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Statistical processes of aggregation and polymerization

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Abstract. We study processes in which units (particles) associate into clusters, which are then also capable of dissociation. Such processes are discussed generally in section 2, where a stochastic kinetic equation (10) is proposed which bridges the gap between the conventional kinetic equations (8) and the statistical equilibrium concept of the Gibbs distribution.

In section 4 we consider the equilibrium behaviour of a process for which the association rate of two units which are already bound to j and k other units respectively has the form (21). This is very much more general than the equi-reactive bond model usually discussed. The principal results are given in Theorem 1; from a single pair of equations (28) and (29) based on the H_j of (21) one can determine critical points, expected number of bonds, the distribution and moments of cluster size, and most other quantities of interest. This is without reference to any other consideration, such as kinetic or stoichiometric relations.

Some particular cases are worked through in section 5. The classic Flory–Stockmayer results for units with f equi-reactive sites are obtained systematically and economically, with all parameters in terms of physically given quantities. Another type of example seems to indicate the existence of a second critical point.

Corresponding results for the case of several types of unit are stated and illustrated in section 6.

1. *Introduction.* We are concerned with processes in which some few elementary types of particle associate according to definite statistical rules to form aggregates, or clusters, these aggregates being then also capable of dissociation. Such processes have been extensively studied in connexion with the polymerization of organic molecules (see Flory (6) for the standard review of this wide subject) virus-antibody agglutination, or the precipitin reaction (Goldberg (7) and (8), Watson (20)) and the so-called 'cluster-theory' of imperfect gases and of liquids (Mayer and Mayer (14), Band (1)).

The process is a more special one than that constituted by a set of interacting particles in that, (i) interparticle forces are assumed to be short-range, so that one has only to consider the existence or non-existence of a bond; (ii) spatial relationships are neglected; in the first approximation the only relationships are those of belonging to the same cluster and of being ordered in some way within this cluster; (iii) cyclic configurations are excluded; that is, no two particles in a cluster can be connected by more than one sequence of bonds, so that the cluster forms a tree rather than a general connected

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graph. However, even with these limitations the process can show interesting co-operative effects, such as condensation (or 'gelation' to use the polymer chemistry term) and provide realistic models for the applications mentioned above.

The fact that the most fully developed application is certainly that of polymer chemistry makes it natural to use the chemical terminology, although in fact our interest is more general than this. Thus, we shall speak of a 'unit' rather than of a particle, and a cluster of one, two, or r units will be termed a monomer, dimer, or r-mer. Occasionally a cluster needs several quantities $r_0, r_1, r_2, \ldots$, for its full description; in such cases it is still convenient to use the term $\mathbf{r}$-mer, with $\mathbf{r}$ understood as a vector. The number of units in the $\mathbf{r}$-mer will still be denoted by r. A unit which can form up to f bonds with other units will be termed f-functional (with f also occasionally to be understood as a vector). The f latent bonds of a unit are sometimes called 'functionalities'; we shall use the simpler term 'site'. The first discontinuous change of state reached as association effects become stronger (corresponding to condensation of a gas to a liquid) will be termed 'gelation', for consistency.

The very successful Flory theory of polymerization was based upon the assumption of 'equi-reactivity', i.e. that the tendency of any given site to form a bond (or, presumably, to break from an existing bond) was uninfluenced by the extent to which other sites on the same or other units had reacted. We shall be much less restrictive and shall assume, in effect, that the potential energy of a unit depends in an arbitrary fashion on the numbers of direct bonds the unit has formed with other units, account being taken in section 6 of the fact that there may be several different types of unit.

Another feature of the Flory theory is the use of the concept 'extent of reaction', i.e. of the proportion of sites of different types that have reacted. This is used as a parameter (or parameters) of the process, and the expected distribution of cluster sizes calculated in terms of it, by maximizing the Gibbs distribution subject to the requirement that the total numbers of units and the extents of reaction have given values. Since the expected extents of reaction can often be calculated as functions of time from kinetic theory, it is then considered that one has determined the cluster size distribution as a function of time.

This seems very like treatment of a non-equilibrium situation by appeal to an equilibrium concept; the Gibbs distribution. The approach may well be valid in a limiting sense, i.e. when the number of units is so large that the proportions of the different $\mathbf{r}$-mers follow virtually deterministic paths. For a finite collection of units it will not in general be true, however, that statistical distributions for a non-equilibrium situation can be derived by conditioning an equilibrium situation; and certainly not for arbitrary initial conditions.

Although the point can doubtless be covered, we shall avoid it by considering only equilibrium conditions. If we allow dissociation then the equilibrium configuration is non-trivial, and 'extent of reaction' becomes meaningful as a measure of the position of balance between association and dissociation, which will shift with varying concentrations and temperature.

A tool that has been used with considerable success is the statistical theory of branching, or cascade, processes (for general references see (3) and (13)). This is the

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theory of processes in which a number of first-generation individuals independently produce progeny which constitute a second generation, these then reproduce independently and according to the same rules, and so on. That some of the distributions occurring in polymer work could be explained by simple processes of this type has been vaguely recognized for some time; Watson ((20)) made the idea explicit in his treatment of the precipitin reaction. However, the concept was first fully explored in a paper by Gordon ((12)). Gordon treats the equi-reactive case, with several types of unit and obtains very direct and simple determinations of the sol-fraction equations, and the critical points. This line has been continued by Good ((11)).

The branching process analysis is suggestive and effective, but its validity has not yet been demonstrated. It is far from self-evident that distributions, etc., calculated from branching considerations will be consistent with those provided by the Gibbs distribution or from the kinetic equations.

This paper began in fact as an attempt (successful) to demonstrate the mutual consistency of these various approaches, and to calculate the parameters of the branching process in terms of quantities which are given physically. However, it gradually became evident that much more general cases than that of equi-reactivity could be treated, concisely and explicitly, and that the branching process technique amounted simply to a disguised treatment of certain combinatorial problems, with an interpretation which, although graphic, could only be carried a certain distance.

For this reason, very little remains in the paper of branching processes.

2. *Methods of specification of an aggregation process.* There are two basic methods: use of the Gibbs distribution, and of the kinetic equations. To those a third will be added below: use of a 'stochastic' kinetic equation (10).

Let $n_{\mathbf{r}}$ be the number of $\mathbf{r}$-mers in a volume V, and let $\epsilon_{\mathbf{r}}$ be the potential energy of an $\mathbf{r}$-mer (this being the 'internal' potential energy, since we suppose that this does not vary with position in space, and that there is no interaction between $\mathbf{r}$-mers). Then, if V is part of a statistically homogeneous infinite volume (i.e. the system is an 'open' one), it follows from the classical Gibbs distribution (see, for example, (1), page 25) that in equilibrium

$$E(n_{\mathbf{r}}) = c_{\mathbf{r}} = \kappa_{\mathbf{r}} W_{\mathbf{r}} \exp(-\epsilon_{\mathbf{r}}/kT), \tag{1}$$

where E is the expectation operator, $W_{\mathbf{r}}$ is a combinatorial factor expressing the number of distinct configurations which lead to an $\mathbf{r}$-mer, and $\kappa_{\mathbf{r}}$ depends on parameters such as the volume density of the different types of unit.

Indeed, it follows further from the Gibbs distribution (see (1), page 321) that the $n_{\mathbf{r}}$ are independent Poisson variables, so that they have joint probability generating function

$$\Pi(\mathbf{z}) = E(\prod_{\mathbf{r}} z_{\mathbf{r}}^{n_{\mathbf{r}}}) = \exp[\Sigma c_{\mathbf{r}}(z_{\mathbf{r}} - 1)]. \tag{2}$$

This result is contingent upon statistical homogeneity, and so is only possible before gelation (condensation) as we shall see in another way later (Appendix B).

The difficulty in this approach is the calculation of the combinatorial coefficients $W_{\mathbf{r}}$; also, to some extent, the summation of series such as $\Sigma c_{\mathbf{r}}$, $\Sigma n_{\mathbf{r}} c_{\mathbf{r}}$ which are required in subsequent work.

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The Gibbs distribution is one consequence of the assumption of a potential energy; an even stronger consequence is the principle of detailed balance (see, for example, (15), page 296). Let an $\mathbf{r}$-mer be denoted $A_{\mathbf{r}}$; consider the reaction

$$A_{\mathbf{r}} + A_{\mathbf{s}} \rightleftharpoons A_{\mathbf{u}}. \tag{3}$$

According to the principle of detailed balance, in equilibrium this individual reaction will itself balance (over any V), so that the expected total rates of reaction to right and left are equal.

