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O S C A R   K N E F L E R   R I C E

*1903—1978*

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*A Biographical Memoir by*

BENJAMIN WIDOM AND RUDOLPH A. MARCUS

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*Biographical Memoir*

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1960

Richard K. Ricci

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Richard K. Ricci, 39, 2nd Lieutenant, Army Signal Corps, was born in New York City on June 1, 1921. He attended the University of Michigan, Ann Arbor, where he received his B.S. degree in 1943. He was graduated from the University of Michigan Law School in 1946.

1960



*Richard K. Ricci*

# OSCAR KNEFLER RICE

*February 12, 1903–May 7, 1978*

BY BENJAMIN WIDOM AND RUDOLPH A. MARCUS

WITH THE DEATH of Oscar Rice at Chapel Hill, North Carolina, in the spring of 1978, physical chemistry lost one of its foremost practitioners, a man who for more than half a century had been a leader and an inspiration in the development of that science. For the last forty-two of those years he had been a member of the chemistry faculty of the University of North Carolina, as Kenan Professor from 1959 and as Kenan Professor Emeritus from 1975. He died the week before he was to have been awarded an Sc.D. degree by his university. The degree was awarded posthumously; he was cited as “very likely the most distinguished chemist ever to have lived in North Carolina.”<sup>1</sup>

Oscar Rice was born in Chicago on February 12, 1903. His parents, Oscar Guido Rice and Thekla Knefler Rice, had been married only six months when his father died of typhoid fever. His mother never remarried, and Oscar never knew a father. He was brought up by his mother and her sister, Amy Knefler, who joined them as homemaker while Thekla Rice supported the household as a secretary. Although the financial resources of the family were strained,

<sup>1</sup> Maurice M. Bursey, *Carolina Chemists: Sketches from Chapel Hill* (Department of Chemistry, University of North Carolina at Chapel Hill, 1982), p. 153.

Oscar's mother and aunt made the sacrifices necessary to enable him to complete his education.<sup>2</sup>

Oscar attended what was then San Diego Junior College (now San Diego State University) from 1920 to 1922, then transferred to the University of California, Berkeley, where he was awarded the B.S. degree in 1924. He stayed on at Berkeley for his graduate studies and by 1926—he was then only 23 years old—had earned his Ph.D. (Two of his contemporaries as graduate students at Berkeley were Henry Eyring and Joseph E. Mayer, also to become important figures in physical chemistry.) After one more year at Berkeley (1926–27) as an Associate in Chemistry, Rice became a National Research Fellow.<sup>3</sup> He spent the first two years of his fellowship, 1927 to 1929, at the California Institute of Technology (with brief stays again in Berkeley); the third, 1929–30, was spent in Leipzig.

On his return from Leipzig, Rice was appointed Instructor in Chemistry at Harvard. He had by then already completed the early versions of his great work on the theory of unimolecular reactions, written at Berkeley and Caltech, so it can hardly have been a surprise when, in 1932—after having been at Harvard for two years—he was given the second American Chemical Society Award in Pure Chemistry. (The first winner, in 1931, was Linus Pauling.) For some years while at Harvard, Rice gave a course of lectures entitled “Advanced Inorganic Chemistry” on which he later based his book *Electronic Structure and Chemical Binding*. The book was not completed, however, until 1939, after Rice’s first three years in Chapel Hill. It was published in 1940.

Rice’s Harvard period was highly productive on the research side. He studied energy exchange in inelastic molec-

<sup>2</sup> From a letter by his wife, Hope Sherfy Rice, to their friend “Cally” (the Reverend Ann Calvin Rogers-Witte), written May 10, 1978, three days after Oscar Rice’s death.

<sup>3</sup> In later years called a National Research Council Fellow.

ular collisions, using creatively the methods of what was then the new quantum mechanics. He continued the work on unimolecular reaction-rate theory and on predissociation and diffuse spectra, which he had begun earlier at Caltech and Leipzig. He wrote his noted papers with Gershinowitz (a Harvard graduate student and a Parker Traveling Fellow at Princeton) on reaction-rate theory, and he pursued his important experimental work on thermal decompositions with the collaboration of D. V. Sickman (a postdoctoral associate), A. O. Allen (his first graduate student), and H. C. Campbell.

Although those years at Harvard could hardly have been more fruitful, Rice seemed not to be very happy there. A. O. Allen believes that the social sophistication of Harvard may not have been well suited to Rice's quiet, solitary, and contemplative style. Later, at Chapel Hill, he found him to be more relaxed and at peace—although otherwise unchanged.<sup>4</sup>

On leaving Harvard in 1935, Rice returned briefly (1935–36) to the Berkeley chemistry department as a research associate. In 1936, with an appointment as associate professor, he began his long and illustrious career at the University of North Carolina at Chapel Hill. He was promoted to full professor in 1943.

Rice was to remain at Chapel Hill, although he traveled widely for conferences and lectures and took an occasional leave of absence. Just after the Second World War, from 1946 to 1947, Rice took a position as Principal Chemist at the Oak Ridge National Laboratory. "The story goes that the Army officer in charge of the laboratory was much concerned about the productivity of this man who sat all day in an armchair thinking. When it was time to review what had been produced, the quality of the work that Dr. Rice had generated in the armchair was so impressive that the officer recom-

<sup>4</sup> Letter of November 8, 1982, by A. O. Allen to the authors.

mended stuffed armchairs for every scientist whom he supervised.”<sup>5</sup> Before that, at Chapel Hill, under contract to the Office of Scientific Research and Development, Rice had worked on the problem of the burning of rocket powders (1950g).<sup>6</sup> In 1947 he was awarded a U.S. Army and Navy Certificate of Appreciation for his war research.

It was at Oak Ridge that Oscar Rice met Hope Ernestyne Sherfy, whom he asked to join him as his wife when he returned to Chapel Hill. They were married in 1947. Hope Rice was Oscar’s constant companion and a source of joy, comfort, and support for their more than thirty years together. They adopted two daughters, Margarita and Pamela, both born in Germany. The Rices adopted them on two separate trips Oscar (accompanied by Hope on the first one) made to Germany to attend scientific congresses. After the death of Oscar’s Aunt Amy, his aged mother came to live with them in a new and larger house they built in Chapel Hill.

The only substantial time Rice spent away from the University of North Carolina, except for his year at Oak Ridge, was in 1968, when he was a visiting professor at the Virginia Polytechnic Institute (now the Virginia Polytechnic Institute and State University) in Blacksburg, and in 1969, when he was Seydel-Woolley Visiting Professor of Chemistry at the Georgia Institute of Technology.

