Toward a Statistical Theory of Catenanes: Distribution of Sizes in Equilibrium Systems with Free Ring Passage

Homer Jacobson

Department of Chemistry, Brooklyn College, Brooklyn, New York 11210.

Received October 7, 1983

ABSTRACT: A polymerizing system is considered to contain chains, rings, and catenanes in equilibrium. Postulating an ad hoc "ring passage" direct equilibrium between rings and catenanes, and allowing them to interpenetrate at rates determined by collision frequencies alone, results in an extension of the Jacobson–Stockmayer (JS) theory to include catenane species, giving specifications of size distributions, concentrations, and number- and weight-average molecular weights for catenanes and ratios of catenanes to rings and chains. All catenane parameters increase monotonically with the degree of reaction. At 100% reaction, the chains disappear, while still of finite size. In contrast with JS, this can occur at any monomer concentration. Quantitative predictions are made for a chain with reactive ends and about 9 Kuhn segments.

This paper presents a simple approach to the specification of geometrical factors governing the frequency of formation of topological bonds in ring-forming polymers synthesizing by random reaction by considering an equilibrium between rings and catenanes free to pass through one another. Although a request for a statistical theory of catenanes was made in 1948 by G. W. Kimball,[1] there does not yet appear to be one. Frisch and Wasserman[2] give the only available estimates for such structures for the case of catenane production by threading of chains through a homogeneous set of rings. I suggest that formation of catenanes by threading may be equivalent to a "ring passage" equilibrium between formed rings and catenanes, leading to the same distribution of sizes of both. The problem, with simplifying assumptions, is solved for a general chain–ring–catenane equilibrium, and for a chain-free system, as a special case, below.

Consider a reversible straight-chain polymer-forming system at equilibrium between chains, rings, and catenanes (for the moment ignoring multiply linked species). Figure 1 illustrates the multiple equilibria present. Six can be recognized during polycondensation: (I) chain formation and breakage; (II) ring closure and opening; (III) ring closure within an existing ring to make catenane and catenane breakage; (IV) chain bond interchange; (V) chain–ring bond interchange; (VI) chain–catenane bond interchange.

The first three of these involve bond formation and breakage; only the third of them is involved in catenane formation. Catenanes can break during equilibrium VI, but their formation by the reverse reaction is very similar to that of III, the threading reaction, differing only by the completion of the linked ring with an interchange, rather than formation of a new bond. Six more types of (unillustrated) equilibria, involving double interchange (i.e., crossover) of internal bonds in chains, rings, and catenanes, are conceivable. Consideration of the geometry, and ultimately the entropy, of catenane formation has focused on the threading reaction, one whose "formidable mathematical difficulties" (FW) of configuration specification have led to crude estimates only, with ring species of a fixed size. A system in equilibrium will most generally have a distribution of ring sizes, and a distribution of singly linked catenane ring pairs, as well as that of any chains, and multiply linked catenanes, present.

It is possible to calculate geometric factors, based upon the prevailing of a seventh equilibrium (Figure 2), a direct ring passage between a ring pair and a catenane, to give or break a topological bond. Such reactions (in the forward direction, though not necessarily in the reverse) have been observed[3,4] with negatively supercoiled DNA in the presence of topoisomerase. We may also consider steps in equilibria III and II, properly ordered and occurring in rapid succession, to be producers of intermediate states in equilibrium VII. Or VII can be considered to be a double interchange of internal bonds between two rings, followed by immediate reinterchange, with topological reorientation. Derivation of the distributions follows.