Thus, suppose that the reaction (3) proceeds to the right (association) at rate $\lambda_{\mathbf{rsu}}$ for a given individual $A_{\mathbf{r}}$ and $A_{\mathbf{s}}$, so that the total rate is $\lambda_{\mathbf{rsu}} n_{\mathbf{r}} n_{\mathbf{s}}$ for $\mathbf{r} \neq \mathbf{s}$, and $\frac{1}{2}\lambda_{\mathbf{rru}} n_{\mathbf{r}}(n_{\mathbf{r}} - 1)$ for $\mathbf{r} = \mathbf{s}$. Let the corresponding dissociation rate for a given $A_{\mathbf{u}}$ be $\mu_{\mathbf{rsu}}$, so that the total rate is $\mu_{\mathbf{rsu}} n_{\mathbf{u}}$. We distinguish the order of $\mathbf{r}$ and $\mathbf{s}$ in dissociation, so that the total dissociation rate in (3), neglecting the order of $\mathbf{r}$ and $\mathbf{s}$ is $(\mu_{\mathbf{rsu}} + \mu_{\mathbf{sru}}) n_{\mathbf{u}}$ $(r \neq \mathbf{s})$ or $\mu_{\mathbf{rru}} n_{\mathbf{u}}$ $(r = \mathbf{s})$. If the reaction (3) is an impossible one, then all these rates are zero.

For reaction (3) the principle of detailed balance leads to the conclusion

$$\lambda_{\mathbf{rsu}} c_{\mathbf{r}} c_{\mathbf{s}} = (\mu_{\mathbf{rsu}} + \mu_{\mathbf{sru}}) c_{\mathbf{u}}. \tag{4}$$

To see this, note first that $c_{\mathbf{r}}$ and $\lambda_{\mathbf{rsu}}$ will be volume dependent, the dependence taking the form

$$c_{\mathbf{r}} = \gamma_{\mathbf{r}} V, \tag{5}$$

$$\lambda_{\mathbf{rsu}} = \frac{\nu_{\mathbf{rsu}}}{V}. \tag{6}$$

The representation (5) is obvious from the definition of $c_{\mathbf{r}}$, while (6) follows from the fact that $\lambda_{\mathbf{rsu}}$ must be proportional to the frequency of encounter between a given $A_{\mathbf{r}}$ and $A_{\mathbf{s}}$, which will be $O(V^{-1})$.

Consider now the detailed balance relation for reaction (3) in an infinitesimal volume δV. The probability of an $A_{\mathbf{r}}/A_{\mathbf{s}}$ encounter in the volume is, by the Poisson distribution (2),

$$\exp[-(\gamma_{\mathbf{r}} + \gamma_{\mathbf{s}})\delta V](\gamma_{\mathbf{r}}\delta V)(\gamma_{\mathbf{s}}\delta V) = \gamma_{\mathbf{r}}\gamma_{\mathbf{s}}(\delta V)^2 + o(\delta V)^2$$

if $\mathbf{r} \neq \mathbf{s}$, and $\qquad \exp(-\gamma_{\mathbf{r}}\delta V)\,\frac{1}{2}(\gamma_{\mathbf{r}}\delta V)^2 = \frac{1}{2}(\gamma_{\mathbf{r}}\delta V)^2 + o(\delta V)^2$

otherwise. Similarly, the probability that an $A_{\mathbf{u}}$ will be present in the volume is $\gamma_{\mathbf{u}}\delta V + o(\delta V)$. Equating the total reaction rates we have then

$$\frac{\nu_{\mathbf{rsu}}}{\delta V}\gamma_{\mathbf{r}}\gamma_{\mathbf{s}}(\delta V)^2 = \gamma_{\mathbf{u}}(\mu_{\mathbf{rsu}} + \mu_{\mathbf{sru}})\delta V + o(\delta V),$$

whence

$$\nu_{\mathbf{rsu}}\gamma_{\mathbf{r}}\gamma_{\mathbf{s}} = (\mu_{\mathbf{rsu}} + \mu_{\mathbf{sru}})\gamma_{\mathbf{u}}. \tag{7}$$

This is equivalent to (4) which will play a central role in succeeding sections.

The kinetic approach could be characterized as follows: the $n_{\mathbf{r}}$ are considered to be so large that they can be regarded as continuous variables which obey the deterministic relations

$$\frac{dn_{\mathbf{u}}}{dt} = \tfrac{1}{2}\sum_{\mathbf{r}}\sum_{\mathbf{s}}(\lambda_{\mathbf{rsu}} n_{\mathbf{r}} n_{\mathbf{s}} - \lambda_{\mathbf{usr}} n_{\mathbf{u}} n_{\mathbf{s}} - \lambda_{\mathbf{rus}} n_{\mathbf{r}} n_{\mathbf{u}}) + \sum_{\mathbf{r}}\sum_{\mathbf{s}}(\mu_{\mathbf{usr}} n_{\mathbf{r}} + \mu_{\mathbf{rus}} n_{\mathbf{s}} - \mu_{\mathbf{rsu}} n_{\mathbf{u}}). \tag{8}$$

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(Since the n_r are regarded as large, we have written $\frac{1}{2}n_r^2$ in the equation, where we might otherwise have written $\frac{1}{2}n_r(n_r-1)$.) The approach is more general than the previous one in that it allows time dependence; less general in that the random character of the variables is lost.

There is a relation between the two approaches, however; if a potential energy is definable, so that the rates λ and μ are consistent with a set of relations (4), then equations (8) will have an equilibrium solution $n_r = c_r$. This solution will not in general be unique. Consider, for example, the case when one is dealing with simple **r**-mers made up of a single kind of unit, so that reaction (3) is permissible only if $u = r+s$. If relations (4), regarded as a set of equations for the c_r, have a solution $c_r = \omega_r$, then

$$c_r = \omega_r \theta^r \tag{9}$$

is also a solution, where θ is an arbitrary parameter whose value will usually be adjusted to give the correct volume-density of units.

Expression (9) will actually constitute the *general* solution of (4) if, for any **r** for which an A_r can physically exist, there is a sequence of reactions by which the A_r can dissociate to r single units, and conversely. For there will then be a sequence of relations (4) which will determine c_r in terms of the single unit c, so that the set of solutions of (4) depends only upon a single parameter.

In this situation any possible grouping of a set of N units can be reached from any other possible grouping, whatever N. A process for which this is so will be termed *irreducible*. The concept of irreducibility can be weakened somewhat further, but only at an unwarranted expense in simplicity.

The indeterminacy in the solution (9) could be attributed to the fact that r is in this case an additive invariant of the reaction (3). In general, if the first k elements $r_1, r_2, \ldots, r_k$ of **r** each correspond to an additive invariant of the reaction, then to any solution $c_r = \omega_r$ of (4) corresponds a more general solution

$$c_r = \omega_r \theta_1^{r_1} \theta_2^{r_2} \ldots \theta_k^{r_k}.$$

This will again be the general solution if the process is irreducible; the appropriate extension of the definition of irreducibility given previously generally being evident.

In order to restore the statistical character of the kinetic process, it is natural for a probabilist to reinterpret the rates λ and μ as *probability intensities of transition* (Bartlett (2), page 50, Parzen (16), page 277). With this interpretation one can establish, either directly or by using the Bartlett formalism ((2), page 83), that the relations (8) have as stochastic analogue a partial differential equation for the p.g.f. of the n_r;

$$\frac{\partial \Pi}{\partial t} = \tfrac{1}{2} \sum_{\mathbf{r}} \sum_{s} \sum_{\mathbf{u}} (z_u - z_r z_s) \left(\lambda_{rsu} \frac{\partial^2 \Pi}{\partial z_r \partial z_s} - 2\mu_{rsu} \frac{\partial \Pi}{\partial z_u} \right). \tag{10}$$

For those unfamiliar with these methods, equation (10) is derived in Appendix A.