Those physical scientists who, like Oscar Rice, were born in the first half of the century’s first decade, reached scientific maturity along with the new quantum theory and wave mechanics. They could thus, still as young men, participate in the glorious crusade that caused one after another famous problem of physics or chemistry to yield to the power of the new ideas and techniques. Writing of the time he began re-

<sup>5</sup> Bursey, *Carolina Chemists*, p. 151.

<sup>6</sup> Here and hereafter, years and letters in parentheses refer to entries in the appended bibliography; thus, (1950g) means the seventh entry for 1950.

search with Rice at Harvard, A. O. Allen says: "Oscar had just recently published his epochal paper with Ramsperger on the theory of unimolecular reactions, which played an important role in the expansion of physical chemistry during what I later heard H. S. Taylor refer to as the 'glorious thirties.' Indeed, a time when the rest of the world was depressed and fearful was just when the physical sciences were most exciting and hopeful. I asked for nothing better than to join the exciting revolution in chemical dynamics under Oscar's tutelage."<sup>7</sup>

Rice's first work at Berkeley was not with quantum mechanics, for the new theory had hardly been born. Instead, he investigated those aspects of colloid stability and surface tension that could be treated by classical methods. In his first published paper (1926a), he acknowledges help from R. C. Tolman of Caltech and J. H. Hildebrand of Berkeley, who were, or were soon to be, recognized as two of the most prominent physical chemists and inspiring teachers in this country. At Berkeley, Rice also knew G. N. Lewis, who held the promising young student in high regard and later recommended him for the faculty position at Harvard.<sup>8</sup> Rice's early work on surface tension was to have important echoes later in his career. Indeed, the combining of microscopic with macroscopic, largely thermodynamic, ideas to create a phenomenological theory or description—the process one sees in these early papers—was also to be the style of much of his later work from the 1940s on.

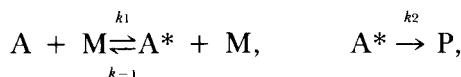
His great work on unimolecular reactions was also, at first (1927b), non-quantum mechanical. It followed and was intended to explain the measurements of H. C. Ramsperger (also then in the Berkeley chemistry department) on the de-

<sup>7</sup> A. O. Allen letter.

<sup>8</sup> As attested by a longtime friend, Professor Milton Burton of Notre Dame, in a letter of November 4, 1983, to the authors.

composition of azomethane. Presumably, it was during Rice's first postdoctoral year, when he was still at Berkeley as an Associate in Chemistry, that he and Ramsperger formulated the theory.<sup>9</sup>

The general problem was accounting for the rates of unimolecular decompositions or isomerizations, particularly for the observed fall-off of the rate at low pressures. Earlier ideas of Lindemann, later elaborated by Hinshelwood (both worked in England), yielded some important clues. A primitive version of that early theory is the following: Suppose A is the molecule that will react to form product P, and that it does so through a high-energy intermediate A\* that is formed by the collision of A with some species M that could be either A or some chemically inert gas with which A is diluted. The reaction scheme is then:



characterized by activation and deactivation rate constants  $k_1$  and  $k_{-1}$  and by the rate constant  $k_2$  for reaction of the activated species. If the population of the latter is assumed to vary only slowly during the reaction (the "steady-state" approximation), the apparent rate coefficient k for the observed reaction  $A \rightarrow P$  is

$$k = k_1 k_2 (M) / [k_{-1} (M) + k_2],$$

where (M) is the concentration of M. Thus k decreases as (M) decreases, which is the characteristic low-pressure fall-off of the rate coefficient.

This scheme accounted qualitatively for what was ob-

<sup>9</sup> The paper was received by the *Journal of the American Chemical Society* in January 1927 so the work was probably done mainly during the latter half of 1926.

served in experiment but not quantitatively: experimentally,  $1/k$  does not vary linearly with  $1/(M)$ . Rice recognized that a proper theory would have to be more explicit about the meaning of  $A^*$  and  $k_2$ . He envisaged the complex molecule A as a collection of coupled oscillators and the activated molecules  $A^*$  as all those that had a great enough total energy to react. However, it was only if that energy were correctly apportioned—particularly, only if some required minimum amount of it found its way into a crucial one of the molecule's vibrational degrees of freedom—that reaction would occur. Rice saw the mean time that had to elapse between the initial energization of A and the favorable reapportionment of that energy as what the primitive versions of the theory had been trying to express as the time lag to reaction,  $1/k_2$ . He could now, however, relate that time explicitly to the complexity of the molecule: the greater the number of active vibrational degrees of freedom, the longer would it take for the required energy to find its way into a particular one of them. The result was not only a theory in better accord with experiment than its predecessors, but a much more detailed and revealing picture of the dynamics of polyatomic molecules. It is a picture that continues to excite the imagination of scientists. The issues raised by it—central to the study of regular versus stochastic behavior of complex mechanical systems—are the object of much current research.

When Rice left Berkeley and went to Caltech as a National Research Fellow, one of his first concerns (1928b) was to rephrase the unimolecular reaction-rate theory, where necessary, in the language of the (older, pre-wave-mechanical) quantum theory. At Caltech he met Louis S. Kassel, who was working on the same problem along similar lines. (In his 1928 paper, Rice expressed his indebtedness to Kassel for discussions of the problem.) Their names were soon to be linked permanently, when the theory came to be known to all chem-

ists first as the RRK (Rice-Ramsperger-Kassel) theory, then later as the RRKM theory (after later work with [1951a] and by<sup>10</sup> R. A. Marcus).

It was also at Caltech that Rice did his first landmark work on predissociation and diffuse spectra (1929a,b). The phenomenon of predissociation has much in common with that of unimolecular decomposition, and Rice elucidated the connection. Some of this work was apparently done during a temporary return to Berkeley (for his 1929 paper, "On the Quantum Mechanics of Chemical Reactions," has a Berkeley byline).

It is clear from the papers of this period that Rice was already mastering and applying the ideas and methods of the new quantum theory originated primarily by German physicists. Since, at that time, the Germans were applying the theory most rapidly and widely, the next major step in his studies—a year at the Institute for Theoretical Physics of the University of Leipzig—was a natural one. While he was there he met and benefitted from discussions with Werner Heisenberg, Michael Polanyi, Eugene Wigner, Felix Bloch, and Hartmut Kallmann.

During his stay in Leipzig, Rice worked on problems of inelastic atomic and molecular collisions (1930a, 1931a) and extended his earlier work (1929a,b,e) on predissociation. On his return to the United States, he continued his studies of inelastic collisions at Harvard. Referring to Rice's papers (1931b,c) on that subject, L. Landau, writing in 1932, said that until then only Rice had correctly recognized the fundamental role that the crossing of potential-energy curves played in those processes.<sup>11</sup> Landau remarked that previous work had implied a strange disappearance of energy. In an-

<sup>10</sup> R. A. Marcus, *Journal of Chemical Physics* 20(1952):359.