Consider two rings, called the i-ring and the j-ring, viewed as freely flailing sets of Kuhn segments, containing i and j monomers, respectively. For ring passage to occur, a reactive site on one monomer (Figure 2) must be contiguous to one on the other. Normally there is one reactive site per monomer; in DNA a base pair can be considered to be one site. An equilibrium constant for the reaction can be calculated from mass action considerations, and the distribution of catenane structures then derived from the known distribution of ring sizes. The degree of necessary contiguity is expressible by some volume element and by some orientation factor, *both of which should be the same for both forward and backward reactions*, and which thus contribute equally to the forward and backward rate constants. Ignoring energetic driving forces, activation energy will be the same in both directions; both rate constants are then identical. The remaining factors in the forward and backward rates are concentration factors and are readily expressed. The forward rate equals the rate factor times the appropriate concentrations of reactive sites (i.e., monomer ends) on i-segments and j-segments, which are iR_i/V and jR_j/V, respectively, where R_i and R_j are the numbers of i-rings and j-rings in total volume V; i.e.

$$r_f = k_f ij(R_iR_j)/V^2 \tag{1}$$

where r_f and k_r are the forward rate and rate constant. The catenane breakup rate, r_r, is

$$r_r = k_r(iCa_{ij}/V)(jc_e) \tag{2}$$

where k_r is the reverse rate constant, Ca_{ij} is the total number of catenanes containing one ring with i monomers and a second with j of them, and jc_e is equivalent to the concentration of j-ring monomer sites constrained into the neighborhood of the i-ring sites by the topological bond. The quantity iCa_{ij}/V represents the concentration of all the reactive sites on the i-ring monomers of such catenanes. However, only sites on j-ring monomers of the *same* catenane can react with each i-ring site, and their concentration is represented by c_e, which must be estimated by reference to the distribution of distances of random j-ring sites from random i-ring sites and particularly to the probability that they are within the contiguity volume element mentioned above. The i-to-j root mean square

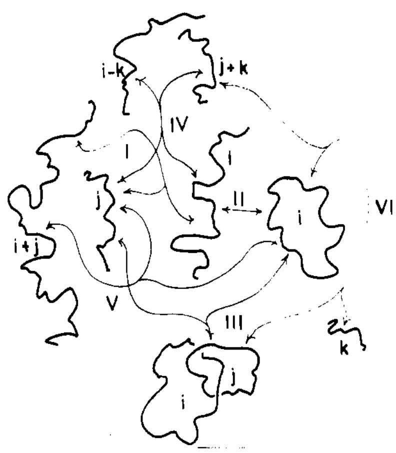

Figure 1. Equilibria in polymerizing system containing rings, chains, and catenanes.

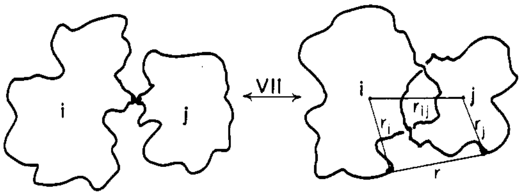

Figure 2. Ring passage equilibrium and its characteristic distances.

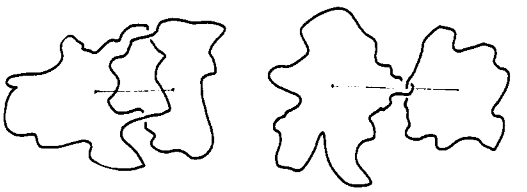

Figure 3. Limitation of intercentric distance: (a) unconstrained ($r_{ij} < r_i + r_j$); (b) constrained ($r_{ij} = r_i + r_j$).

distance, r, is a result of vector addition of three distances, taken at first approximation to be independent in direction from one another (Figure 2), in a random three-step walk. The three distances are (1) r_i, the root mean square radius of the i-ring, (2) r_j, the root mean square radius of the j-ring, and (3) r_{ij}, the root mean square of the distances of the ring centers, or intercentric distance, as limited by ring constraints.

The overall mean square distance is

$$r^2 = r_i^2 + r_j^2 + r_{ij}^2 \tag{3}$$

r_i and r_j are radii of gyration and readily calculated for the Kuhn model. Evaluation of r_{ij} requires some consideration. It appears to be approximately the sum of r_i and r_j. Figure 3 shows two rings of a catenane, in projection on a plane passing through their centers, in unconstrained and constrained position. The instantaneous size of r_{ij} varies from zero to the instantaneous value of $r_i + r_j$. At the larger of the values, the rings are in constraint. Simply viewed, we may consider the intercentric distance r_{ij} to be confined to a sphere of radius $r_i + r_j$ at any point of time. Both r_i and r_j are separately variable and distributed Gaussianly.

