30	51.34	23	120	24.80	24.92	17
150.86(T_c)	48.34	47.28	5.3	126.26(T_c)	33.56	33.34	5.2
	$\sigma = 0.85\%$				$\sigma = 1.26\%$		
Oxygen^a				Water^b			
54.35(T_{tp})	0.001500	0.001693	1,200,000	0°C(t_{tp})	0.006027	0.007519	2,000,000
70	0.06140	0.05932	24,000	50	0.1217	0.1202	100,000
85	0.5610	0.5249	2,300	100	1.000	.9138	11,000
100	2.509	2.415	460	150	4.698	4.303	2,100
115	7.454	7.459	130	200	15.35	14.60	540
130	17.25	17.76	48	250	39.26	39.23	170
145	34.02	35.35	18	300	84.79	88.70	61
154.77(T_c)	50.14	51.51	4.8	350	163.2	176.0	21
	$\sigma = 4.75\%$			374.15(t_c)	218.0	235.8	6.1
					$\sigma = 7.84\%$		

^a Data from H. M. Roder, R. D. McCarty, and V. J. Johnson, *Nat. Bur. Stand. Tech. Note 361* (1968).

^b Data from N. E. Dorsey, *Properties of Ordinary Water-Substance*, Reinhold, New York, 1940.

^c These numbers are rounded off from an 8-digit calculation.

^d From a least-squares fit of experimental data (rounded off).

^e $\sigma = \left(\frac{1}{n} \sum [P - P_{\text{calc}}/P]^2 \right)^{1/2}$; measure of goodness of fit of experimental data in P to least-squares equation.

Table 2. Atomic radii of the alkali metals calculated from compressibility data and knowledge of the crystal form (bcc)
Pressure = 1 kg/cm², T = 300°K, N₀ = 6.02283 x 10²³

Metal	r(A) ^a	r(A) ^b	r(A) ^c
Lithium	1.437	1.45	1.50
Sodium	1.752	1.80	1.77
Potassium	2.099	2.20	2.07
Rubidium	2.295	2.35	2.25
Cesium	2.541	2.60	2.37

(low pressure form)

^a Ginell and Quigley, ref. 12 from compressibility and knowledge of crystal form.

^b J. C. Slater, *J. Chem. Phys.*, **41**, 3199, (1964), from X-ray measurements.

^c W. L. Bragg, *Phil. Mag.*, **40**, 169 (1920), from X-ray measurements.

assumption made in this calculation was that α was the average size of the liquid cluster rather than the minimum size. This we feel is a good assumption since the range of sizes in the liquid α -mers is probably small.

Second: We have shown that the equation of state (Equation 3) can be converted exactly into the Tait-Tamann Law for the isothermal compressibility of liquids (7). This law is

$$-\left(\frac{\partial v}{\partial P}\right)_T = \frac{J}{L + P} \quad (8)$$

where J and L are constants. This law has been found to hold well for most liquids. For example, it holds for methyl, ethyl, propyl, isobutyl, and amyl alcohols, acetone, ethyl ether, ethyl chloride, bromide, and iodide, benzene, chloro-, bromo-, nitro-benzene, aniline, carbon disulfide, phosphorus trichloride, and helium I and II (8). It also holds for solutions such as: ethylene glycol/water and concentrated aqueous sodium chloride and bromide. It has even been shown to hold for solids such as the alkali metals: lithium, sodium, potassium, rubidium, and cesium (9).

The integrated form of this equation

$$(P + L)e^{v/J} = H \quad (9)$$

where H is a constant of integration, gives excellent fit to the P - v curves of many liquids (10) and of the alkali metals (9).

Third: From the Tait-Tamann Law there can be obtained the relationship (11) at the critical point

$$P_c = -L \quad (10)$$

The data necessary to examine this equation are rather sparse. Long extrapolations are necessary; however, in the case of He - 4, a least-squares extrapolation over half the liquid range gives

$$P_c = 2.26 \text{ atm (experimental)}$$

$$P_c = 2.258 \text{ (calculated)}$$

Calculations with other liquids (e.g., ethyl ether) for which the extrapolation is more difficult and for which the data are very scant give results agreeing to about 1/2%.

Fourth: We have calculated the atomic radii of the alkali metals (12). The results of this calculation are shown in Table 2. As can be seen the results that are calculated from compressibility data (P - v) and a knowledge of crystal form (bcc) agree very well with the results from

direct measurement by X-rays. In order to make this calculation we assumed that the free volume was negligible.

Fifth: As mentioned previously the equation of state (Equation 3) can be expanded directly without approximations into the virial equation of state and yields the composition of the various virial coefficients. Hence this equation of state is the closed form of the virial equation of state.

Sixth: A plausible theory of nucleation has been presented (2). Using this theory Brown and Ginell (13) have derived an equation describing the rate of growth of crystals from a glass. Since many of the parameters in the theory are thus far unknown, the equation has been treated as if it were an empirical equation and it was fitted to the available data. In the paper (13) four sets of data were fitted and the fit was excellent. One set of data contained not only values for the rate of crystallization but also for the rate of decrystallization (change from devitrified to vitrified). Even here the fit is excellent.

Conclusion: Like all theory this one is not completely developed. Problems remain to be solved and more comparisons with experimental data need to be made. However at this point I feel that association theory is a logical comprehensive picture of the states of matters and the nature of the transitions from state to state. Further work is in progress to develop this point of view.

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