<sup>11</sup> L. Landau, *Physikalische Zeitschrift der Sowjetunion* 1(1932):88.

other direction, Rice's method for treating problems in which the collision partners approach slowly but interact strongly (1931e) anticipated what later came to be called the "method of perturbed stationary states."<sup>12</sup>

Recent evaluations have also recognized the perceptiveness of Rice's pioneering work on predissociation (1929a,b,e, 1930c).<sup>13</sup> Wilse Robinson, referring to Rice's work of this period, noted: "Many persons, myself included, working on radiationless transitions in large molecules 30 years later unfortunately were not fully aware, even though we should have been, of the beautiful physical insight into this problem already recorded, dust-covered and forgotten, in the library. Who would guess that one of the best intuitive descriptions of the process whereby a discrete state 'prepared by the absorption of light' interacts with a continuum is contained in that great paper of September 10, 1929 . . . ?"<sup>14</sup>

In collaboration with Harold Gershinowitz at Harvard, Rice also made an early contribution toward the now famous transition-state theory of chemical reactions (1934c). In addition, he mastered the new ideas of valency and molecular structure that arose from the quantum theory. His course in advanced inorganic chemistry at Harvard must have been one of the first in the country to give a systematic presentation of those ideas for young students; now such courses are standard in the chemistry curriculum. Rice's influential book, *Electronic Structure and Chemical Binding* (1940a), which was based on his Harvard lectures, has come to be regarded as a highly original contribution to the pedagogy of chemistry.

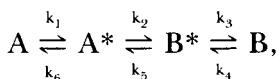
After moving to Chapel Hill, Rice continued to pursue his

<sup>12</sup> N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions*, 2d ed. (Oxford, 1949), pp. 153–57.

<sup>13</sup> R. A. Harris, *Journal of Chemical Physics* 39(1963):978; G. W. Robinson, in *Excited States*, vol. 1, ed. E. C. Lim (New York: Academic Press, 1974), p. 1.

<sup>14</sup> G. W. Robinson, in *Excited States*, p. 1.

interests in chemical reaction kinetics (both its theoretical and experimental aspects) with vigor. In the early 1960s, he again took up the problem of the kinetics and mechanism of atomic recombination (and its inverse, diatomic dissociation), to which he had been giving intermittent attention since 1941. He presented arguments of great subtlety and generality (1961b) to clarify the question of equality between the equilibrium constant in a reaction and the ratio of forward and reverse rate constants (the "rate-quotient law"). These can be best appreciated in a simple example. In the kinetic scheme



with  $A^*$  and  $B^*$  being transient high-energy intermediates, the concentrations of which can be treated in steady-state approximation, the rate constants  $k_f$  and  $k_r$  for the forward and reverse reactions  $A \rightarrow B$  and  $B \rightarrow A$  are:

$$k_f = k_1 k_2 k_3 / (k_3 k_6 + k_5 k_6 + k_2 k_3)$$

$$k_r = k_4 k_5 k_6 / (k_3 k_6 + k_5 k_6 + k_2 k_3).$$

The "equilibrium" approximations to these rate constants (obtained for the forward reaction as  $k_2$  times the ratio of the concentrations of  $A^*$  and  $A$  at equilibrium, and analogously for the reverse reaction) are  $k_f^{eq} = k_1 k_2 / k_6$  and  $k_r^{eq} = k_5 k_4 / k_3$ . These exceed the true (i.e., the steady-state) rate constants by the common factor  $1 + k_5/k_3 + k_2/k_6$ . Thus, although the true rate constants  $k_f$  and  $k_r$  are less than they are estimated to be by the equilibrium approximation, they deviate from the latter by identical factors, so that  $k_f/k_r$ , like  $k_f^{eq}/k_r^{eq}$ , is just  $k_1 k_2 k_3 / k_4 k_5 k_6$ , which is the equilibrium constant for the reaction  $A \rightleftharpoons B$ .

This illustrates what Rice found to be a general phenom-

enon (not only in steady-state approximation): that the ratio  $k_f/k_r$  of the rate constants in a chemical reaction remains equal to the equilibrium constant of the reaction even though  $k_f$  and  $k_r$  separately are less (sometimes *much* less) than what one would have estimated for them from the equilibrium approximation. Our understanding of the very meaning of a rate constant is now much deeper than it was before Rice's analysis.

Impressive as were Rice's accomplishments in quantum collision theory, energy exchange, and chemical kinetics, they were nevertheless matched in depth and originality by his work on phase transitions and critical phenomena, the dominant interest of his later 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 showed (1955b) that when a pure liquid and its vapor are in equilibrium, the isothermal compressibility  $K$  of one of those phases at any point  $T, V$  on the temperature-volume coexistence curve; the discontinuity  $\Delta C_v$  that the constant-volume heat capacity undergoes when the coexistence curve is crossed at that point from the one- to the two-phase region; and the rate  $dV/dT$  at which the volume varies with the temperature along the coexistence curve at that point, are related by

$$KV \Delta C_v = T(dV/dT)^2.$$

If we suppose that as  $T, V$  approaches the critical point at  $T_c, V_c$  the discontinuity  $\Delta C_v$  diverges proportionally to a negative power,  $(T_c - T)^{-\alpha}$ , of the temperature difference

$T_c - T$ ; that  $K$  diverges proportionally to another negative power,  $(T_c - T)^{-\gamma}$ ; and that  $V - V_c$  on the coexistence curve vanishes proportionally to  $(T_c - T)^\beta$ ; then we conclude from Rice's relation that the critical-point exponents  $\alpha$ ,  $\beta$ , and  $\gamma$  are related by  $\alpha + 2\beta + \gamma = 2$ . This exact relation underlies the slightly more conjectural one (called a "scaling law") that is in common use in present day critical-point theory, in which  $\beta$  and  $\gamma$  are as above while  $\alpha$  is the exponent characterizing the divergence of the heat capacity  $C_v$  itself rather than that of the discontinuity  $\Delta C_v$ . If, along the same lines, the pressure  $p$  on the critical isotherm deviates from the critical pressure  $p_c$  proportionally to a power  $|V - V_c|^\delta$  of the distance  $|V - V_c|$  from the critical point, then Rice may be seen to have discovered, in that same paper (1955b), the special case  $\gamma = 1$  of a second scaling law,  $\delta = 1 + \gamma/\beta$ . (Four years later, M. E. Fisher<sup>15</sup> reported finding that  $\gamma = 7/4$  in the two-dimensional Ising or lattice-gas model. Until then, however, it was universally believed that  $\gamma$  is always 1, as it is in any of the classical equations of state, explaining Rice's implicit assumption in 1955 that it was 1.)