As derived this equation has no basis in statistical mechanics, but it is certainly a natural analogue of (8), and is consistent with both the Gibbs and the kinetic approaches. To see this, note that if c_r is a solution of (4), then (2) is certainly an equilibrium solution of (10), so that (10) is consistent with the Gibbs distribution. It is

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consistent with the kinetic equations (8) almost by construction; the exact relation is that (8) still holds with n_r, $n_r n_s$ and n_r^2 replaced by

$$E(n_r), \quad E(n_r n_s) \quad \text{and} \quad E(n_r^2 - n_r) \quad \text{respectively} \quad (\mathbf{r} \neq \mathbf{s}).$$

If we regard relations (4) as a set of equations for the c_r, then from their general solution one can generate the general equilibrium solution of (12). (We restrict ourselves to processes which are irreducible, and subject to the law of detailed balance.) For example, let us return to the simple **r**-mer case, when (9) is the general solution of (4). Then (10) will have an equilibrium solution

$$\Pi(\mathbf{z}) = \int \phi(\theta) \exp(\Sigma \omega_r \theta^r z_r)\, d\theta, \tag{11}$$

where the integral may include complex θ values. That this is indeed the *general* solution may be seen by the following argument. First, on account of irreducibility the equilibrium distribution is unique in that it is fully determined once the distribution of the total number of units $N = \Sigma r n_r$ has been prescribed. (In fact, for fixed N the process is irreducible in the Markov sense; see (5), page 350.) If $\phi(\theta)$ can be chosen in (11) such that N has the prescribed distribution, then (11) does indeed represent the general equilibrium solution. Note that the p.g.f. of N is

$$\Phi(\zeta) = [\Pi(\mathbf{z})]_{z_r = \zeta^r} = \int \phi(\theta) \exp[\Sigma \omega_r (\theta\zeta)^r]\, d\theta. \tag{12}$$

Now, consider the case when N has a fixed value, so that $\Phi(\zeta) = \zeta^N$. The integral in (12) must thus effectively select the coefficient of θ^N in $\exp[\Sigma \omega_r (\theta\zeta)^r]$ and multiply it by a constant such that the result is unity when $\zeta = 1$. We can thus write (11) for this particular case as

$$\Pi(\mathbf{z}) = \frac{\oint \exp(\Sigma \omega_r \theta^r z_r)\, \theta^{-N-1}\, d\theta}{\oint \exp(\Sigma \omega_r \theta^r)\, \theta^{-N-1}\, d\theta}, \tag{13}$$

where the integration contour encircles the origin in the complex θ-plane, but no singularities of $\omega(\theta) = \Sigma \omega_r \theta^r$ (if this is possible). Expression (13) thus represents the unique equilibrium p.g.f. for the case $\Sigma r n_r = N$, and the case of randomly distributed N can be generated from it.

Another interesting special case of solution (11) is the simple one

$$\Pi(\mathbf{z}) = \exp[\Sigma \omega_r \theta^r (z_r - 1)], \tag{14}$$

corresponding exactly to (2).

It is shown in Appendix B that this describes the equilibrium distribution of numbers in an open uncondensed system. If the expected number of units in V is N, then θ will be determined by the equation

$$\Sigma r \omega_r \theta^r = N \tag{15}$$

(see Appendix B).

Usually expression (13) can only be evaluated by some method such as that of steepest descents. It follows from (6), (5) and (9) that the ω_r will be proportional to V,

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and so to N if N and V are varied subject to constant density, $N/V = \rho$. Thus, the integrands of (13) are exponential in N, and the method of steepest descents seems applicable for N large. Equation (15) essentially locates the saddle-point of the lower integral; that of the upper integral would be located by a similar equation with $\omega_r z_r$ substituted for ω_r. However, if one is interested only in expectation values, then these will be given asymptotically by

$$c_r = \omega_r \theta^r,$$

where θ is determined by (15).

At least, this is so before gelation occurs, a phenomenon which comes about analytically as follows. Normally the function $\omega(\theta)$ and its derivatives will have a finite positive radius of convergence, say θ_0. If $\lim_{\theta \uparrow \theta_0} \omega'(\theta) = \infty$, then equation (15) will always have a solution, which approaches the value θ_0 from below as N increases, but never attains it.

However, if $\lim_{\theta \uparrow \theta} \omega'(\theta) < \infty$ (as will often happen if θ_0 is a branch point of $\omega(\theta)$, rather than a pole) then the value θ_0 is attained in (15) for a finite N, and after that point there is strictly no θ solution. This corresponds to the occurrence of gelation, which is brought about when the density crosses the critical value corresponding to a solution θ_0 of (15).

A rigorous discussion of the statistics of the condensed phase (i.e. once gelation has occurred) must be based upon a consideration of the closed system, and expression (13).

The branch point in $\omega(\theta)$ often stems from the fact that $\omega(\theta)$ is determined implicitly as the root of an equation; the critical value $\theta = \theta_0$ is that at which the equation for ω develops a multiple root. (Consider, for example, the determination of θ from the pair of equations (54), (55).)

The kinetic approach, either in the deterministic form (8) or the stochastic form (10), presents one considerable difficulty. This lies in the determination of the coefficients λ_{rsu} and μ_{rsu}, particularly the latter. In order to calculate μ_{rsu} one must determine the number of ways in which an A_u can dissociate into an A_r and an A_s. This is a combinatorial problem of almost exactly the same degree of difficulty as the determination of the terms W_r in (1), which are required for specification of the Gibbs distribution.

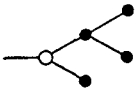
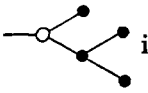
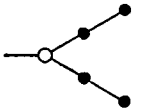
3. *Some auxiliary results.* All the combinatorial results are immediately related to the enumeration of trees, and we use the following generating function (g.f.) approach.

Consider the 'rooted tree' obtained by taking an existing bond, and considering the cluster lying to one particular side of the bond. Denote a unit which is bound to j other units by a_j. Let $U(x_1, x_2, \ldots) = U(\mathbf{x})$ be the g.f. of such trees, in that the coefficient of $\prod_1^\infty x_j^{r_j}$ is the number of trees with r_j a_j's ($j = 1, 2, \ldots$). Then $U(\mathbf{x})$ obeys the equation

$$U(\mathbf{x}) = \sum_{j=1}^{\infty} x_j U(\mathbf{x})^{j-1}, \tag{16}$$

as can be seen by considering whether the first unit is an a_j ($j = 1, 2, \ldots$; it cannot be an a_0 as it is known to have at least one satisfied bond), and noting that it will then have $j-1$ distinct further trees rooted in it. $U(\mathbf{x})$ must be the root of (16) which tends to zero with the x's, and so will be the smallest root if the x's are sufficiently small.

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Note that the trees are *ordered* trees rather than *free* trees (see (19), page 125). That is, a tree such as  is considered as distinct from  in that the two configurations together contribute $2x_1^3x_3^2$ to U, whereas for a free tree the joint contribution would be simply $x_1^3x_3^2$. A configuration such as  contributes $x_1^2x_2^2x_3$ in either case. The appropriateness of the ordered version for our purposes will be explained after equation (40).

The actual coefficients in the expansion of $U(\mathbf{x})$, or in any sufficiently regular function of it, $F[U]$, can be determined by Lagrange's expansion. In fact,

$$F[U(\mathbf{x})] = \frac{1}{2\pi i}\oint \frac{F(z)[1-\Sigma(j-1)x_jz^{j-2}]dz}{z-\Sigma x_jz^{j-1}}, \tag{17}$$

if $F(z)$ is regular in a region containing the smallest root of the denominator in the integrand, where the integration contour encircles just this root. If this region can be extended to a circle centred at the origin, then one can expand in powers of the x's under the integral, For example, in the case $F[U] = U^s$ we have

$$\begin{aligned} U_s(\mathbf{r}) &= \text{coefficient of } \prod_j x_j^{r_j} \text{ in } U(x)^s \\ &= \text{coefficient of } \Pi x_j^{r_j} \text{ in } \frac{1}{2\pi i}\oint [1-\Sigma(j-1)x_jz^{j-2}] \sum_{k=0}^{\infty} (\Sigma x_jz^{j-1})^k z^{s-k-1}dz \\ &= \frac{r!}{\Pi r_j!}\left[1-\frac{1}{n}\Sigma(j-1)r_j\right]\frac{1}{2\pi i}\oint z^{\Sigma(j-1)r_j+s-r-1}dz \\ &= \frac{(r-1)!\,s}{\prod_1^{\infty} r_j!}\delta_{\Sigma jr_j-2r+s}. \end{aligned} \tag{18}$$

Here $r = \Sigma r_j$.