The distribution of intracentric distances is not Gaussian but is more nearly a uniform volume density within a sphere of radius $r_i + r_j$. Mathematical simplification, with small inaccuracy (relative to other assumptions made), results from replacing this non-Gaussian length by a Gaussian distribution which has an equal probability at short distance. Multiplying $r_i + r_j$ by the factor $a = (6/\pi)^{1/6} = 1.114$ accomplishes this.

The complete walk is now described as more-or-less Gaussian, with a mean square length

$$r^2 = r_i^2 + r_j^2 + a^2(r_i + r_j)^2 \tag{4}$$

Mean square radii within a ring containing n monomers, each of which in turn contains v Kuhn segments, are known[5] to equal $nvb^2/12$, where b is the length of the segment. The mean square walk length is thus approximately

$$r^2 = (vb^2/12)(1 + a^2)(i + j + q(ij)^{1/2}) \tag{5}$$

where $q = 2a^2/(1 + a^2) = 1.1074$.

The effective concentration of the end of a random Gaussian walk of mean square length r^2 is

$$(3/2\pi)^{3/2}r^{-3}$$

Substituting (5) into this value

$$c_e = (18/\pi)^{3/2}v^{-3/2}b^{-3}[(1 + a^2)(i + j + q(ij)^{1/2})]^{-3/2} \tag{6}$$

From classical ring–chain equilibrium theory[6]

$$R_n/V = Bn^{-5/2}x^n \tag{7}$$

where R_n is the number of rings containing n segments,

$$B \equiv \tfrac{1}{2}(3/2\pi)^{3/2}(v^{1/2}b)^{-3}$$

and x is the fraction of reacted end groups on the chains alone. The system treated here corresponds to JS's case I, the dimethylsilanediol type, a homopolymer with a symmetric monomer. Cases II and III, with unsymmetric homopolymer and two-monomer alternating copolymer will not be considered.

Equating forward and backward rates and constants in (1) and (2)

$$Ca_{ij}/V = (R_i/V)(R_j/V)/c_e \tag{8}$$

Now substituting for c_e from (6) and for R_i and R_j from (7)

$$Ca_{ij}/V = C(i + j + q(ij)^{1/2})^{3/2}(ij)^{-5/2}x^{i+j} \tag{9}$$

where

$$C = \frac{(1 + a^2)^{3/2}(v^{1/2}b)^{-3}}{(2^{13}\pi^3)^{1/2}} = 0.0067(v^{1/2}b)^{-3}$$

The factor $(v^{1/2}b)^{-3}$ depends on the monomer. It is a reciprocal volume, corresponding to a cube one Kuhn segment, times the square root of the number of segments per monomer, on a side. The factors containing i and j give a distribution for catenane sizes, insofar as the model is correct, and (9) can be used as the basis for calculating number and weight fractions of catenanes in such an equilibrium mixture of chains, rings, and catenanes. Summation over i and j in (9) gives the total number of catenanes in unit volume; summation after multiplication by $i + j$ gives their total monomer content. To avoid redundant summation, the i-ring is declared to be the bigger (or equal) one, and summation over j is carried on only up to i. The number of catenanes, defined as I'', and number of monomer units in catenanes, defined as N'', are given by the summations cited over Ca_{ij}:

$$I'' = CV\phi'(x, \tfrac{5}{2}) \tag{10}$$

and

$$N'' = CV\phi'(x, \tfrac{3}{2}) \tag{11}$$

where the ϕ' functions represent the summations

$$\phi'(x, \tfrac{5}{2}) \equiv \sum_{i=1}^{\infty}\sum_{j=1}^{i}[(i + j + q(ij)^{1/2})^{3/2}(ij)^{-5/2}x^{i+j}]$$

and

$$\phi'(x, \tfrac{3}{2}) \equiv \sum_{i=1}^{\infty} \sum_{j=1}^{i} [(i + j)(i + j + q(ij)^{1/2})^{3/2}(ij)^{-5/2}x^{i+j}]$$