Rice was also the first to point out that what might have been a lambda transition in a lattice had the lattice been incompressible, might actually, in a compressible lattice, prove to be a first-order phase transition (1954d). This idea gave rise to a substantial body of literature—first, Cyril Domb,<sup>16</sup> following Rice, then many others—and was also confirmed by experiment.<sup>17</sup> Rice's address, "Secondary Variables in Critical Phenomena," delivered in 1970 when he received the American Chemical Society's Peter Debye Award in Physical Chemistry, was an extension of that same theme (1972a). Rice used his ideas about secondary variables to analyze the

<sup>15</sup> M. E. Fisher, *Physica* 25(1959):521.

<sup>16</sup> C. Domb, *Journal of Chemical Physics* 25(1956):783.

<sup>17</sup> C. W. Garland and R. Renard, *Journal of Chemical Physics* 44(1966):1130.

lambda transition in liquid helium (1971a), and also the phase transitions in liquid solutions of the two helium isotopes,  $^3\text{He}$  and  $^4\text{He}$  (1967d, 1972b, 1973a), thus contributing to the understanding of what, following Griffiths,<sup>18</sup> is now called a tricritical point. Rice's interest in quantum fluids was of long standing; he had collaborated with Fritz London (1948b), a great pioneer in the subject of superfluidity (as, earlier, in the theories of chemical bonding and intermolecular forces). Both spiritually and geographically, Rice was close to London, for London was at Duke University in Durham, easy commuting distance from Chapel Hill.

Rice was one of the first to treat seriously the fundamental problem of determining intermolecular forces from bulk, macroscopic properties (1941b). His program was continued by Guggenheim and McGlashan,<sup>19</sup> Barker,<sup>20</sup> and others, 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 (1944a); and his was among the pioneering studies of the equation of state of such a hard-sphere fluid (1942d), long predating the accurate determination of that equation of state by computer simulation.

Oscar Rice's experimental studies of critical consolute points in liquid mixtures, including his careful determinations of the shapes of the two-phase coexistence curves, were fully as important for the development of our understanding of critical phenomena as were his theoretical ideas. His aim in making those measurements was to test some controversial ideas then current about condensation and critical points.

<sup>18</sup> R. B. Griffiths, *Physical Review Letters* 24(1970):715.

<sup>19</sup> E. A. Guggenheim and M. L. McGlashan, *Proceedings of the Royal Society of London, Series A: Mathematical and Physical Sciences* 255(1960):456.

<sup>20</sup> J. A. Barker, in *Rare Gas Solids*, vol. 1, ed. M. L. Klein and J. A. Venables (New York: Academic Press, 1976).

During the 1940s there was much talk of the "derby hat" region<sup>21</sup> near a critical point. Rice did not accept the whole of that picture but was led independently, by his own arguments (1947b), to accept one aspect of it—a flat-topped coexistence curve—as plausible. From Guggenheim's influential paper<sup>22</sup> on the law of corresponding states, which appeared in 1945, it was widely known that as the temperature  $T$  approaches the critical temperature  $T_c$ , the difference in the densities of a pure liquid and its equilibrium vapor vanishes proportionally to  $(T_c - T)^\beta$  (vid. sup.), with  $\beta \cong 1/3$ . Rice thought that this law might break down just before  $T$  reached  $T_c$  and that the two phases might still be distinct—in particular, have different densities—when the meniscus between them disappeared; that is, that the coexistence curve would be flat-topped rather than rounded.

Rice gave several particularly illuminating accounts of his and Mayer's ideas: in the paper he presented at a 1948 American Chemical Society symposium on solutions (1949a); the next year in an invited address at the ACS symposium on critical phenomena (1950h); and in his masterly review of critical phenomena (1955j) prepared for Rossini's *Thermodynamics and Physics of Matter*.<sup>23</sup> He pointed out that the same issues arise at the consolute point of a liquid mixture. In the second of the reviews noted above, he reported preliminary results on the coexistence curve for aniline-cyclohexane, the beginning of his famous series of studies on this system (1951c, 1952a, 1953d, 1954b, 1959a, 1960b), some of which have not been surpassed in care and precision to this day. Although he never definitively established the flat top—it is

<sup>21</sup> The term came from a famous diagram that Harrison and Mayer published in 1938 in the *Journal of Chemical Physics*, a figure that bore a fancied resemblance to a hat.

<sup>22</sup> E. A. Guggenheim, *Journal of Chemical Physics* 13(1945):253.

<sup>23</sup> F. D. Rossini, ed., *Thermodynamics and Physics of Matter*, vol. 1 of *High Speed Aerodynamics and Jet Propulsion* (Princeton: Princeton University Press, 1955).

now believed that if there is a flattening it is due only to gravity—his measurements were among the most important in establishing the universality of the critical phenomenon, particularly the underlying identity between the liquid-vapor critical point in a pure fluid and the liquid-liquid consolute point in a mixture.

Among the measurements in Rice's aniline-cyclohexane series was that of the interfacial tension and the rate at which it vanishes as the consolute point is approached (1953d). That was the first such measurement (and is still among the very few) to determine the critical-point exponent for surface tension at a liquid-liquid consolute point. To within experimental error the exponent is identical with that at a liquid-vapor critical point, further confirming the essential identity of those two kinds of critical point. Rice had long recognized the central role of surface tension in critical phenomena; indeed, it had played a prominent part in his earlier theory (1947b). To the end of his life he continued to return to the problems of the structure and tension of interfaces. For him it was the closing of a circle: Some of his earliest papers, dating from his student days at Berkeley and published between 1926 and 1928, were on that theme, as were his last six papers, published between 1976 and (posthumously) 1979.

Rice's *Electronic Structure and Chemical Binding*, to which we have already referred, was his first full-length book. More than a quarter of a century—and a hundred research papers—later, he wrote his second, *Statistical Mechanics, Thermodynamics, and Kinetics* (1967a). There is hardly a topic in it to which he himself had not made a major contribution. It is a particularly original text.

We have had occasion above to mention some of the honors that came to Oscar Rice, including the ACS Award in Pure Chemistry and the ACS Peter Debye Award. There

were others. He was given the Southern Chemist Award in 1961; the North Carolina Award in Science, presented by the governor, in 1966; the award of the American Chemical Society's Florida section in 1967; and the Charles H. Stone Award of the ACS's Carolina Piedmont section in 1972. He was elected to serve successively as secretary-treasurer, vice-chairman, and chairman of the Division of Physical and Inorganic Chemistry of the ACS from 1942 to 1944, and he was elected chairman of the ACS's North Carolina section for 1946. He was twice an associate editor of the *Journal of Chemical Physics*, first from 1934 to 1936, starting with the second volume of the *Journal*, and again just after the war, from 1945 to 1947. He was named a fellow of the American Physical Society and a member of the Board of Sponsors of the Federation of American Scientists. He served on the National Science Foundation's Advisory Panel on Chemistry (1958–1961), on the North Carolina Governor's Scientific Advisory Committee (1961–1964), and on the chemistry panel of the Army Research Office, in nearby Durham (1967–1972). He was elected to the National Academy of Sciences in 1964.

