This Week's Citation Classic ™

This paper and one published concurrently by the late M.L. Huggins[1] provided the basis for the statistical-thermodynamic theory of solutions of molecules dissimilar in size. Known as the Flory-Huggins theory, the results of these investigations and the works that followed them have found numerous applications, especially in the interpretation of the thermodynamic behavior of polymer solutions. [The *SCI®* indicates that this paper has been cited in over 645 publications since 1955.]

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The paper cited above was one of two that formed the basis for what has come to be known as the Flory-Huggins theory. The other paper was published by the late Maurice L. Huggins.[1] Our investigations had been carried out independently. I first became aware of Huggins's work when he presented it at the Colloid Symposium held at Cornell University in June 1941. At that symposium, I presented a paper on the theory of gelation and networks formed in nonlinear polymers, a subject unrelated to the above but one that, like it, has gained widespread acceptance. I was surprised to learn from the lecture delivered by Huggins that he had carried out work very similar to that which I was then preparing for publication on the thermodynamics of polymer solutions. After his lecture, I approached him to point out that I had been engaged in a similar investigation. He was most gracious and encouraged me, a mere fledgling at the time, to publish my work and to communicate it to him.

This was our first meeting; it proved to be the beginning of a lifelong friendship. We subsequently engaged in many scientific discussions on various topics and developments, not always with full concurrence but invariably with respect and good rapport.

As I have often stated, the theory credited to us should bear our names in the reverse order; his first publication preceded mine by a month or two. His initial contribution dealt with the lattice theory in greater detail; mine may have been more comprehensive in certain respects.

The ramifications of the so-called Flory-Huggins theory are many, and it continues to find further applications in new areas concerning mixtures of macromolecules and their solutions. At the time of our original publications on the subject, there was an urgent need for a theory capable of dealing with mixtures of molecules grossly dissimilar in size. I had read *Solubility of Non-Electrolytes*[2] in its second edition by the late Joel Hildebrand and was much impressed by the broad applicability of the ideal solution law. It was readily apparent, both on theoretical and experimental grounds, that this law could not be applied generally to polymer solutions, although rigorous thermodynamic arguments demonstrated that ideality must hold in the limit of infinite dilution. Various devices had been tried to amend the fairly obvious limitations on application of the ideal solution law to mixtures of molecules differing in size. None was appropriate at all concentrations.

The potentialities of lattice methods applied to mixtures came to be appreciated in the late 1930s, especially by Guggenheim and his followers. It was in this context that Huggins and I, independently, sought to find a basis for understanding and interpreting the equilibrium properties of polymer solutions.

1. **Huggins M L.** Thermodynamic properties of solutions of long-chain compounds. *Ann. NY Acad. Sci.* 43:1-32. 1942. (Cited 315 times since 1955.)
2. **Hildebrand J H.** *Solubility of non-electrolytes.* New York: Reinhold. 1936. 203 p.