An extremely useful result is a multivariate extension of Lagrange's expansion, due to Good ((10)) which we quote:

If $\zeta_j = u_j/f_j(\mathbf{u})$, *where* $f_j(\mathbf{u})$ *is analytic in a neighbourhood of the origin and*

$$f_j(0) \neq 0 \quad (j = 1, 2, \ldots, n),$$

and $F(\mathbf{u})$ *is meromorphic in a neighbourhood of the origin, then the coefficient of* $\zeta_1^{m_1}\ldots\zeta_n^{m_n}$ *in* $F[u(\zeta)]$ *is equal to that of* $u_1^{m_1}\ldots u_n^{m_n}$ *in*

$$F(\mathbf{u})\prod_j f_j(\mathbf{u})^{m_j}\det\left[\delta_{jk}-\frac{u_j}{f_j(\mathbf{u})}\frac{\partial f_k(\mathbf{u})}{\partial u_j}\right]. \tag{19}$$

Finally, although we make very little use of branching process theory, it is worthwhile defining two basic probability generating functions (p.g.f.'s), $G_0(z)$ and $G_1(z)$.

Suppose one selects a unit at random; $G_0(z)$ is the p.g.f. of the number of units directly bound to it. Suppose one selects a bond at random and then a unit connected

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to it; $G_1(z)$ is the p.g.f. of the number of *further* bonds attached to the unit. If these p.g.f.'s have expansions $\Sigma g_{0j}z^j$, $\Sigma g_{1j}z^j$ then it follows from the method of sampling that

$$g_{1,j-1} = \text{const.}\, jg_{0j},$$

so that

$$G_1(z) = \frac{G_0'(z)}{G_0'(1)}. \tag{20}$$

This consistency relation does not seem to have always been observed; some authors have proposed formulae in conflict with it (although relation (20) appears explicitly in an unpublished manuscript communicated to me by Dr M. Gordon).

4. *General results; one type of unit.* We shall relax the assumption of equi-reactivity by abandoning the idea of sites altogether, and postulating that: (i) all bonds have the same probability intensity of dissocation, μ; but (ii) a given unrelated a_j and a_k have probability intensity of mutual association of the form

$$\lambda \frac{H_{j+1}H_{k+1}}{H_jH_k}. \tag{21}$$

By 'unrelated' we mean that the two units lie in distinct clusters.

Postulates (i) and (ii) together with the detailed balance relations imply that a configuration of N units in which there is a total of N_j a_j's ($j = 0, 1, 2, \ldots$) has a probability proportional to $\prod_j H_j^{N_j}$ (the proportionality factor will be a complicated combinatorial term, to determine it is the essence of the problem!). Since by the Gibbs distribution this probability will also be proportional to $\exp(-\epsilon/kT)$, where ϵ is the potential energy of the configuration, we see that $-kT\log H_j$ is the potential energy of an a_j. The function H_j is allowed to vary arbitrarily with j, but the variation is to affect rates of association rather than of dissociation. This rather irksome requirement could probably be relaxed; the reason for it will emerge later.

We now classify an $\mathbf{r}$-mer by the number of a_j's it contains ($j = 0, 1, 2, \ldots$); the subscript $\mathbf{r}$ in $n_\mathbf{r}$, $c_\mathbf{r}$, etc., will be assumed to contain all this information. If we can determine the $c_\mathbf{r}$'s, then in virtue of (2) or (13) we have virtually solved the problem of the determination of the probability distribution of the $n_\mathbf{r}$'s.

Define the two functions

$$H(\xi) = \sum_0^\infty \frac{H_j\xi^j}{j!}, \tag{22}$$

$$H^*(\xi) = \sum_0^\infty \frac{H_jx_j\xi^j}{j!}, \tag{23}$$

and set

$$\kappa = \mu/\lambda. \tag{24}$$

We shall also use a notation

$$S[f(\mathbf{r})] = \sum_\mathbf{r} c_\mathbf{r} f(\mathbf{r}), \tag{25}$$

so that $S[f(\mathbf{r})]/S[1]$ would be the expected value of the random function, $f(\mathbf{r})$, of a cluster.

The results of this section are summarized in the following theorem. They are asserted for the non-gelation region, although some of them may hold beyond it.

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THEOREM. (i)

$$c_r = \begin{cases} \kappa\theta H_0 & (r=1) \quad (26a) \\ \kappa v_r \theta^r \prod_{j=1}^{\infty} \left[\frac{H_j}{(j-1)!}\right]^{r_j} & (r>1) \quad (26b) \end{cases}$$

where

$$v_r = \frac{(r-2)!}{\prod_1^{\infty} r_j!} \delta_{\Sigma j r_j - 2r + 2}, \tag{27}$$

and θ is determined by the solution of the equations

$$N = \kappa\theta H(\xi), \tag{28}$$

$$\xi = \theta \frac{\partial H(\xi)}{\partial \xi}, \tag{29}$$

corresponding to the smallest ξ root.

(ii) *The weight average number of bonds is*

$$\frac{S[r(r-1)]}{S[r]} = \frac{2}{1-\psi}, \tag{30}$$

where

$$\psi = \theta \frac{\partial^2 H(\xi)}{\partial \xi^2}, \tag{31}$$

the value of ξ being that determined in (i), *and gelation sets in when $\psi > 1$.*

(iii) *The expected number of bonds is*

$$S[r-1] = \tfrac{1}{2}\kappa\xi^2. \tag{32}$$

(iv) *If ξ^* is determined by the smallest root of*

$$\xi^* = \theta \frac{\partial H^*(\xi^*)}{\partial \xi^*}, \tag{33}$$

then the generating function of the weight distribution is

$$S\left[\prod_0^{\infty} x_j^{r_j}\right] = \kappa\theta H^*(\xi^*) - \tfrac{1}{2}\kappa(\xi^*)^2, \tag{34}$$

and this is partitionable into the 'unit number' and the 'bond number' g.f.'s:

$$S[r \Pi x_j^{r_j}] = \kappa\theta H^*(\xi^*), \tag{35}$$

$$S[(r-1)\,\Pi x_j^{r_j}] = \tfrac{1}{2}\kappa(\xi^*)^2. \tag{36}$$

(v) *These results are consistent with those for a branching process for which*

$$G_0(z) = \frac{H(\xi z)}{H(\xi)}, \tag{37}$$

$$G_1(z) = \frac{\theta H'(\xi z)}{\xi}, \tag{38}$$

respectively, so that $\psi = G_1'(1)$.

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Expression (34) has a striking resemblance to the Lagrangian difference between potential and kinetic components of energy; (33) is obviously a demand that expression (34) shall have an extremal value with respect to ξ^*. A deeper analysis would probably demonstrate equations (29) and (33) as conditions for a saddle-point in the steepest descent evaluation of an integral; this will be covered in another publication by the author ((21)).

The equations (28), (29) are reminiscent of the Born–Fuchs treatment of the imperfect gas (Born and Fuchs (4); Mayer and Mayer (14), page 277) with the H_j playing somewhat the role of the elementary cluster integrals. However, the treatment here is very much more explicit, because, as emphasized in the introduction, the present process is so much simpler than the general interacting-particle process.

The occurrence of the δ term in (27) is, physically, a consequence of the fact that the number of bonds in a cluster can be written either as $r-1$ or as $\frac{1}{2}\Sigma j r_j$, so that these two quantities must be equal.

Proof of the theorem. This is based upon evaluation of the coefficients in the kinetic equation (10). Consider the possible association of an $\mathbf{r}$-mer and an $\mathbf{r}'$-mer into an $\mathbf{r}''$-mer, this to happen in such a way that an a_j in the $\mathbf{r}$-mer combines with an a_k in the $\mathbf{r}'$-mer. We shall thus have

$$r''_p = r_p + r'_p + \delta_{p,j+1} - \delta_{pj} + \delta_{p,k+1} - \delta_{pk} \quad (p = 0, 1, 2, \ldots). \tag{39}$$

Assumption (21) yields the association rate for a given a_j and a_k; we shall supplement it by supposing that the rate for association of a given $\mathbf{r}$-mer and $\mathbf{r}'$-mer by formation of an a_{j+1}/a_{k+1} bond is

$$\lambda_{jk}(\mathbf{r}, \mathbf{r}') = \lambda r_j r'_k \frac{H_{j+1} H_{k+1}}{H_j H_k}. \tag{40}$$

The inclusion of the combinatorial term $r_j r'_k$ seems reasonable, since this is the number of ways in which an a_{j+1}/a_{k+1} bond could be formed. This point has an implication; that one can distinguish between the r_j different a_j's of an $\mathbf{r}$-mer, and it is for this reason the trees we deal with are *ordered* trees. Had we assumed that distinction was impossible, we should have had to modify the rate (40) to

$$\lambda \eta(r_j)\, \eta(r'_k) \frac{H_{j+1} H_{k+1}}{H_j H_{jk}}, \tag{41}$$

where $\eta(0) = 0$, $\eta(r) = 1$ $(r = 1, 2, 3, \ldots)$ and should have had the much more difficult combinatorial problem of dealing with free trees. The choice between (40) and (41) is rather like the choice between Boltzmann and Bose–Einstein statistics; however, (40) seems the more plausible assumption physically, for the polymer case at least.