Similarly defined for use with weight averages is

$$\phi'(x, \tfrac{1}{2}) \equiv \sum_{i=1}^{\infty} \sum_{j=1}^{i} [(i + j)^2(i + j + q(ij)^{1/2})^{3/2}(ij)^{-5/2}x^{i+j}]$$

These summations are arbitrarily denoted with the numbers $^5/_2$, $^3/_2$, and $^1/_2$ in parallel with those of Truesdell,[7] as computed for use in JS. I designate them, tentatively and generically, as "second-order Truesdell (T2) functions" and the simple summations $\phi(x, {}^5/_2)$, etc., as "first-order Truesdell (T1) functions". The form of the T2 functions will change with further refinements, and they may require additional parameters in their definition, e.g., the value of q. A convolutional summation proves more convenient for computation and for detailed distribution functions.

A simple calculation gives the ratio of numbers of catenanes to rings and of numbers of monomers in catenanes to those in rings:

$$I''/I' = (C/B)\phi'(x, \tfrac{5}{2})/\phi(x, \tfrac{5}{2}) \tag{12}$$

and

$$N''/N' = (C/B)\phi'(x, \tfrac{3}{2})/\phi(x, \tfrac{3}{2}) \tag{13}$$

where I' is the number of rings, and N' the number of monomer units in rings, respectively.

Further discussion of the entire system requires definition of the following in terms of N, the total number of monomers present, M, the total number of molecules, and N', N'', I', and I'', defined above: $D \equiv$ the number-average degree of polymerization of the whole system $\equiv N/M$, $\rho_w \equiv$ the weight fraction of rings in the system $\sigma_w \equiv$ the weight fraction of catenanes in the system $\equiv N''/N$, $\sigma_n \equiv$ the number fraction of catenanes in the system $\equiv I''/M$, $p \equiv$ the fraction of reacted functional groups in the system $\equiv$ $(N - M + I' + I'')/N = (N - I)/N$, $D_{ca} \equiv$ the number-average degree of polymerization of the catenanes $\equiv N''/I''$, and $D_{caw} \equiv$ the weight-average degree of polymerization of the catenanes $\equiv N'/I'$.

It is now possible to specify many of the fractions and averages above, by reference to (9)–(11), the definitions above, and the parameters x, B, and C. The distributions and average sizes of chains have long been known,[8] as have those of the ring fraction.[6]

The catenane number- and weight-average molecular weights, D_{ca} and D_{caw}, in monomer units, are

$$D_{ca} = \phi'(x, \tfrac{3}{2})/\phi'(x, \tfrac{5}{2}) \tag{14}$$

and

$$D_{caw} = \phi'(x, \tfrac{1}{2})/\phi'(x, \tfrac{3}{2}) \tag{15}$$

The derivable formulas for the number- and weight-average molecular weights of the chain and ring fractions, separately, in this work, are identical with those of JS. To find the overall weight fraction of chains, rings, of catenanes, define, as in JS

$$c \equiv 1000N/(N_0V)$$

where N_0 is Avogadro's number, and c the molar concentrations of monomers, i.e., the "ground molarity" of the system. For both constant factors B and C associated with rings and catenanes, let

$$B' \equiv 1000B/N_0$$

$$C' \equiv 1000C/N_0$$

converting to concentrations expressed in moles/liter, instead of molecules per cm^3.

