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LETTER TO THE EDITOR

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LETTER TO THE EDITOR

In a recent paper in your journal [1] J. W. Stafford concludes that "in any bimolecular reaction which is at equilibrium, i.e.,

$$A + B \rightleftharpoons C + D \tag{1}$$

complete conversion cannot be achieved no matter how efficient the removal of a by-product may be." As will be shown below, this is a fallacious conclusion, arrived at by neglecting the statistical nature of thermodynamics.

The author uses a model system, condensation of a hydroxyacid,

$$HO{-}R_i{-}COOH + HO{-}R_j{-}COOH \rightleftharpoons HO{-}R_{i+j}{-}COOH + H_2O \tag{2}$$

to pursue his argument. A hypothetical experiment starts with one mole of hydroxyacid in a given volume, which polymerizes as water is removed stepwise. After each incremental water removal the system relaxes to a new equilibrium position. Eventually there is a single free water molecule left in the equilibrium mixture, though there are roughly 4 × 10^{11} potential water molecules in the form of hydroxyl and carboxyl groups. It is asserted that this is the state of maximum DP and that no further water can be removed. The system is purportedly incapable of achieving a new equilibrium position because this would involve less than one water molecule in the given volume, which the author supposes to be the lowest theoretically possible equilibrium concentration.

This is where the fundamental fallacy of the argument lies. It is a basic principle that equilibrium is a dynamic state and that equilibrium concentrations are time-averages of fluctuating instantaneous concentrations. An equilibrium concentration of, say, one half water molecule in the given volume means that there are no molecules at some instants and one, two, or even more at others. Thus there is absolutely no theoretical obstacle to reestablishment of equilibrium, no matter how low the equilibrium water concentration, nor is there a theoretical limit to the DP, as long as any hydroxyl and carboxyl groups are unreacted.

Stafford was led to the above consideration of condensation polymerization by an apparent paradox. Both kinetic and statistical approaches lead to a polydispersity $\overline{X}_w/\overline{X}_n$ equal to (1 + p), where p is the extent of reaction, i.e., 2 for complete reaction. Yet at completion there would be only a single giant macrocyclic molecule, i.e. $\overline{X}_w/\overline{X}_n$ equal to unity. This apparent paradox is again the result of applying thermodynamic principles to a non-statistical situation. Equilibrium (2) has meaning only as long as there are at least a few polymer molecules capable of undergoing reaction. These molecules continually change in DP, as the forward and back reactions take place, and the time-average concentration of each DP obeys the "most probable" distribution with $\overline{X}_w/\overline{X}_n = 2$.

As Stafford rightly recognizes, his conclusions are of little practical importance, for his maximum extent of reaction is immeasurably close to completion and cannot be attained in practice. Nevertheless, he chooses to consider hypothetical situations involving small numbers of molecules in non-statistical terms. It seemed necessary to demonstrate that this treatment did not invalidate LeChatelier's principle which implies that equilibrium reactions can be driven to completion by removal of product.

REFERENCE

[1] J. W. Stafford, J. Macromol. Sci.-Chem., A5, 1297 (1971).

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