

Figure 2. Collision of a 2-mer and a 1-mer. Partial transfer of kinetic momentum to rotational momentum. If the energy of impact is slight, collision may stop at step C. For a collision a little higher in energy, termination step may be step D. Step D is in equilibrium with step C and molecule will alternately have structure D and C. (A) approach; (B) collision: formation of first bond; (C) formation of second bond due to rotation (may stop at this stage); (D) degradation: breaking first bond. (Energy of collision too great to stop at C but may stop at this stage and oscillate between C and D); (E) complete degradation: breaking of second bond: (likelihood good that some rotational momentum remains, in part, in the molecule).

tum of the particles. Since every collision, except a direct line collision (Figure 1) results in the transfer of some of the kinetic momentum into rotational momentum, there is time for additional bonds to form. From geometric concepts, direct line collisions are rare, hence extra bonds are usually formed (see Figure 2). This means that as higher  $j$ -mers form, they tend to be more complex in terms of the number of bonds that an individual atom shares. The situation in the case of the formation of the 4-mer from the 3-mer and the 1-mer is shown in Figure 3. Here the 3-mer is triangular, and the rotation momentum of the 4-mer forces the formation of first, 1 additional bond and then 2 additional bonds. We would refer to such a bonding type as three-hole bonding (3-hole) since the triangular array of the 3-mer forms a hole bounded by 3 atoms. The breakup of such a bonded arrangement is simple. The bond was formed one bond at a time and breaks up one bond at a time. If we consider the energy of formation of a single bond to be the same, no matter where it occurs, and this is a plausible assumption at least as a first approximation, then the formation of a 3-hole bond consists of a series of three equally energetic steps while the reverse reaction of breakup of a 3-hole bond consists of the same three steps.

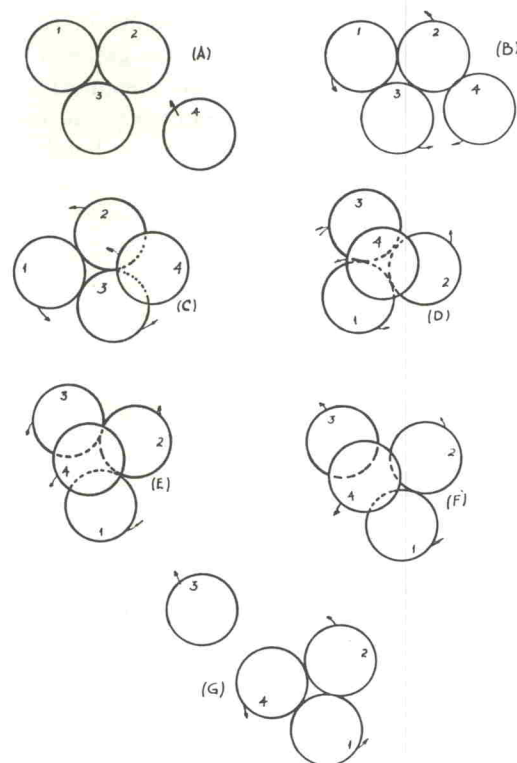


Figure 3. Bond formation in a 3-hole molecule: (A) approach; (B) first bond forms; (C) second bond forms; (D) third bond forms; (E) first bond breaks; (F) second bond breaks; (G) third bond breaks (departure). Process may stop at any of several stages. Transfer of kinetic momentum to rotational momentum most likely. Most stable structure (least energy) is D. The stages that are gone through and the amount of energy transferred depends largely on the quantity of energy in the collision and the exact geometry of the collision.

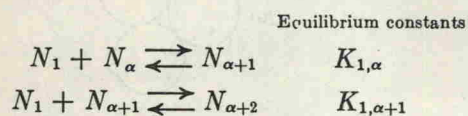
As the temperature is lowered and still higher compact forms have time to form,  $j$ -mers with 4 and 5 holes appear. The behavior of such bonds is in one way similar and in another way quite different from the formation of 3-hole bonds. In the formation of 4-hole bonds, the energy of the first step and the second step (Figure 4) is the same as in the 3-hole bond. However, the third step is different. In the 4-hole bond two bonds are formed simultaneously in the third step, while in the 3-hole bond only one bond is formed. The important difference is when we consider the process of breakup. In the 4-hole bond the first step demands that 2 bonds be broken simultaneously. This is energetically more difficult than breaking one bond. Hence energetics favor the 4-hole bond. It is more stable than the three-hole bond. In the 5-hole bond the stability of the bond increases still more, since 3 bonds are formed in the last step. Similar reasoning holds for the 6- and higher hole bonds. We call such highly stable particles multiply bonded structures. As the temperature of the gas is lowered, the point is reached where such multiply bonded structures start forming. Since they are more stable, they rapidly drain the gas of simply bonded



structures. Shortly this process results in the depletion of the simply bonded  $j$ -mers in the gas, and first the 2-mer and then the 3-mer and 4-mer disappear from the gas. The concentration of 1-mers is also decreased at this time. At this point where multiply bonded structures form there is an extra release of energy due to their formation. This compensates for the uniform dropping of the temperature, and a halt in the temperature drop ensues while the multiply bonded  $j$ -mers for either the liquid or the solid are forming. The fact that the species, 2-mer, 3-mer, etc. go to zero concentration results in a breakdown of the mathematics of the continuous case and results in a gap, giving rise to the discontinuous case.

