

at equilibrium. The validity of doublet closure may then be examined in the analogous manner as the triplet closure. It suffices to quote the result. Whereas in the latter case it was at least possible to compare appropriate terms with each other, we now observe that *different* rate parameters appear in the two equations to be compared. For example, in considering the triplet 001, we note in eq 3c the appearance of k_1 , k_2 , k_2' , and k_3' . But from eq 3a and 3b and the assumption

$$n(001) = n(00)n(01)/n(0)$$

an equation for $dn(001)/dt$ results, which involves all rates. This inadmissible consequence of doublet closure is not surprising.

In conclusion, we have provided proof that any assertion of *rigorous* closure at the triplet level⁶ is erroneous. This, of course, does not necessarily exclude a *numerical* adequacy of the closure approximations used previously by us² or others, involving longer sequences. Indeed, results of type (5a–5b) are encouraging in this respect by demonstrating partial identities. Numerical comparisons of the remaining terms in these and analogous equations for longer sequences may prove useful.

At this point one may inquire whether special cases exist other than the trivial one of noncooperativity, where some form of closure of our rate eq 2 for infinite chains is rigorous. For example, consider the special case constructed by Glauber.⁴ In our notation, and setting his scale factor a equal to two, it implies

$$k_2 = k_2' = 1; \quad k_1 = k_1' = (1 - \gamma); \quad k_3 = k_3' = (1 + \gamma)$$

and satisfies, of course, the general condition on the rate constants^{1,2}

$$(k_2/k_2')^2 = (k_3/k_1')(k_1/k_3')$$

On substituting into the right-hand side of eq 3a, we observe that the coefficients of $n(01)$, $n(011)$, and $n(001)$ all vanish and only the coefficient of $n(0)$ survives, which renders eq 3a immediately integrable. On the other hand, in eq 3b, the analogous substitution does not eliminate the dependence on the triplet sequences. The situation in the further relations of the hierarchy, eq 1, follows the analogous pattern. However, Glauber has shown⁴ that in his special case a further closed differential equation for at least pair correlations can be obtained. It should be noted, however, that even the most general mechanism formulated by him represents a special case, namely

$$k_i/k_i' = k_j/k_j' \quad i, j = 1, 2, 3$$

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CORRECTIONS

"Polymer-Solvent Interactions for Homopolypeptides in Aqueous Solution," by A. J. Hopfinger, Volume 4, Number 6, November–December 1971, page 731.

On page 733, equation 3, the upper limit on the second integral should read $r_j + r_{ij}$. In equation 6, the upper limit on the sum should be n instead of N . The same error occurs in the text two lines above the equation.