About every great man legends grow, often reflecting quirks of habit or personality. Oscar Rice was famous for apparently sleeping through seminars and then asking perceptive and penetrating questions of the speakers. He was notorious for the clutter of his office, piled high with books and papers in seemingly random array—which did not keep him from laying his hands instantly on whatever was sought. Then there was the famous armchair, which, as we saw, even made its mark on the Oak Ridge establishment.

In manner Rice was quiet, gentle, and modest, but never hid his enthusiasm for science, which was obvious to all. His writings show how great was his strength—the firmness of his grip on his subject and the clarity and certainty of his vision. But even his published papers, powerful and compel-

ling as they are, have a calmness and restraint that reflect the reasoned judgment of their author.

The careers of Oscar Rice and the late Henry Eyring (1901–1981) ran closely parallel. They were nearly the same age (Eyring was two years older); they were contemporaries as graduate students in the Berkeley chemistry department; they both witnessed the development of quantum and statistical mechanics and applied them widely through physical chemistry; and they shared abiding interests in problems of chemical kinetics, liquid structure, and phase transitions. Although their public styles could hardly have been more different, their personal habits were much alike: “Henry . . . was abstemious to the extreme, no coffee, no tea, no alcohol, no very hot or very cold foods. Commenting on this Oscar said that the only difference between him and Henry was that he ate coffee ice cream.”<sup>24</sup> On hearing that remark, anyone who knew Oscar would have recognized its tone. His humor was never caustic but was as gentle as his manner, yet it was sudden and spontaneous. His quips were always accompanied by a smile and a sparkle that are still recalled by friends and family.

Rice’s counsel was sought and valued by his students and associates. He gave them generous help at the start of their careers and loyal support thereafter. He was a selfless and devoted teacher, more interested, we recall from personal experience, in the development of his coworkers than in his own aggrandizement. In our regular individual meetings with him to discuss papers in the literature, he was always careful to point out the tacit assumptions the papers made and that we might have missed. Those were valuable lessons.

By all who knew him Oscar Rice was loved as a friend, held in the highest esteem for his accomplishments as a sci-

<sup>24</sup> Letter of October 18, 1982, by H. Gershinowitz to the authors.

tist, and admired for his courage. He withstood years of painful illness without complaint and with thought only for the welfare of others. He fought injustice and intolerance wherever he saw it, without thought to the popularity of his cause. When none would speak out with him, he spoke out alone.

He is remembered for his concern for the rights and freedoms of people everywhere, for his tolerance, for his patience with persons with whom he disagreed, for his unwillingness to be reconciled to injustice . . . [He] championed scholars who were denied academic freedom, he worked for the elimination of racial segregation, he defended the rights of all citizens to freedom of expression and action in the redress of grievances.<sup>25</sup>

In the following statement of regard for his university, Rice speaks eloquently of his concern for human rights: "I should acknowledge my indebtedness to the University of North Carolina, which for the past 25 years has provided good working conditions, an interesting and stimulating teaching program, and a situation both pleasant and conducive to research. I value not only these aspects of my life at this University, but also the atmosphere of free and open discussion which I have found there, the acceptance of new ideas, and the growth of a new cosmopolitanism, which now encompasses not only people of the far corners of the world, but also some Americans who until recently have been partially excluded from the world of culture through irrelevant circumstances, not connected with their own worth and value."<sup>26</sup> Oscar Rice served his fellow man as he served his science—with courage and distinction.

<sup>25</sup> From a memorial resolution proposed by Rice's colleagues and adopted by the faculty of the University of North Carolina at its meeting of September 15, 1978.

<sup>26</sup> O. K. Rice, on receiving the Southern Chemist Award of the Memphis section of the American Chemical Society, in New Orleans, 1961; quoted in the August 28, 1981 edition of the *University Gazette* (University of North Carolina, Chapel Hill), in an article about the establishment of the Oscar K. Rice Lectureship in the Department of Chemistry.

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## SELECTED BIBLIOGRAPHY

1926

- Equilibrium in colloid systems. *J. Phys. Chem.*, 30:189–204.  
The surface tension of charged surfaces. *J. Phys. Chem.*, 30:1348–55.  
A study of the electrocapillary curve near its maximum. *J. Phys. Chem.*, 30:1501–9.  
Equilibrium in colloid systems. II. Coagulation. *J. Phys. Chem.*, 30:1660–68.

1927

- Dynamic surface tension and the structure of surfaces. *J. Phys. Chem.*, 31:207–15.  
With H. C. Ramsperger. Theories of unimolecular gas reactions at low pressures. *J. Am. Chem. Soc.*, 49:1617–29.

1928

- With H. C. Ramsperger. Theories of unimolecular gas reactions at low pressures. II. *J. Am. Chem. Soc.*, 50:617–20.  
The quantum theory of quasi-unimolecular gas reactions. *Proc. Natl. Acad. Sci. USA*, 14:113–18.  
The theory of the decomposition of azomethane. *Proc. Natl. Acad. Sci. USA*, 14:118–24.  
The surface tension and the structure of the surface of aqueous ammonia solutions. *J. Phys. Chem.*, 32:583–92.  
Application of the Fermi statistics to the distribution of electrons under fields in metals and the theory of electrocapillarity. *Phys. Rev.*, 31:1051–59.  
Energy distribution of complex molecules. *Phys. Rev.*, 32:142–49.  
On the theory of unimolecular gas reactions. In: *L'Activation et la Structure des Molécules*, pp. 298–318. Paris: Réunion Internationale de Chimie Physique.

1929

- With G. E. Gibson. Diffuse bands and predissociation of iodine monochloride. *Nature*, 123:347–48.  
Perturbation in molecules and the theory of predissociation and diffuse spectra. *Phys. Rev.*, 33:748–59.

The temperature coefficient of radioactive disintegration. Proc. Natl. Acad. Sci. USA, 15:593–95.

Types of unimolecular reactions. Proc. Natl. Acad. Sci. USA, 15: 459–62.

On the quantum mechanics of chemical reactions: Predissociation and unimolecular decompositions. Phys. Rev., 34:1451–65.

1930

Einige Bemerkungen über Energieaustausch innerhalb Molekülen und zwischen Molekülen bei Zusammenstoss. Z. Phys. Chem. Abt. B, 7:226–33.

A contribution to the quantum mechanical theory of radioactivity and the dissociation by rotation of diatomic molecules. Phys. Rev., 35:1538–50.

Perturbations in molecules and the theory of predissociation and diffuse spectra. II. Phys. Rev., 35:1551–58.