### Mathematical Derivation

The problem is now to put these ideas into mathematical form. For simplicity we shall consider the case where a gap exists between the 1-mers and the  $\alpha$ -mer where  $\alpha$  is some larger number. The general reactions existing are



$$N_1 + N_{m-1} \rightleftharpoons N_m \quad K_{1,m-1}$$

$$N_1 = N_1$$

$$N_j = 0 \quad 2 \leq j < \alpha$$

$$= N_j \quad \alpha \leq j \leq m$$

$$= 0 \quad m < j$$

where  $N_j$  = number of moles of particles of size  $j$  in a mass of substance of  $w$  grams.

The kinetic equations<sup>2</sup> or equilibrium equations<sup>8</sup> are the same as for the continuous case (where all species are present) as is the solution, if certain definitions are modified. In Table I are to be found the equations and definitions for both the continuous case and the discontinuous case (gap exists). As can be seen from the table, the discontinuous case can be considered a singular case of the continuous case; a case where  $K_x$  becomes zero as soon as any one of the species disappears, or better, the continuous case can be considered a special case of the discontinuous case where  $\alpha = 1$ . As can be seen, the discontinuous case reduces to the continuous case when  $\alpha = 1$ .

**Equation of State.** The derivation for the equation of state does not change, and the equation of state for both cases is

$$P(1 - B/v) = CRT \quad (1)$$

where  $C$  is  $\sum_1^m C_x$  and  $B/v = \sum_1^m B_x C_x$  where  $B_x$  is the

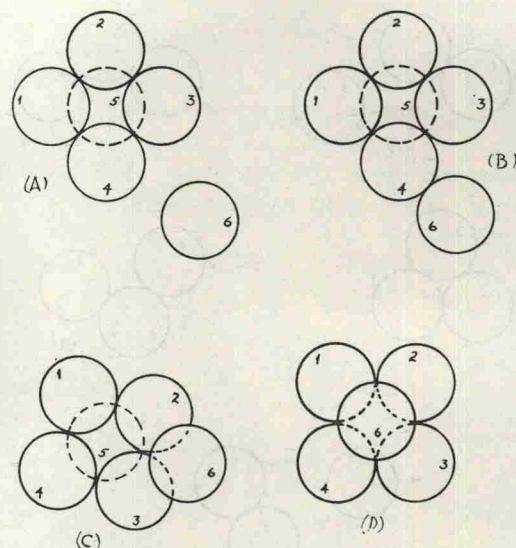


Figure 4. Bond formation in a 4-hole molecules: (A) approach; (B) first bond forms; (C) second bond forms; (D) third and fourth bonds form simultaneously. Degradation in reverse order. 2 bonds breaking simultaneously is the first step. Atom 5 as shown is necessary since without atom 5 the square planar structure of 1, 2, 3, 4 is not stable to kinetic forces and will rearrange to a tetrahedral structure. In a collision of this sort kinetic momentum is transferred to rotational momentum. Loss of this energy may be by the same mechanism or by colliding with a more complex  $j$ -mer.

covolume of a mole of  $x$ -mers. Hence this equation of state is valid for gases, liquids, and solids.

**The Compressibility Equation.** The point where the serious changes occur is in the equations derived from the compressibility equation. If one takes the derivative of the equation of state (eq 1) at constant temperature and rearranges it, one has

$$-\frac{dv}{dP} = \frac{u \frac{du}{dv}}{\left(-RT \frac{dC}{dv} \frac{du}{dv}\right) + P} \quad T = \text{constant} \quad (2)$$

where  $u = (1 - B/v)$ , letting

$$u \frac{du}{dv} = J \quad (3)$$

and

$$\frac{-RTdC}{dv} \frac{du}{dv} = L \quad (4)$$

one has

$$-\frac{dv}{dP} = \frac{J}{L + P} \quad T = \text{constant} \quad (5)$$

If  $J$  and  $L$  are constant with pressure changes then the equation is identical with the so-called Tait equation. We say so-called Tait equation because as explained by