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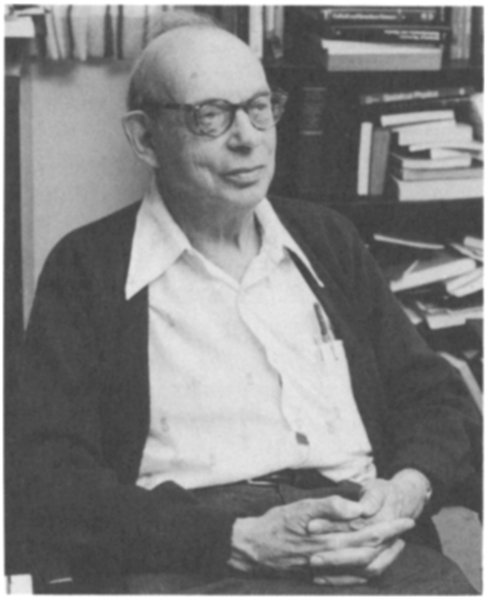
In Memorium: Oscar Knefler Rice, 1903–1978

Oscar K. Rice, late Kenan Professor of Chemistry in the University of North Carolina, was born in Chicago on February 12, 1903. He received his B.S. degree in 1924 and his Ph.D. in 1926, both from the University of California at Berkeley. He was for three years a National Research Council Fellow at the California Institute of Technology and at Leipzig, and then Instructor of Chemistry at Harvard University, 1930–1935. He was at the University of North Carolina from 1936. He died May 7, 1978.

Rice's scientific work spanned the full range of modern physical chemistry: quantum theory, chemical kinetics, equilibrium and nonequilibrium thermodynamics, and statistical mechanics. In each of these fields he was a



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pioneer, frequently the first to identify and attack a problem of far-reaching significance.

His early work in unimolecular reaction-rate theory is classic. Its decisive importance was recognized at once, and led to his being chosen to receive the second American Chemical Society Award in Pure Chemistry, in 1932. (The first, in 1931, went to Linus Pauling). It is, in its present form as the RRKM theory (Rice–Ramsperger–Kassel–Marcus), the standard formulation of unimolecular reaction rates, and its foundations are still the object of much study, both in theory and in experiment.

Rice's work in molecular quantum mechanics was equally important. His theory of predissociation and diffuse spectra was accepted as fundamental, as were his ideas on electronic transitions and the intersection of potential energy surfaces. He was the first to account for the quenching of electronic fluorescence in those terms. His theoretical studies of inelastic molecular collisions and vibrational excitation included the discovery of what is now known as the method of perturbed stationary states (though it is often credited to others, who, some time later, developed it independently). Rice made basic contributions to the theory of the electronic structure of molecules. His book, *Electronic Structure and Chemical Binding* (1940), which appeared within a year of Pauling's *Nature of the Chemical Bond*, was one of the first expositions of this subject for students, had a very wide influence, and was a highly original contribution to the pedagogical literature of science.

In the early 1960s Rice took up again the problem of the kinetics and the mechanism of atomic recombination (and its inverse, diatomic dissociation), which had long been one of his interests. He presented arguments of great power and subtlety to clarify the question of equality between the equilibrium constant and the ratio of forward and reverse rate constants. He showed how a rate constant may be substantially smaller than the coefficient in the unidirectional flux at equilibrium, but showed also that the rate constants of the two opposing processes are decreased by exactly equal factors, so that their ratio is still the equilibrium constant. Our understanding of the very meaning of a rate constant is now incomparably deeper than it had been prior to Rice's analysis.

Impressive as all those accomplishments were, they were nevertheless matched in depth and originality by his work on phase transitions and critical phenomena, Rice's dominant interest in his last years. Some of the roots of the scaling and homogeneity principles, which have been important heuristic ideas for understanding the relations connecting thermodynamic singularities at a critical point, are to be found in Rice's studies of the thermodynamics of critical-point and lambda-point phenomena. He was the first to show that the compressibility, the specific heat, and the shape of the coexistence curve bear a necessary relation to each other, so that the singularity in any one may be determined from the singularities in the other two. Along the same lines, it was Rice who first found a connection between the shapes of the coexistence curve and the critical isotherm. (In modern terms, he discovered the special case $\gamma = 1$ of the relation $\delta = 1 + \gamma/\beta$.) It was also Rice who was the first to point out that what might have been a lambda transition in a lattice, had the lattice been incompressible, may actually, in a compressible lattice, prove to be a first-order phase transition. Those theoretical ideas were subsequently confirmed by experiment, and have since given rise to a substantial literature in which the theory has been further elaborated by many others. His address, "Secondary Variables in Critical Phenomena," which he delivered on the occasion of being given the American Chemical Society's 1970 Peter Debye Award in Physical Chemistry, was an extension of that same theme. Rice also made extensive application of his ideas on phase transitions and liquid structure to the problem of structure and superfluidity in liquid helium.

He was the first, also, to treat seriously the fundamental problem of determining intermolecular forces from bulk macroscopic properties. His program has been brought up-to-date by others, using modern thermodynamic data, and has culminated in the accurate rare-gas potentials that are now available. Rice was also among the first to recognize the relevance of the gas of hard spheres to the problem of the structure of simple liquids, and his was one of the pioneering studies of the equation of state of such a hard-sphere fluid, pre-dating the accurate determination of that equation of state by computer simulation.

Again in regard to his studies of critical phenomena, it should be recorded that his experimental work on critical consolute points of binary liquid mixtures was fully as important as his theoretical work. His determinations of the coexistence curves and other properties in the cyclohexane–aniline and perfluoromethylcyclohexane–carbon tetrachloride systems are classics of their kind, have hardly been surpassed in care and precision, and provide some of our most valuable data for testing theoretical ideas.

It was Rice who made the first experimental determination of the rate of vanishing of the interfacial tension near a consolute point, providing data important for the subsequent development of the theory of interfaces near critical points. Indeed, he himself contributed significantly to that theory, starting with his early recognition of the importance of interfacial tension and structure in phase equilibrium, and continuing with his deep and strikingly original suggestions to elucidate some aspects of the structure of interfaces by studying the effect of "impurities" on the critical point.

Rice was the author of *Statistical Mechanics, Thermodynamics, and Kinetics* (W. H. Freeman, 1967), one of the most original of the modern texts on statistical mechanics. There is not a topic in it that he did not think through for himself and put his signature on.

Thoughts about the structure of interfaces and the theory of interfacial tension, further ideas on how the diverging range of concentration fluctuations manifests itself in singular thermodynamic properties at critical points, and continuing experiments on binary mixtures near their consolute points were the preoccupations of this remarkable scientist, when he died, at the age of seventy-five. He was in the fifty-second year of his extraordinarily productive career—ending it as he started it, thinking deeply about science.

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