If $\mu_{jk}(\mathbf{r}, \mathbf{r}')$ is similarly defined as the rate at which a given $\mathbf{r}''$-mer dissociates into an $\mathbf{r}$-mer and an $\mathbf{r}'$-mer by dissolution of an a_{j+1}/a_{k+1} bond (the order of $\mathbf{r}$, $\mathbf{r}'$ being distinguished), then the only statement one can make immediately is that

$$\Sigma \mu_{jk}(\mathbf{r}, \mathbf{r}') = \mu(r'' - 1), \tag{42}$$

where the sum covers all possible dissociations of the $\mathbf{r}''$-mer by severance of a single bond (there are $r'' - 1$ bonds). In order to determine what proportion $\mu_{jk}(\mathbf{r}, \mathbf{r}')$ constitutes of this sum, we must solve the combinatorial problem of determining the

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proportion of cases in which the cutting of a randomly chosen bond in the $\mathbf{r}''$-mer would separate an a_{j+1} and an a_{k+1}, the a_j and a_k thus newly created lying respectively in an $\mathbf{r}$-mer and an $\mathbf{r}'$-mer.

Now the number of trees of composition $\mathbf{r}$ starting with an a_{j+1} which has been transformed into an a_j by severance of a bond is

$$T^{(j)}(\mathbf{r}) = \text{coefficient of } \prod_k x_k^{r_k} \quad \text{in} \quad x_j U(\mathbf{x})^j,$$

and by equation (18) this is

$$T^{(j)}(\mathbf{r}) = \frac{jr_j(r-2)!}{\Pi r_j!}\delta_{\Sigma jr_j-2r+2}. \tag{43}$$

The number of trees of composition $\mathbf{r}''$ obtainable by working out in both directions from a bond is $U_2(\mathbf{r}'')$. From these considerations and equation (27) we thus see that

$$\mu_{jk}(\mathbf{r},\mathbf{r}') = \mu(r''-1)\frac{T^{(j)}(\mathbf{r})T^{(k)}(\mathbf{r}')}{U_2(\mathbf{r}'')}$$

$$= \frac{\mu r_j r'_k jk}{2}\frac{v_{\mathbf{r}}v_{\mathbf{r}'}}{v_{\mathbf{r}''}}. \tag{44}$$

Expression (26b) now follows as the solution of the detailed balance equation

$$\frac{c_{\mathbf{r}}c_{\mathbf{r}'}}{c_{\mathbf{r}''}} = \frac{\mu_{jk}(\mathbf{r},\mathbf{r}')+\mu_{kj}(\mathbf{r}',\mathbf{r})}{\lambda_{jk}(\mathbf{r},\mathbf{r}')}$$

$$= \kappa jk\frac{v_{\mathbf{r}}v_{\mathbf{r}'}}{v_{\mathbf{r}''}}\frac{H_jH_k}{H_{j+1}H_{k+1}}, \tag{45}$$

and relations (39). Relations (39) of course imply that $\mathbf{r}''$ is determined by $\mathbf{r},\mathbf{r}',j$ and k, so that the left-hand member of (45) is not independent of j and k, as it may appear to be. Equation (26a) follows from the equation corresponding to (45) when $r = 1$, which is relatively trivial.

In order to evaluate θ in (26), and obtain the remaining results of the Theorem, we need a few summation formulae. Let us write

$$\phi_j = \frac{H_j}{(j-1)!}.$$

We see from (26) and formula (18) for $U_2(\mathbf{r})$ that

$$S[(r-1)\Pi x_j^{r_j}] = \tfrac{1}{2}\kappa\sum_{\mathbf{r}}U_2(\mathbf{r})\prod_j(\phi_j x_j\theta)^{r_j}$$

$$= \tfrac{1}{2}\kappa[U(\theta\phi_1 x_1,\theta\phi_2 x_2,\ldots)]^2$$

$$= \frac{\kappa}{4\pi i}\oint\frac{z^2[1-\theta\Sigma(j-1)\phi_j x_j z^{j-2}]\,dz}{z-\theta\Sigma\phi_j x_j z^{j-1}}$$

$$= \tfrac{1}{2}\kappa(\xi^*)^2, \tag{46}$$

where ξ^* is the unique pole of the integrand, i.e. the smallest root of (33). This proves (36); setting all the $x_j = 1$ we obtain assertion (iii) of the Theorem.

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Similarly,

$$S[r(r-1)\,\Pi x_j^{r_j}] = \kappa \sum_r \frac{r!}{\prod_1^\infty r_j!}\,\theta^r\,\Pi(\phi_j x_j)^{r_j}\,\delta_{\Sigma j r_j - 2r+2}$$

$$= \kappa \sum_r \{\text{coefficient of } z^{r-2} \text{ in } P(z)^r\},$$

where

$$P(z) = \theta\Sigma\phi_j x_j z^{j-1} = \theta\frac{\partial H^*(z)}{\partial z}. \tag{47}$$

We can thus write

$$S[r(r-1)\,\Pi x_j^{r_j}] = \frac{\kappa}{2\pi i}\oint z^2 dz \Big/ \left(z - \theta\frac{\partial H^*(z)}{\partial z}\right)$$

$$= \kappa(\xi^*)^2 \Big/ \left(1 - \theta\left[\frac{\partial^2 H(z)}{\partial z^2}\right]_{z=\xi^*}\right).$$

Setting all the $x_j = 1$ we obtain, in accordance with equation (30),

$$\frac{S[r(r-1)]}{S[r-1]} = 2\Big/\left(1-\theta\frac{\partial^2 H(\xi)}{\partial\xi^2}\right) = \frac{2}{1-\psi}.$$

This expression gives the average size of the polymer within which a randomly chosen bond finds itself, so that $\psi > 1$ does indeed indicate gelation.

Finally,

$$S[r\Pi x_j^{r_j}] = \kappa\theta H_0 + \kappa \sum_{r>1} \frac{1}{r-1}\{\text{coefficient of } z^{r-2} \text{ in } P(z)^r\}. \tag{48}$$

The sum in (48) can alternatively be written

$$-\text{coefficient of } z^{-2} \text{ in } \frac{P}{z}\log\left(1-\frac{P}{z}\right) = -\frac{1}{2\pi i}\oint P(z)\log\left(1-\frac{P(z)}{z}\right),$$

where the integral is a contour enclosing the two logarithmic singularities of the integral, $z = 0$ and $z = \xi^*$. A partial integration throws integral (49) in the form

$$\frac{1}{2\pi i}\oint\left[\int^z P(\zeta)\,d\zeta\right]\frac{\partial}{\partial z}\left[1-\frac{P(z)}{z}\right]\Big/\left[1-\frac{P(z)}{z}\right]dz = \int_0^{\xi^*} P(\zeta)\,d\zeta = \theta\int_0^{\xi^*}\frac{\partial H^*(\zeta)}{\partial\zeta}\,\partial\zeta, \tag{49}$$

which together with (48) yields

$$S[r\Pi x_j^{r_j}] = \kappa\theta H^*(\xi^*). \tag{50}$$

Equations (46) and (50) establish (35) and (36) and equation (28) follows.

Assertion (v) of the theorem follows if one converts enumerative g.f. relations such as (16) into p.g.f. relations by substituting $g_{1,j-1}x_j$ for x_j, g_{1j} being later identified with $\theta H_{j+1}\xi^{j-1}/(j!)$. Since this approach is not central to our method, we shall not follow through the details. It is worth noting, however, that expressions (37), (38) obey the consistency condition (20).

The basic pair of relations (28) and (29) bear some analogy to the relations (11), (12) of Gordon's paper ((12)). The analogy is only a loose one, however; Gordon's relations are not tied at all to physically given quantities (such as N, κ or the H_j), do not observe the consistency condition (20), and must be supplemented by kinetic and stoichiometric considerations. These considerations are built into the theory given here.