The calculation of p and the weight fractions of rings and catenanes is possible directly from the definitions above. The weight fraction of catenanes, σ_w, is seen to be

$$\sigma_w = (C'/c)\phi'(x, \tfrac{3}{2}) \tag{16}$$

in parallel with the corresponding result for rings from JS:

$$\rho_w = (B'/c)\phi(x, \tfrac{3}{2}) \tag{17}$$

To calculate p, the overall fraction of reacted end groups, several more relations are needed. Given the known[8] distribution of chain sizes

$$C_n = Ax^n \tag{18}$$

where C_n is the number of chains of length n, and A a normalizing factor, and the summed forms of (18)

$$I = \sum C_n = Ax/(1 - x) \tag{19}$$

and

$$N_c = \sum nC_n = Ax/(1 - x)^2 \tag{20}$$

where I is the total number of chains, and N_c the total number of monomers in chains, there now results, using the overall relations

$$M = Ax/(1 - x) + BV\phi(x, \tfrac{5}{2}) + CV\phi'(x, \tfrac{5}{2}) \tag{21}$$

and

$$N = Ax/(1 - x)^2 + BV\phi(x, \tfrac{3}{2}) + CV\phi'(x, \tfrac{3}{2}) \tag{22}$$

and the definitions of p, I, B', and C', with elimination of A

$$p = x + (1 - x)[(B'/c)\phi(x, \tfrac{3}{2}) + (C'/c)\phi'(x, \tfrac{3}{2})] \tag{23}$$

Expression of fractions and averages in terms of p, the overall fraction of reacted end groups, rather than of x, the fraction of reacted end groups *on the chains alone*, must be done numerically, rather than in closed form.

The weight-average molecule weight of the entire system can be found from the weight fractions of catenanes and rings in (16) and (17) and from the weight averages of catenanes given above and those of the chains and rings, given suitable summations over (7) and (8), as performed in JS.

From (23), it can be seen that $p = 1$ at a point when

$$c = B'\phi(x, \tfrac{3}{2})[1 + N''/N'] \tag{24}$$

This value of x is designated x^*; here, for this value of c, all end groups have reacted.

A special case of importance arises when no chains are present, nor involved in the equilibria, but only a homogeneous set of rings, defined to contain n ($=i = j$) monomers each. For this case, (7) is invalid, and c_r, the concentration of rings, is used instead of R_i/V and R_j/V. Instead of summing over (9), a substitution of (6) into (8) gives c_{ca}, the catenane concentration:

$$c_{ca} = (\pi/18)^{3/2}(1 + a^2)^{3/2}(2 + q)^{3/2}(v^{1/2}b)^3n^{3/2} \tag{25}$$

The number ratio of catenanes to rings (the weight ratio is just twice this) is thus

$$c_{ca}/c_r = 1.34c_r(nvb^2)^{3/2} \tag{26}$$

The last factor is recognizable as the volume of a cube whose sides equal the Gaussian root mean square distance between the ends of a chain made by opening the n-mer ring. Note that c_r is expressed in (26) as molecules per cm^3; the ratio on the left-hand side is dimensionless. Note also

Table I
Values of Second-Order Truesdell Sums and Quotients

x	$\phi'(x, {}^5/_2)$	$\phi'(x, {}^3/_2)$	$\phi'(x, {}^1/_2)$	I''/I' [a]	N''/N' [b]	D_{ca}	D_{caw}
0.1	0.0566	0.1153	0.2371	0.02244	0.04485	2.036	2.056
0.2	0.2355	0.4903	1.045	0.04575	0.09161	2.082	2.132
0.3	0.5537	1.186	2.651	0.07026	0.1414	2.142	2.236
0.4	1.036	2.299	5.472	0.09641	0.1959	2.219	2.380
0.5	1.718	3.992	10.32	0.1249	0.2577	2.324	2.586
0.6	2.651	6.563	19.03	0.1567	0.3317	2.471	2.899
0.7	3.948	10.63	36.40	0.1938	0.4276	2.693	3.424
0.75	4.779	13.64	52.48	0.2154	0.4904	2.856	3.845
0.8	5.785	17.82	79.84	0.2402	0.5713	3.081	4.480
0.85	7.039	24.06	133.6	0.2698	0.6849	3.420	5.549
0.9	8.687	34.86	269.5	0.3077	0.8711	4.013	7.732
0.95	11.14	60.94	892.2	0.3644	1.305	5.472	14.64
0.97	12.66	89.91	2202	0.4011	1.780	7.100	24.49
0.99	15.33	210.1	1660_{0}	0.4693	3.731	13.71	79.0
0.995	16.70	370.7	620_{00}	0.5069	6.311	22.19	167
0.996	17.10	447.7	952_{00}	0.5183	7.545	26.17	213
0.997	17.62	574	166_{000}	0.5327	9.554	32.6	289
0.999	19.40	1540	142_{0000}	0.5845	24.9	79.8	919