1931

On the transfer of energy between atoms at collision. Proc. Natl. Acad. Sci. USA, 17:34–39.

On the effect of resonance in the exchange of excitation energy. Phys. Rev., 37:1187–89.

On the effect of resonance in the exchange of excitation energy. Phys. Rev., 37:1551–52.

The structure of the  $\alpha$ -particle. J. Am. Chem. Soc., 53:2011–12.

On collision problems involving large interactions. Phys. Rev., 38:1943–60.

1932

The mechanism of energy exchange in unimolecular reactions. Chem. Rev., 10:125–34.

Energy exchange in unimolecular gas reactions. J. Am. Chem. Soc., 54:4558–81.

With D. V. Sickman. The decomposition of diethyl ether at low pressures. J. Am. Chem. Soc., 54:3778–79.

1933

Predissociation and the crossing of molecular potential energy curves. J. Chem. Phys., 1:375–89.

A remark on Rosen's paper: "Lifetimes of Unstable Molecules." *J. Chem. Phys.*, 1:625–26.

With G. E. Gibson and N. S. Bayliss. Variation with temperature of the continuous absorption spectrum of diatomic molecules. Part II. *Theoretical. Phys. Rev.*, 44:193–200.

On the binding forces in the alkali and alkaline earth metals according to the free electron theory. *J. Chem. Phys.*, 1:649–55.

### 1934

With H. Gershinowitz. On the activation energy of unimolecular reactions. *J. Chem. Phys.*, 2:273–82.

With D. V. Sickman. The homogeneous decomposition of diethyl ether at low pressures; with some remarks on the theory of unimolecular reactions. *J. Am. Chem. Soc.*, 56:1444–55.

With H. Gershinowitz. Entropy and the absolute rate of chemical reactions. I. The steric factor of bimolecular associations. *J. Chem. Phys.*, 2:853–61.

The kinetics of homogeneous gas reactions. In: *Annual Survey of American Chemistry*, vol. 9, pp. 35–48.

### 1935

With D. V. Sickman. The thermal decomposition of propylamine. *J. Am. Chem. Soc.*, 57:22–24.

With A. O. Allen. The explosion of azomethane. *J. Am. Chem. Soc.*, 57:310–17.

With H. C. Campbell. The explosion of ethyl azide. *J. Am. Chem. Soc.*, 57:1044.

On the Stokes phenomenon for the differential equations which arise in the problem of inelastic atomic collisions. *J. Chem. Phys.*, 3:386–98.

With H. Gershinowitz. Entropy and the absolute rate of chemical reactions. II. Unimolecular reactions. *J. Chem. Phys.*, 3:479–89.

With H. Gershinowitz. The activation energy of unimolecular reactions. II. *J. Chem. Phys.*, 3:490–92.

With A. O. Allen and H. C. Campbell. The induction period in gaseous thermal explosions. *J. Am. Chem. Soc.*, 57:2212–22.

With D. V. Sickman. The polymerization of ethylene induced by methyl radicals. *J. Am. Chem. Soc.*, 57:1384–85.

1936

On the zero-point energy of an activated complex and the reaction



With D. V. Sickman. Studies on the decomposition of azomethane.

I. Description of the apparatus. *J. Chem. Phys.*, 4:239-41.

With D. V. Sickman. Studies on the decomposition of azomethane.

II. Pure azomethane and azomethane in the presence of helium. *J. Chem. Phys.*, 4:242-51.

On the thermodynamic properties of nitric oxide. An example of an associated liquid. *J. Chem. Phys.*, 4:367-72.

With G. E. Gibson. The electric moment of the  $'\Sigma_+$  to  $\text{O}^+$  transition in the continuum of  $\text{Cl}_2$ . *Phys. Rev.*, 50:380 (erratum 50:871).

With D. V. Sickman. Studies on the decomposition of azomethane.

III. Effect of various inert gases. *J. Chem. Phys.*, 4:608-13.

1937

With R. A. Ogg, Jr. Factors influencing rates of reaction in solution. *J. Chem. Phys.*, 5:140-43.

Internal volume and the entropy of vaporization of liquids. *J. Chem. Phys.*, 5:353-58.

On transitions in condensed systems. *J. Chem. Phys.*, 5:492-99.

1938

The solid-liquid equilibrium in argon. *J. Chem. Phys.*, 6:472-75.

On communal entropy and the theory of fusion. *J. Chem. Phys.*, 6:476-79.

1939

Further remarks on the solid-liquid equilibrium in argon. *J. Chem. Phys.*, 7:136-37.

With H. C. Campbell. The explosion of ethyl azide in the presence of diethyl ether. *J. Chem. Phys.*, 7:700-709.

The nature of the fusion process in argon. *J. Chem. Phys.*, 7:883-92.

1940

*Electronic Structure and Chemical Bonding: With Special Reference to Inorganic Chemistry*. New York: McGraw-Hill Book Company. (Reprinted with corrections, Mineola, N.Y.: Dover, 1969).

The role of heat conduction in thermal gaseous explosions. *J. Chem. Phys.*, 8:727–33.

With W. L. Haden, Jr., and E. P. H. Meibohm. Note on the chain photolysis of acetaldehyde in intermittent light. *J. Chem. Phys.*, 8:998.

#### 1941

A note on the entropy of fusion of argon. *J. Chem. Phys.*, 9:121.  
The interatomic potential curve and the equation of state for argon. *J. Am. Chem. Soc.*, 63:3–11.

On the recombination of iodine and bromine atoms. *J. Chem. Phys.*, 9:258–62.

With C. V. Cannon. The photolysis of azomethane. *J. Am. Chem. Soc.*, 63:2900.

#### 1942

The effect of intermittent light on a chain reaction with bimolecular and unimolecular chain-breaking steps. *J. Chem. Phys.*, 10:440–44.

With W. L. Haden, Jr. The chain photolysis of acetaldehyde in intermittent light. *J. Chem. Phys.*, 10:445–60 [erratum 12(1944):521].

With C. V. Cannon. A monochromator using a large water prism. *Rev. Sci. Instrum.*, 13:513–14.

The partition function of a gas of hard elastic spheres. *J. Chem. Phys.*, 10:653–54.

The partition function of a simple liquid. *J. Chem. Phys.*, 10:654.

#### 1944

On the statistical mechanics of liquids, and the gas of hard elastic spheres. *J. Chem. Phys.*, 12:1–18 [errata 12:521].

The thermodynamic properties and potential energy of solid argon. *J. Chem. Phys.*, 12:289–95.

#### 1946

The thermodynamic properties and potential energy of solid argon. II. *J. Chem. Phys.*, 14:321–24.

The thermodynamic properties of liquid argon. *J. Chem. Phys.*, 14:324–38.

