New Developments in the Principle of Detailed Balancing

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The principle of detailed balancing states that $K = k_{forward}/k_{reverse}$. It imposes 1) relationships between the forms of the rate expressions for the forward and reverse processes of a mechanistic step, 2) the requirement of reversible loops to obey closure, and 3) the requirement to remove illegal loops. The recent development of DETBAL, a software application, greatly simplifies the task of identifying situations where the principle of detailed balancing is relevant.

DETBAL has been applied to a 109-step mechanism for the radiation chemistry of nitrate solutions, and it revealed a significant error in reversible loop closure and the presence of 6 illegal loops. Correction of these errors led to significant changes in the modeled kinetic behavior.[1]

Application of DETBAL to a 169-step mechanism for the UV photolysis of NH_2Cl solutions led to identification of a reversible loop that violated closure and 6 illegal loops.[2]

Published mechanisms for the Fenton reaction have reversible steps with rate-constant ratios that disagree with the equilibrium constant and reversible steps where the form of the forward and reverse rate expressions disagree with the form of the equilibrium expression. 59 unique illegal loops have been found in published reports on the Fenton reaction, and over 200 publications have been found with mechanisms violating the principle of detailed balancing.[3]

Use of DETBAL led to the identification of over 100 publications with mechanisms that included $HClOH^{\bullet}$ in reversible loops that violate closure or in illegal loops.[4]

$BrCl^{\bullet-}$ appeared in a 150-step mechanism for aquatic chemistry, and DETBAL showed that the mechanism has a reversible loop involving $BrCl^{\bullet-}$ that violates closure by a factor of 800,000.[5] Similar violations of closure involving $BrCl^{\bullet-}$ occur in approximately 50 subsequent publications.

References

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