[a] $=(C/B)[\phi'(x, {}^5/_2)/\phi(x, {}^5/_2)]$. [b] $=(C/B)[\phi'(x, {}^3/_2)/\phi(x, {}^3/_2)]$.

that c_r is not the ground-molar concentration c, except in the case of monomeric rings.

Similar calculations can be made for any chain-free system whose ring size distribution is known.

Results

The calculations of (10)–(17) and (23) have been computed for a range of reacted fractions x, with especial reference to an arbitrary prototype system, a flexible-chain carbon polymer with 36 carbons per monomer ring, each containing 9 Kuhn segments, 5 Å long. For such a polymer, C' is calculated to be 0.00323 M, and B', 0.081 M.

Numerical calculations using (26) for the chain-free, homogeneous-monomer-ring case with this polymer are immediately performable. Using a c_r of 1.8 M, corresponding to 100% hydrocarbon, we find the number ratio of catenanes to rings to be 4.9; the weight ratio is twice this, predicting an approximate 90% conversion of ring monomers to catenanes!

Table I gives the values of the T2 sums, the ratios of numbers of $\phi'(x, m)/\phi'(x, m + 1)$, the quotients $(C/B)\phi'(x, m)/\phi(x, m)$ (m is ${}^5/_2$ or ${}^3/_2$), and the ratios of number- and weight-average molecular weights of catenanes to rings for the prototype example as a function of x, the fraction of chain end groups reacted. The original tabulations of the T1 sums are in ref 6 and 7. Multiplying the quotients by C/B (=0.0403), gives the number- and weight-average ratios of catenanes to rings for *any* polymer of this model, as tabulated. The T2 sums and the quotients diverge at $x = 1$ and are not tabulated, although the first two T1 sums converge to 1.34 and 2.61 for this value of x. Table II gives a set of calculated number and weight concentrations and fractions for the prototype chain–ring–catenane system at equilibrium with various values of x.

Discussion

Although primitive, this model leads to some interesting conclusions, which are worth examining even before any desired corrections are derived and applied:

1. The concentration of catenanes (at a fixed value of x) predicted by (9) in a completely equilibrated ring–chain–catenane system is independent of dilution. This is due to an increase of rings with dilution which just compensates for the expected decrease in the bimolecular catenane formation reaction rate. The catenane breakup rate is monomolecular and unaffected by concentration. The concentration of rings, as given in eq 5 of JS, is also independent of dilution. The concentration and weight fraction of both rings and catenanes continuously increase during the reaction.

Table II
Parameters of Hydrocarbon-Type Chain–Ring–Catenane System with 5-Å Kuhn Segment and 9 Segments/Monomer (c = 1.8 M)

x	I''/N	N''/V	ρ_{w}	σ_{w}	p
0.1	0.000185	0.000378	0.00468	0.000210	0.104
0.2	0.000771	0.00160	0.00973	0.000892	0.208
0.3	0.00181	0.00388	0.0152	0.00216	0.312
0.4	0.00339	0.00753	0.0213	0.00418	0.415
0.5	0.00562	0.0131	0.0282	0.00726	0.518
0.6	0.00870	0.0215	0.0360	0.0119	0.619
0.7	0.0129	0.0348	0.0452	0.0193	0.719
0.75	0.0156	0.0447	0.0506	0.0248	0.769
0.8	0.0189	0.0583	0.0567	0.0324	0.818
0.85	0.0230	0.0788	0.0639	0.0438	0.866
0.9	0.0284	0.114	0.0728	0.0634	0.9136
0.95	0.0365	0.199	0.0849	0.111	0.9598
0.97	0.04146	0.294	0.0988	0.163	0.9797
0.99	0.05018	0.688	0.102	0.382	0.9948
0.995	0.05468	1.21	0.107	0.674	0.9989
0.996	0.0560	1.47	0.108	0.814	0.9997