A note on communal entropy. Remarks on a paper by Henry S. Frank. *J. Chem. Phys.*, 14:348–50.

With G. W. Murphy. Corresponding states in the frozen rare gases. *J. Chem. Phys.*, 14:518–25.

Review of *Photosynthesis and Related Processes*, vol. 1, *Chemistry of Photosynthesis, Chemosynthesis, and Related Processes in Vitro and in Vivo*, by Eugene I. Rabinowitch. *Rev. Sci. Instrum.*, 17:145–46.

### 1947

With L. White, Jr. The thermal reaction of hexafluoroethane with quartz. *J. Am. Chem. Soc.*, 69:267–70.

On the behavior of pure substances near the critical point. *J. Chem. Phys.*, 15:314–32 [errata 15:615].

The effect of pressure on surface tension. *J. Chem. Phys.*, 15:333–35.

Activation in unimolecular reactions. *J. Chem. Phys.*, 15:689–90.

A note on the relation between entropy and enthalpy of solution. *J. Chem. Phys.*, 15:875–79.

### 1948

Quantum corrections to the thermodynamic properties of liquids, with application to neon. *J. Chem. Phys.*, 16:141–47.

With F. London. On solutions of He<sup>3</sup> in He<sup>4</sup>. *Phys. Rev.*, 73:1188–93.

### 1949

Critical phenomena in binary liquid systems. *Chem. Rev.*, 44:69–92.

The thermodynamics of liquid helium on the basis of the two-fluid theory. *Phys. Rev.*, 76:1701–7.

### 1950

Effect of He<sup>3</sup> on the λ-point of He<sup>4</sup>. *Phys. Rev.*, 77:142–43.

With O. G. Engel. Lambda-temperatures of solutions of He<sup>3</sup> in He<sup>4</sup>. *Phys. Rev.*, 78:55–57.

The partial molal entropy of superfluid in pure He<sup>4</sup> below the λ-point. *Phys. Rev.*, 78:182–83.

With O. G. Engel. Thermodynamics of He<sup>3</sup>-He<sup>4</sup> solutions. *Phys. Rev.*, 78:183.

- The thermodynamics of liquid helium and of He<sup>3</sup>-He<sup>4</sup> solutions. *Phys. Rev.*, 79:1024–25.
- With V. E. Lucas. The chain-breaking process in acetaldehyde photolysis. *J. Chem. Phys.*, 18:993–94.
- With R. Ginell. The theory of the burning of double-base rocket powders. *J. Phys. Colloid Chem.*, 54:885–917.
- Introduction to the symposium on critical phenomena. *J. Phys. Colloid Chem.*, 54:1293–1305.

## 1951

- With R. A. Marcus. The kinetics of the recombination of methyl radicals and iodine atoms. *J. Phys. Colloid Chem.*, 55:894–908.
- With R. W. Rowden. Critical phenomena in the cyclohexane-aniline system. *J. Chem. Phys.*, 19:1423–24.
- The solid-liquid transition in argon. In: *Phase Transformations in Solids* (Proceedings of a symposium at Cornell University, August 1948), ed. R. Smoluchowski, J. E. Mayer, and W. A. Weyl. New York: John Wiley & Sons.

## 1952

- With R. W. Rowden. Phénomène critique dans le système cyclohexane-aniline. In: *Changements de Phases*. Comptes Rendus de la Deuxième Réunion Annuelle de la Société de Chimie Physique, Paris, June 2–7, 1952.
- With J. L. Weininger. The photolysis of azoethane. *J. Am. Chem. Soc.*, 74:6216–19.

## 1953

- Reply to Careri's "Note on the rate of recombination of free atoms." *J. Chem. Phys.*, 21:750–51.
- Irreversible processes with application to helium II and the Knudsen effect in gases. *Phys. Rev.*, 89:793–99.
- With B. Widom. The thermodynamics of the helium film. *Phys. Rev.*, 90:987.
- With D. Atack. The interfacial tension and other properties of the cyclohexane-aniline system near the critical solution temperature. *Discuss. Faraday Soc.*, 15:210–18.
- Contributions to the discussion. *Discuss. Faraday Soc.*, 15:110, 276, 286, 287.

1954

- With J. C. Morrow. Solutions of nonelectrolytes. *Annu. Rev. Phys. Chem.*, 5:71.
- With D. Atack. Critical phenomena in the cyclohexane-aniline system. *J. Chem. Phys.*, 22:382-85.
- The nature of higher-order phase transitions with application to liquid helium. *Phys. Rev.*, 93:1161-68.
- Thermodynamics of phase transitions in compressible solid lattices. *J. Chem. Phys.*, 22:1535-44.
- With D. Atack. Thermodynamics of vapor-phase mixtures of iodine and benzene, with application to the rate of recombination of iodine atoms. *J. Phys. Chem.*, 58:1017-23.
- Statistical mechanics of helium II near 1°K. *Phys. Rev.*, 96:1460-63.
- Heat and entropy of mixing of He<sup>3</sup> and He<sup>4</sup> on the basis of the two-fluid theory of He<sup>4</sup>. *Phys. Rev.*, 96:1464-65.

1955

- Shape of the coexistence curve near the critical temperature. *J. Chem. Phys.*, 23:164-68.
- Relation between isotherms and coexistence curve in the critical region. *J. Chem. Phys.*, 23:169-73.
- Interpretation of the magnetic behavior of liquid helium-3. *Phys. Rev.*, 97:263-66.
- Can helium-3 be expected to exhibit superfluidity at sufficiently low temperatures? *Phys. Rev.*, 97:558-59.
- Energy levels in liquid He<sup>3</sup>. *Phys. Rev.*, 97:1176.
- Comparison of the energy excitations in liquid He<sup>3</sup> and He<sup>4</sup>. *Phys. Rev.*, 98:847-51.
- With B. Widom. Critical isotherm and the equation of state of liquid-vapor systems. *J. Chem. Phys.*, 23:1250-55.
- With H. A. Hartung. Some studies of spontaneous emulsification. *J. Colloid Sci.*, 10:436-39.
- With R. Gopal. Shape of the coexistence curve in the perfluoromethylcyclohexane-carbon tetrachloride system. *J. Chem. Phys.*, 23:2428-31.
- Critical phenomena. In: *High Speed Aerodynamics and Jet Propulsion*, vol. 1, *Thermodynamics and Physics of Matter*, ed. F. D. Rossini, pp. 419-500. Princeton: Princeton University Press.

1956

Elementary theory of the excitations in liquid helium: New model for rotons. *Phys. Rev.*, 102:1416.

Reversible flow phenomena and thermodynamic properties of liquid helium and the two-fluid hypothesis. *Phys. Rev.*, 103: 267-74.