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If the 'open' distribution (2) holds, which it only can do before gelation, then by determining the c_r's in Theorem 1 we have determined the joint distribution of the n_r's In particular, if $z_r = \Pi x_j^{rj}$ then it follows from the summation formulae that

$$\Pi(\mathbf{z}) = \exp\{\kappa\theta[H^*(\xi^*) - H(\xi)] - \tfrac{1}{2}\kappa[(\xi)^{*2} - \xi^2]\}, \tag{51}$$

and this, as a function of the x's, is the p.g.f. of the total number of a_j's ($j \geqslant 0$). The expression $\exp[\kappa\theta H(\xi) - \frac{1}{2}\kappa\xi^2]$ is closely related to the partition function of the process.

If, on the other hand, we have a closed system with a fixed number of units, N, then, in virtue of (13), determination of the c_r's, or equivalently the ω_r's, still determines in principle the full equilibrium statistics of the process.

One could not make the dissociation rate depend upon the type of bond, because specification of the numbers $r_0, r_1, r_2, \ldots$ does not determine the number of a_j/a_k bonds within a cluster. However, the case of a variable dissociation rate can certainly be treated if one is prepared to work with a more detailed description of an r-mer; we hope to return to this point.

5. *Some particular cases.* Let us first see how the theory of the preceding section works out for the case when each unit bears f equi-reactive sites, so that

$$H_j = \frac{f!}{(f-j)!}, \tag{52}$$

and the association rate (21) is $\lambda(f-j)(f-k)$. This case has been fully treated by Flory ((6)) and Stockmayer ((17)), at least for the case of zero dissociation, and so is well understood.

We have
$$H(\xi) = (1+\xi)^f, \tag{53}$$

so that equations (28), (29), can be written

$$N = \kappa\theta(1+\xi)^f, \tag{54}$$

$$\xi(1+\xi) = Nf/\kappa. \tag{55}$$

The expected number of bonds is

$$\tfrac{1}{2}\kappa\xi^2 = \frac{Nf}{2}\frac{\xi}{1+\xi}, \tag{56}$$

so that if we work with
$$p = \frac{\xi}{1+\xi} \tag{57}$$

instead of ξ, this will have the interpretation of the 'extent of reaction', the expected proportion of sites which have reacted. In terms of p, equations (55) and (54) can be rewritten as

$$p/q^2 = Nf/\kappa, \tag{58}$$

$$\theta = \frac{\xi}{f(1+\xi)^{f-1}} = \frac{pq^{f-2}}{f}, \tag{59}$$

respectively, where $q = 1-p$. The first determines p uniquely as an increasing function of Nf/κ, the second determines θ as a function of p, increasing as long as $(f-1)p < 1$. Since by (31)

$$\psi = \frac{(f-1)\xi}{1+\xi} = (f-1)p, \tag{60}$$

we see that $(f-1)p = 1$ does indeed locate the critical point.

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We have only claimed validity of our results up to gelation; but p continues to increase with Nf/κ in a reasonable fashion past this point. θ decreases, however, so that formula (26) presumably then expresses the distribution of cluster size in the sol-fraction (i.e. the uncondensed phase) rather than in the entire material.

Equation (58) has an immediate kinetic interpretation. Let b be the total number of bonds, so that the number of unreacted sites is $Nf-2b$. For large N one might expect a kinetic equation

$$\frac{db}{dt} = \tfrac{1}{2}\lambda(Nf-2b)^2-\mu b. \tag{61}$$

(This neglects the statistical variation of b, and also the fact that not all site pairs can form bonds.) Setting $b = \frac{1}{2}Nfp$ and equating the right-hand member of (61) to zero, we recover (58).

The g.f. relations of the theorem make calculation of cluster-size distribution simple. If c_r is the expected number of clusters of size r, then by (33), (35)

$$\Sigma r c_r x^r = \kappa\theta x(1+\xi^*)^f, \tag{62}$$

where

$$\xi^* = f\theta x(1+\xi^*)^{f-1}. \tag{63}$$

By Good's theorem (19) we then have

$$\begin{aligned} c_r &= \frac{\kappa\theta}{r}\{\text{coefficient of } x^{r-1} \text{ in } (1+\xi^*)^f\} \\ &= \frac{\kappa\theta}{r}\left\{\text{coefficient of } \zeta^{r-1} \text{ in } (f\theta)^{r-1}\left[1-\frac{(f-1)\zeta}{1+\zeta}\right](1+\zeta)^{fr-r+1}\right\} \\ &= \frac{\kappa(f\theta)^r(fr-r)!}{r!(fr-2r+2)!} \\ &= \frac{Nfq^2}{p}\frac{(fr-r)!}{r!(fr-2r+2)!}(pq^{f-2})^r, \end{aligned} \tag{64}$$

in agreement with Stockmayer ((17)). (See also Good (11).)

Since κ will be of the form $\sigma V e^{-\epsilon/kT}$, where σ is a constant and ϵ the 'bond energy', we see from (58) and the inequality $(f-1)p < 1$ that the region of non-gelation is

$$\rho e^{-\epsilon/kT} < \frac{\sigma(f-1)}{f(f-2)^2}, \tag{65}$$

ρ and T being density and absolute temperature, respectively.

As an example of something new, consider a situation for which

$$H(\xi) = (1-\xi)^{-f}. \tag{66}$$

This has strong formal similarities with the one just treated, but is qualitatively rather different.

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The association rate is now $\lambda(f+j)(f+k)$, and so increases indefinitely with j. The equations corresponding to (55), (56), (59), (60) and (64) are

$$\xi(1-\xi) = Nf/\kappa, \tag{67}$$

$$\text{expected number of bonds} = \tfrac{1}{2}\kappa\xi^2 = \frac{Nf}{2}\frac{\xi}{1-\xi}, \tag{68}$$

$$\theta = \frac{\xi(1-\xi)^{f+1}}{f}, \tag{69}$$

$$\psi = \frac{(f+1)\xi}{1-\xi}, \tag{70}$$

$$c_r = \frac{\kappa(f\theta)^r(fr+2r-3)!}{r!(fr+r-1)!}, \tag{71}$$

respectively, as can be seen by calculations completely analogous to the previous ones. The difference arises from the fact that, whereas (55) always has just one solution, (67) sometimes has two (of which the smaller is the appropriate one) and sometimes none.

As Nf/κ increases from zero the smaller solution of (67) also increases. When ξ passes the value $(f+2)^{-1}$ then by (70) $\psi > 1$ and gelation occurs. As Nf/κ continues to increase so does the bonding parameter ξ, until for a finite value of Nf/κ it reaches the value $\frac{1}{2}$, which by (68) corresponds to the existence of $\frac{1}{2}Nf$ bonds. There is no ξ solution for larger values of Nf/κ.

This suggests the occurrence of a second critical point. At the first point infinite trees become possible (at least if N is infinite); at the second the trees become 'saturated', in that the maximum possible degree of branching takes place. One is tempted to identify these two points with the two phenomena of liquefaction and solidification, but a much more careful treatment of expression (13) in the 'condensation' region is necessary before one can be certain of either the existence or interpretation of a second critical point. That some caution is needed is evident from the fact that, with the non-cyclic restriction, the number of bonds cannot exceed $N-1$. Thus expression (68) can hardly exceed the value N, which it reaches for $\xi = 2/(f+2)$.

It would be interesting to study the dependence of θ and of ξ, which is determined by the equation

$$\xi = \frac{N}{\kappa}\frac{\partial}{\partial\xi}\log H(\xi)$$

upon the form of $H(\xi)$. For example, if $H_1 = 0$, then $\xi = 0$, indicating that the only equilibrium state is that in which all material is in monomer form.

6. *The case of several types of unit.* The case of m types of unit ($m > 1$) is by no means an immediate generalization of the case of one, and we shall defer its full consideration to another paper by the author, ((21)), using another method. However, we shall summarize the analogues of the results of the last section, and demonstrate their application. We shall refer to a unit of type α as an α-unit ($\alpha = 1, 2, \ldots, m$).

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Denote an α-unit which is bound to j_β β-units ($\beta = 1, 2, \ldots, m$) by $\alpha_{\alpha\mathbf{j}}$, and suppose that the analogue of the H_j of section 4 for such a unit is $H_{\alpha\mathbf{j}}$. Define

$$H_\alpha(\xi_1, \ldots, \xi_m) = \sum_{\mathbf{j}} H_{\alpha\mathbf{j}} \prod_{\beta=1}^{m} \frac{\xi_\beta^{j_\beta}}{j_\beta!}, \tag{72}$$

$$H_\alpha^*(\xi_1, \ldots, \xi_m) = \sum_{\mathbf{j}} H_{\alpha\mathbf{j}} x_{\alpha\mathbf{j}} \prod_{\beta=1}^{m} \frac{\xi_\beta^{j_\beta}}{j_\beta!}. \tag{73}$$

Suppose that there are N_α α-units, let $n_\mathbf{r}$ be the number of units in which there are $r_{\alpha\mathbf{j}}$ $a_{\alpha\mathbf{j}}$'s ($\alpha = 1, 2, \ldots, m$; $\mathbf{j} \geqslant 0$) and, as usual, denote $E_0(n_\mathbf{r})$ by $c_\mathbf{r}$.