2. The ratios of catenanes to rings, both number and weight, are increasing functions of x and independent of both the segment parameters of the molecule and the concentration, as the ratios of C/B (=C'/B') are size independent. The number- and weight-average catenane molecular weights are also size independent, as are the molecular weights of the chain and ring fractions. The ratios of chains to either rings or catenanes, however, are concentration dependent, with higher dilution equally favoring rings and catenanes. With increasing x, the catenanes become much larger than twice the average size of the rings; this means that the larger rings are the ones most likely to become catenanes.

3. The T2 sums diverge when $x = 1$, i.e., at chain end-group disappearance. Moreover, the ratios given by (12) and (13) also diverge. At first glance, this seems to correspond to an increase in the catenane-to-ring ratios without limit as the reaction proceeds; later we will see that this is not generally true.

4. The overall fraction of reaction, p, is, of course, always at least as great as that of the chain fraction, x. From (24), however, it can be seen that when x is big enough, or c small enough, the chain fraction vanishes. Here $x^* < 1$, and the (vanished) chains are of finite size. The phenom-

enon in the ring–chain system was described in JS as a "critical concentration" below which a system of 100% rings could appear. The extension of theory in this paper provides a similar prediction for nonchains (rings + catenanes). Unlike the situation with chain–ring system, the chain–ring–catenane system can go to 100% nonchains at *any* concentration, *provided that the reaction is driven far enough, i.e., x is large enough.* After the chains have disappeared, the system will not change by any equilibrium process, as catenanes and rings are already in the distribution pattern dictated by the kinetic considerations of (1) and (2). Given any particular concentration, x^* is given by (24). For the hydrocarbon model system used, at a concentration of 1.8 ground molar, the undiluted maximum, x^* is slightly above 0.996. This corresponds to a number-average chain molecular weight of about 250 monomers, with number-average molecular weights of about 100 000, 600, and 10 000 for the chain, ring, and catenane fractions, respectively. At this point, there is about half a catenane for each ring, but the molecular weight of the catenanes is about 15 times that of the rings, and most of the monomers are in catenanes. At lower concentrations, the value of x^* is smaller, and the ratio of catenanes to rings and the relative molecular weights of catenanes and rings decrease, as can be seen in Table I. Thus a maximum catenane fraction will be generated by driving the reaction to completion at the highest possible concentration.

A final interpretation of this theory can be applied to the possibility of an interpenetrating network (IPN) or catenane gel in such systems. Preliminary calculations indicate that no system containing chains, rings, and catenanes in equilibria can produce a gel; but sufficiently large chain-free rings in equilibria with catenanes, e.g., circular DNA of biological size, would do so.

It remains a major question whether this model can be considered relevant to real catenane-forming systems; it describes systems at equilibrium only. Although similar models have proven useful in dealing with other systems with kinetic determinants, in this case there is, except for the topoisomerase–DNA system, no demonstrable such reversible reaction. In fact, FW specifically demonstrates the unlikelihood, from quantum arguments, of ring passage. Nonetheless, the results are in good agreement with those of FW for the special case of the flexible hydrocarbon-type monomers. Their eq 2, prior to excluded volume considerations, leads to an expression identical with (26), except for numerical factor. When the effect of their using $r = nb^2/8$ rather than $nb^2/12$ for the mean square radius of a ring is taken into account, their factor leads to a result within 15% of this work. In view of theoretical imprecision in both works, this is most comforting. Does this calculation apply to nonpassage systems? It seems intuitively likely, considering the purely geometric quality of the states involved in the equilibria. For a ring which freely passes in and out of a set of other rings should have the same number and distribution of catenane structures at equilibrium as would a chain of equal length, with approximated ends, among the same set of rings and awaiting some ring-closure reaction which threads it. This strategem, then, may prove useful for systems beyond just those with free ring passage.

