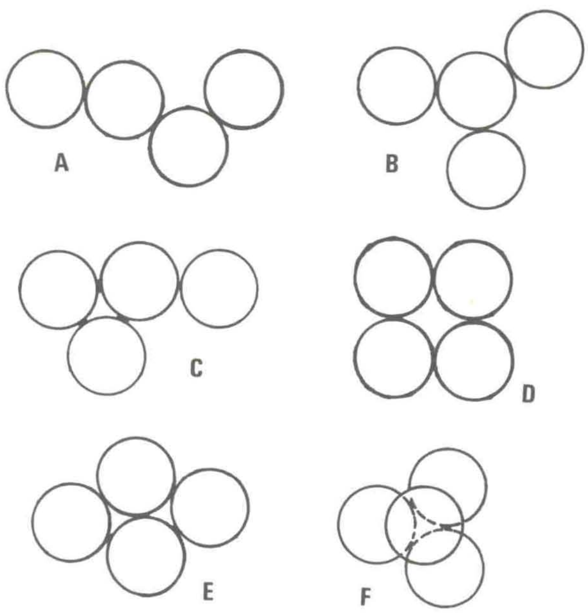

Figure 4. Forms of the 4-mer

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,

$$G_m = б_{m-1} - (m - 1)K_{1,m-1} \qquad (6)$$

The first few virial coefficients are

$$G_2 = B = б_1 - K_2$$

$$G_3 = \{[C - 4K_2 + 3б_1K_2 + б_1^2]/K_2\} = б_2 - 2K_{1,2}$$

$$G_4 = \frac{[D + 20K_2^3 - 18K_2K_3 - K_2^2(14б_1 - 5б_2) - K_2(2б_1б_2 - 5б_1^2) + 5б_1K_3 - б_1^3]}{K_3}$$

$$G_4 = б_3 - 3K_{1,3}$$

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

The fact that the successive $б_x$ 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 $б_x$ and $K_{1,x}$ can be determined for each step successively and in principle, the total б and $\Sigma\ C_j$ 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

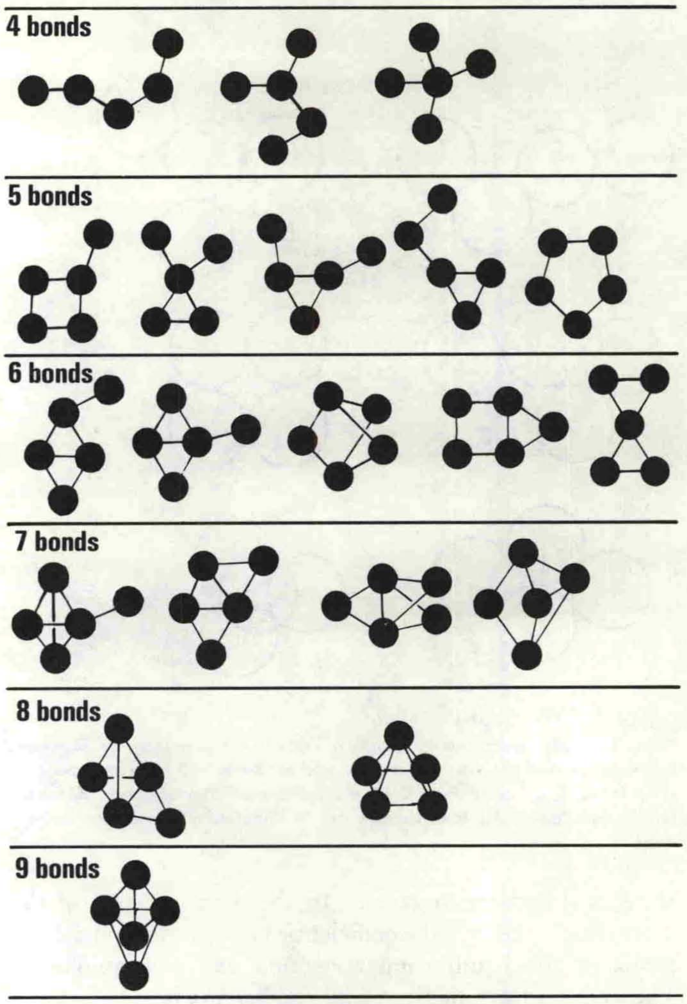

Figure 5. Forms of the 5-mers
Some of these forms are drawn in 3-dimensional projection. Although all the connected unimers really touch, they are shown with bonds joining them to make the spatial relationship clearer

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 $\alpha \geqq 5$.

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