THEOREM 2. *Consider the quantities θ_α, $\xi_{\alpha\beta}$ and $\psi_{\alpha\beta\gamma}$ determined by*

$$N_\alpha = \theta_\alpha H_\alpha(\xi_{\alpha 1}, \ldots, \xi_{\alpha m}), \tag{74}$$

$$\xi_{\beta\alpha} = \theta_\alpha \frac{\partial}{\partial \xi_{\alpha\beta}} H_\alpha(\xi_{\alpha 1}, \ldots, \xi_{\alpha m}), \tag{75}$$

$$\psi_{\alpha\beta\gamma} = \theta_\alpha \frac{\partial^2}{\partial \xi_{\alpha\beta} \partial \xi_{\alpha\gamma}} H_\alpha(\xi_{\alpha 1}, \ldots, \xi_{\alpha m}) \quad (\alpha, \beta, \gamma = 1, 2, \ldots, m). \tag{76}$$

Then (i) *Gelation occurs if the maximum eigen-value ψ of the linear system*

$$\sum_{\beta} \zeta_{\beta\alpha} \psi_{\alpha\beta\gamma} = \psi \zeta_{\alpha\gamma} \tag{77}$$

is greater than unity.

(ii) *The expected number of bonds between α-units and β-units is*

$$\kappa \xi_{\alpha\beta} \xi_{\beta\alpha} \ (\alpha \neq \beta) \quad \text{or} \quad \tfrac{1}{2}\kappa \xi_{\alpha\alpha}^2 \ (\alpha = \beta).$$

(iii) *If $\xi_{\alpha\beta}^*$ ($\alpha, \beta = 1, 2, \ldots, m$) is the solution of the equations*

$$\xi_{\alpha\beta}^* = \theta_\alpha \frac{\partial}{\partial \xi_{\alpha\beta}^*} H_\alpha^*(\xi_{\alpha 1}^*, \ldots, \xi_{\alpha m}^*) \tag{78}$$

then the **r**-*mer weight g.f. is*

$$S[\prod_{\alpha} \prod_{\mathbf{j}} x_{\alpha\mathbf{j}}^{r_{\alpha\mathbf{j}}}] = \kappa \sum_{\alpha} \theta_\alpha H_\alpha^*(\xi_{\alpha 1}^*, \ldots, \xi_{\alpha m}^*) - \tfrac{1}{2}\kappa \sum_{\alpha} \sum_{\beta} \xi_{\alpha\beta}^* \xi_{\beta\alpha}^*. \tag{79}$$

This is partitionable as follows:

$$S[\mathbf{r}^{(\alpha)} \prod x_{\alpha\mathbf{j}}^{r_{\alpha\mathbf{j}}}] = \kappa H_\alpha^*(\xi_{\alpha 1}^*, \ldots, \xi_{\alpha m}^*), \tag{80}$$

$$S[\mathbf{r}^{(\alpha\beta)} \prod x_{\alpha\mathbf{j}}^{r_{\alpha\mathbf{j}}}] = \kappa \xi_{\alpha\beta}^* \xi_{\beta\alpha}^* \quad (\alpha \neq \beta), \tag{81a}$$

$$S[\mathbf{r}^{(\alpha\alpha)} \prod x_{\alpha\mathbf{j}}^{r_{\alpha\mathbf{j}}}] = \tfrac{1}{2}\kappa (\xi_{\alpha\alpha}^*)^2, \tag{81b}$$

where $\mathbf{r}^{(\alpha)}$ is the number of α-units in the **r**-*mer, and $\mathbf{r}^{(\alpha\beta)}$ the number of $\alpha\beta$-bonds.*

The reason why ξ generalizes to an $m \times m$ matrix rather than to a vector is that there are now m^2 conceivable types of linkage The system (77) is distinctly more complex than (31). From a branching process point of view the reason is that the distribution of units 'descending' from a α-unit will in general depend upon the type of unit from which the α-unit itself descended, so that one has a two-step dependence.

Again, the values $\xi_{\alpha\beta}^*$ determined by (78) correspond to a stationary point of expression (79).

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As an example, consider the case $m = 2$ in which type 1 has f equi-reactive A-sites, type 2 has g equi-reactive B-sites, and the only possible reaction is an AB bond. Then

$$H_{1j_1j_2} = \begin{cases} \dfrac{f!}{(f-j_2)!} & (j_1 = 0, j_2 \leqslant f), \\ 0 & \text{(otherwise)}, \end{cases}$$

$$H_{2j_1j_2} = \begin{cases} \dfrac{g!}{(g-j_1)!} & (j_1 \leqslant g, j_2 = 0), \\ 0 & \text{(otherwise)}, \end{cases}$$

and

$$H_1(\xi_{11}, \xi_{12}) = (1+\xi_{12})^f,$$
$$H_2(\xi_{21}, \xi_{22}) = (1+\xi_{21})^g.$$

The equation system (75) becomes

$$\left.\begin{aligned} \xi_{11} &= 0, \\ \xi_{12} &= \theta_2 g(1+\xi_{21})^{g-1}, \\ \xi_{21} &= \theta_1 f(1+\xi_{12})^{f-1}, \\ \xi_{22} &= 0, \end{aligned}\right\} \tag{82}$$

and equations (74) are

$$\left.\begin{aligned} N_1 &= \kappa\theta_1(1+\xi_{12})^f, \\ N_2 &= \kappa\theta_2(1+\xi_{21})^g. \end{aligned}\right\} \tag{83}$$

If we perform the reparametrization

$$\xi_{12} = \frac{p}{1-p} = \frac{p}{q}, \quad \xi_{21} = \frac{p'}{1-p'} = \frac{p'}{q'},$$

then

$$\theta_1 = \frac{p'q^{f-1}}{fq'}, \quad \theta_2 = \frac{p(q')^{g-1}}{gq}.$$

Substitution in (83) leads to the two determining equations for p and p':

$$N_1 = \frac{\kappa p'}{fqq'}, \quad N_2 = \frac{\kappa g}{gqq'}. \tag{84}$$

The expected number of bonds is

$$\kappa\xi_{12}\xi_{21} = N_1 fp = N_2 gp' \tag{85}$$

so that p, p' are in fact the expected proportions of reacted A and B sites respectively, and equations (84), like (58), can be verified immediately on kinetic/stoichiometric grounds. The linear system (77) is simply

$$\psi\zeta_{12} = \theta_2 g(g-1)(1+\xi_{21})^{g-2}\zeta_{21} = \frac{(g-1)pq'}{q}\zeta_{21},$$

$$\psi\zeta_{21} = \frac{(f-1)p'q}{q'}\zeta_{12}$$

so that

$$\psi^2 = (f-1)(g-1)pp'$$

and gelation occurs when this quantity exceeds unity; a relation with an immediate branching interpretation.

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Let us now determine c_{rs}, the expected number of rs-mers. From (80) we shall have

$$\Sigma r c_{rs} x^r y^s = \kappa\theta_1 x(1+\xi_{12}^*)^f,$$

where ξ_{12}^* is determined by

$$\xi_{12}^* = y\theta_2 g(1+\xi_{21}^*)^{g-1},$$
$$\xi_{21}^* = x\theta_1 f(1+\xi_{12}^*)^{f-1}.$$

Thus, by Good's theorem (19)

$$\begin{aligned} c_{rs} &= \frac{\kappa\theta_1}{r}\Big\{\text{coefficient of } \alpha^{r-1}\beta^s \text{ in } (f\theta_1)^{r-1}(g\theta_2)^s(1+\beta)^f \\ &\qquad \times\left[1-\frac{(f-1)(g-1)\alpha\beta}{(1+\alpha)(1+\beta)}\right](1+\beta)^{(r-1)(f-1)}(1+\alpha)^{s(g-1)}\Big\} \\ &= \frac{\kappa(fr-f)!\,(gs-g)!}{r!s!\,(fr-r-s+1)!\,(gs-r-s+1)!}(f\theta_1)^r(g\theta_2)^s \\ &= \frac{\kappa(fr-f)!\,(gs-g)!}{r!s!\,(fr-r-s+1)!\,(gs-r-s+1)!}\left(\frac{p'q^{f-1}}{q'}\right)^r\left(\frac{p(q')^{g-1}}{q}\right)^s \end{aligned}$$

in agreement with Stockmayer ((17), (18)). The derivation is, of course, much simpler and more systematic than Stockmayer's. Furthermore, treatments of particular equi-reactive cases give little hint of the structure involved and methods required for the general case of Theorem 2.