For practical results, excluded volume corrections are essential. The enormous values for catenane-to-ring ratios calculated with (26) indicate how out of range simple applications of the uncorrected theory is (as was application of JS). Two problems arise. The first is prominent with small rings and stems from the finite breadth of the polymer chains (FW estimated that hydrocarbon chains have a radius of 2.2 Å from the density of packed chains at 0 K). There is a variable decrease in the distance between any two segments in the i- and j-chains, as used to compute r in (5). This difference is twice the chain radius, times a mean secant factor of the order of 2, due to random mutual orientation of the colliding chains. Subtracting this total of 8.8 Å from the uncorrected value of 11.4 Å for r calculated with the prototype system reduces the value of r^3 to 1.2% of its original value and leads to a value of 0.06 for c_{ca}/c_r. This is still nearly an order of magnitude higher than that experimentally observed;[9] for rings of prototype size, the excluded volume is highly sensitive to the effective chain radius. One of 2.5 Å, for instance, would lead to less than 1% catenanes, in line with the cited observations.

A second problem associated with excluded volume arises with large rings. Use of Gaussian formulas for end-to-end distances leads to underestimates. Corrections using appropriate exponents for the probability of segment collisions, derived from random walks under non-self-intersecting restrictions,[10,11] would be appropriate. The T2 sums and ratios may change their divergence properties when so corrected.

Further corrections to the model must include possible energetic effects, existence of multiply linked catenanes at high catenane fraction, and uncertainties in the constraint distances, particularly elastic effects. These, refining of kinetic assumptions and consistent treatment of excluded volume, will require other contributions.

Note Added in Proof: I have failed to cite two works[12,13] which, contrary to the first paragraph of this paper, consider the important chain-free special case, and offer estimates of catenane production. Equations in both works bear a formal similarity to eq 26, predicting a linear increase in the catenane *fraction* with increase in concentration; both support the contention that configurational factors are correctly derived under equilibrium assumptions. Each paper deals with a system different from the small prototype of this paper; consequently no quantitative comparisons will be made here.

Acknowledgment. I gratefully acknowledge 40 years of help and inspiration from W. H. Stockmayer, as teacher and friend. Even in absentia, his spirit has permeated my current zeal.

References and Notes

(1) Oral doctoral examination of author, as witnessed by W. H. Stockmayer.
(2) Frisch, H.; Wasserman, E. *J. Am. Chem. Soc.* **1961**, *83*, 3789 (hereinafter referred to as FW).
(3) Kreuzer, K. N.; Cozzarelli, N. R. *Cell* **1980**, *20*, 245.
(4) Mizuuchi, K.; Gellert, M.; Weisberg, R. A.; Nash, H. *J. Mol. Biol.* **1980**, *14*, 485.
(5) Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301.
(6) Jacobson, H.; Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 1600 (hereinafter referred to as JS).
(7) Truesdell, C. A. *Math. Ann.* **1945**, *46*, 144.
(8) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137.
(9) Wasserman, E. *J. Am. Chem. Soc.* **1960**, *82*, 4433.
(10) Domb, C. *J. Chem. Phys.* **1963**, *38*, 2957.
(11) Fisher, M. E. *J. Chem. Phys.* **1969**, *45*, 1469.
(12) Wang, J. C.; Schwartz, H. *Biopolymers* **1967**, *5*, 953.
(13) Volgogodskii, A. V.; Lukashin, A. V.; Frank-Kamenetskii, M. D. *Zh. Eksp. Teor. Fiz.* **1974**, *67*, 1875.