APPENDIX A

Derivation of equation (10)

An event is said to have *probability intensity* λ if the probability of its occurrence in a time-interval $(t, t+\delta t)$ is $\lambda\delta t + o(\delta t)$, and if the probability of its multiple occurrence in the same interval is $o(\delta t)$, the course of the process before t affecting these probabilities only in so far as it affects the value of λ.

We assume in the present case the intensity with which a *particular* $A_\mathbf{r}$ and $A_\mathbf{s}$ associate to form an $A_\mathbf{u}$ is $\lambda_{\mathbf{rsu}}$ and the intensity with which a *particular* $A_\mathbf{u}$ dissociates into an $A_\mathbf{r}$ and an $A_\mathbf{s}$ (the order of $\mathbf{r}$ and $\mathbf{s}$ being relevant if $\mathbf{r} \neq \mathbf{s}$) is $\mu_{\mathbf{rsu}}$.

Then, if individual associations and dissociations are statistically independent, the total intensity of the reaction

$$A_\mathbf{r} + A_\mathbf{s} \to A_\mathbf{u}$$

(the individual identities of the $A_\mathbf{r}$ and $A_\mathbf{s}$ now being disregarded) will be $\lambda_{\mathbf{rsu}} n_\mathbf{r} n_\mathbf{s}$ ($\mathbf{r} \neq \mathbf{s}$) or $\frac{1}{2}\lambda_{\mathbf{rru}} n_\mathbf{r}(n_\mathbf{r}-1)$ ($\mathbf{r} = \mathbf{s}$). The corresponding total intensity for the reverse reaction (with $\mathbf{r}$ and $\mathbf{s}$ in a given order for $\mathbf{r} \neq \mathbf{s}$) will be $\mu_{\mathbf{rsu}} n_\mathbf{u}$.

The process described by the vector variable $\mathbf{n}(t)$ will now be Markov, and the probabilities

$$P(\mathbf{n}, t) = \text{prob } (\mathbf{n}(t) = \mathbf{n}) \tag{A 1}$$

obey the equations

$$\begin{aligned} \frac{\partial P}{\partial t} &= \tfrac{1}{2}\sum_\mathbf{r}\sum_\mathbf{s}\sum_\mathbf{u}\lambda_{\mathbf{rsu}}[(n_\mathbf{r}+1)(n_\mathbf{s}+1-\delta_{\mathbf{rs}})D_\mathbf{u}^{-1}D_\mathbf{r}D_\mathbf{s}P - n_\mathbf{r}(n_\mathbf{s}-\delta_{\mathbf{rs}})P] \\ &\quad + \sum_\mathbf{r}\sum_\mathbf{s}\sum_\mathbf{u}\mu_{\mathbf{rsu}}[(n_\mathbf{u}+1)D_\mathbf{u}D_\mathbf{r}^{-1}D_\mathbf{s}^{-1}P - n_\mathbf{u}P] \end{aligned} \tag{A 2}$$

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(cf. (5), page 426, or (15), page 296). Here we have used D_r for the operator which increases the argument n_r of a function of $\mathbf{n}$ by one. Multiplying equation (A 2) by $\prod_r z_r^{n_r}$ and summing over all $\mathbf{n}$, we obtain equation (10) for the p.g.f.

$$\Pi(\mathbf{z}) = \sum_{\mathbf{n}} P(\mathbf{n}) \prod_r z_r^{n_r}. \tag{A 3}$$

APPENDIX B

A proof that expression (14) *describes the equilibrium distribution of numbers in an open system*

We shall consider events in a volume V, and to make the dependence on V explicit we shall write (14) as

$$\Pi(\mathbf{z}) = \exp[V\Sigma\gamma_r\theta^r(z_r - 1)], \tag{B 1}$$

where the γ_r satisfy (7).

Suppose now that one has two neighbouring regions of volumes V and V', within each of which association and dissociation are proceeding as hitherto and between which there is migration of molecules. If n_r, n_r' denote the numbers of $\mathbf{r}$-mers in V, V' respectively, then we shall suppose that the total emigration intensity of $\mathbf{r}$-mers from V to V' is $\eta_r V' n_r$, that from V' to V being $\eta_r V n_r'$.

Then, if

$$\Pi(\mathbf{z}, \boldsymbol{\zeta}) = E(\prod_r z_r^{n_r}\zeta_r^{n_r'}), \tag{B 2}$$

one finds by a derivation analogous to that of (10) that

$$\frac{\partial\Pi}{\partial t} = \tfrac{1}{2}\sum_r\sum_s\sum_u (z_u - z_r z_s)\left(\frac{\nu_{rsu}}{V}\frac{\partial^2\Pi}{\partial z_r \partial z_s} - 2\mu_{rsu}\frac{\partial\Pi}{\partial z_u}\right)$$
$$+ \tfrac{1}{2}\sum_r\sum_s\sum_u (\zeta_u - \zeta_r\zeta_s)\left(\frac{\nu_{rsu}}{V'}\frac{\partial^2\Pi}{\partial\zeta_r\partial\zeta_s} - 2\mu_{rsu}\frac{\partial\Pi}{\partial\zeta_u}\right) + \sum_r \eta_r(\zeta_r - z_r)\left(V'\frac{\partial\Pi}{\partial z_r} - V\frac{\partial\Pi}{\partial\zeta_r}\right). \tag{B 3}$$

This possesses a solution

$$\exp[\Sigma\gamma_r\theta^r(Vz_r + V'\zeta_r)], \tag{B 4}$$

and, if the process is irreducible, the general solution can be obtained from it as in (11).

If the total number of units in $V + V'$ is fixed at N then the solution corresponding to the unique equilibrium distribution is

$$\Pi(\mathbf{z}, \boldsymbol{\zeta}) = \text{const.} \oint \exp[\Sigma\gamma_r\theta^r(Vz_r + V'\zeta_r)]\,\theta^{-N-1}\,d\theta \tag{B 5}$$

(cf. the derivation of (13)). Suppose now that we consider only the distribution of the n_r (and so set all the ζ_r equal to 1) and that we set

$$N = \rho(V + V'), \tag{B 6}$$

where the density, ρ, is to be held constant as V', N increase. We have then

$$\Pi(\mathbf{z}) = \text{const}\oint \frac{\exp(V\Sigma\gamma_r\theta^r z_r)}{\theta^{\rho V+1}}\left(\frac{\exp(\Sigma\gamma_r\theta^r)}{\theta^\rho}\right)^{V'} d\theta. \tag{B 7}$$

Considering now V' to be very large, we can evaluate the integral (B 7) by steepest descents, obtaining

$$\Pi(\mathbf{z}) = \text{const.}\exp(V\Sigma\gamma_r\theta^r z_r), \tag{B 8}$$

the value of θ being the saddle-point value determined by

$$\Sigma r\gamma_r\theta^r = \rho. \tag{B 9}$$

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If the conditions for the validity of the steepest descents method are fulfilled (and the case where they are not is just that where some kind of condensation has taken place), then expression (B 8) becomes exact in the limit of large V', proving the assertion expressed after equation (14). The constant in (B 8) is evaluated from the consideration that $\Pi(1, 1, \ldots) = 1$.

By assuming the emigration rate from V' to V to be $\eta_{\mathbf{r}} V n'_{\mathbf{r}}$ we have implicitly assumed that *any* **r**-mer in V' has an equal chance (proportional to V) of emigrating into V. More realistically, one would have to suppose that only local motion was possible, so that space would have to be divided into small elements of volume V_j, the rate of **r**-mer emigration from V_j to V_k being $\eta_{\mathbf{r}jk} V_k n_{\mathbf{r}j}$ (in an obvious notation) where $\eta_{\mathbf{r}jk}$ falls to zero with increasing distance between the two elements. V and V' will each be made up of a number of these V_j. However, if only $\eta_{\mathbf{r}jk} = \eta_{\mathbf{r}kj}$ then one again reaches the same conclusion as above; that the joint p.g.f. of numbers in V and V' is obtained by linear superpositions of the solution (B 4), and that conclusion (B 8) follows from this under the same conditions as before.

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