1957

A kinetic approach to the thermodynamics of irreversible processes. *J. Phys. Chem.*, 61:622-29.

With F. Kohler. Coexistence curve of the triethylamine-water system. *J. Chem. Phys.*, 26:1614-18.

Some remarks on solutions of  $\text{He}^3$  in  $\text{He}^4$ . In: *Proceedings of the Symposium on Liquid and Solid Helium Three*, pp. 173-80. Columbus: Ohio State University Press.

Elementary theory of liquid helium: Refinement of the theory and comparison with Feynman's theory. *Phys. Rev.*, 108:551-60.

1958

Energy fluctuations in liquid helium and its flow properties. *Nuovo Cimento Suppl.*, 9(ser. 10):267-85.

1959

With F. R. Meeks and R. Gopal. Critical phenomena in the cyclohexane-aniline system: Effect of water at definite activity. *J. Phys. Chem.*, 63:992-94.

Reaktionen mit intermolekularem Energieaustausch. *Monatsh. Chem.*, 90:330-56.

The recombination of atoms, and other energy-exchange reactions. In: *Proceedings of the Ninth International Astronautics Congress*, Amsterdam, 1958, pp. 9-19. Vienna: Springer-Verlag KG.

Gas of hard nonattracting spheres. *J. Chem. Phys.*, 31:987-93.

1960

Note on the equation of state for hard spheres. *J. Chem. Phys.*, 32:1277-78.

With M. E. Jacox and J. T. MacQueen. A dilatometric study of the cyclohexane-aniline system near its critical separation temperature. *J. Phys. Chem.*, 64:972-75.

- The thermodynamics of non-uniform systems, and the interfacial tension near a critical point. *J. Phys. Chem.*, 64:976–84.
- Conditions for a steady state in chemical kinetics. *J. Phys. Chem.*, 64:1851–57.
- The principle of minimum entropy production and the kinetic approach to irreversible thermodynamics. *J. Phys. Chem.*, 64:1857–60.
- Clausius-Clapeyron equation. In: *Encyclopaedic Dictionary of Physics*, vol. 1, pp. 695–96. London: Pergamon Press.
- Continuity of state. In: *Encyclopaedic Dictionary of Physics*, vol. 2, pp. 71–72. London: Pergamon Press.

## 1961

- With J. T. MacQueen and F. R. Meeks. The effect of an impurity on the phase transition in a binary liquid system as a surface phenomenon. *J. Phys. Chem.*, 65:1925–29.
- On the relation between an equilibrium constant and the non-equilibrium rate constants of direct and reverse reactions. *J. Phys. Chem.*, 65:1972–76.
- Effects of quantization and of anharmonicity on the rates of dissociation and association of complex molecules. *J. Phys. Chem.*, 65:1588–96.

## 1962

- With J. T. MacQueen. The effect of an impurity on the phase transition in a binary liquid system. II. *J. Phys. Chem.*, 66:625–31.
- With W. Forst. Entropy of activation in the thermal decomposition of azomethane. *Ann. Assoc. Can.-Fr. Av. Sci. Montreal*, 28:47.

## 1963

- Further remarks on the “rate-quotient law.” *J. Phys. Chem.*, 67:1733–35.
- Non-equilibrium effects in the dissociation of diatomic molecules by a third body. *J. Phys. Chem.*, 67:6–11.
- With W. Forst. The thermal decomposition of azomethane. I. Effect of added olefin and nitric oxide. *Can. J. Chem.*, 41:562–85.
- With A. W. Loven. Coexistence curve of the 2,6-lutidine + water system in the critical region. *Trans. Faraday Soc.*, 59:2723–27.

1964

Some problems in energy exchange related to chemical kinetics.

In: *Transfert d'Energie dans les Gaz*, Douzième Conseil de Chimie Solvay, Brussels, November 1962, pp. 17–86. New York: Interscience Publishers.

With D. R. Thompson. Shape of the coexistence curve in the perfluoromethylcyclohexane-carbon tetrachloride system. II. Measurements accurate to 0.0001°. *J. Am. Chem. Soc.*, 86:3547–53.

The thermodynamic properties and interatomic potential energy of solid argon. *J. Elisha Mitchell Sci. Soc.*, 80:120.

1965

Energy fluctuations and the nature of the rotons in helium II. In: *Proceedings of the Ninth International Conference on Low Temperature Physics*, p. 88. New York: Plenum Press.

1966

With W. C. Worsham and M. T. Jaquiss. High pressure capillary thallium-amalgam arc for use in ultraviolet. *Rev. Sci. Instrum.*, 37:1084–85.

1967

*Statistical Mechanics, Thermodynamics, and Kinetics*. San Francisco: W. H. Freeman and Company.

Statistical thermodynamics of  $\lambda$ -transitions, especially of liquid helium. *Phys. Rev.*, 153:275–79.

With N. F. Irani. Coexistence curve of the cyclohexane + methylene iodide system in the critical region. *Trans. Faraday Soc.*, 63:2158–62.

Possible relation between phase separation and the  $\lambda$ -transition in  $^3\text{He}$ - $^4\text{He}$  mixtures. *Phys. Rev. Lett.*, 19:295–97.

With W. C. Worsham. Deactivation by collision in the photolysis of azoethane. *J. Chem. Phys.*, 46:2021.

With B. W. Davis. Thermodynamics of the critical point: Liquid-vapor systems. *J. Chem. Phys.*, 47:5043–53.

1968

With E-C. Wu. The photolysis of perfluoroazomethane. *J. Phys. Chem.*, 72:542–46.

On charge-transfer complexes in the vapor phase. Int. J. Quantum Chem. Symp., 2:219–24.

1969

Some remarks on the foundations of thermodynamics and statistical mechanics. J. Phys. Soc. Jpn., 26(suppl.):219.

With D. R. Chang. The thermal decomposition of azomethane-d<sub>6</sub>. Int. J. Chem. Kinet., 1:171–91.

On the motion of a sphere in a perfect fluid with application to liquid helium. Proc. Natl. Acad. Sci. USA, 63:1055–62.

Statistical thermodynamics of the  $\lambda$  transition in liquid helium. J. Am. Chem. Soc., 91:7682–84.

Melting phenomena in simple solids. Physikertag. Phys. Ges. (Salzburg), Vorabdrucke Kurzfassungen Fachber., 34:73–78.

1971

With D. R. Chang. Secondary variables in critical phenomena, with application to  $\lambda$  transition in liquid helium. In: *Critical Phenomena in Alloys, Magnets, and Superconductors*, ed. R. E. Mills, E. Ascher, and R. I. Jaffee, pp. 105–24. New York: McGraw-Hill Book Company.

On the relation between unimolecular reaction and predissociation. J. Chem. Phys., 55:439–46.

1972

Secondary variables in critical phenomena. Acc. Chem. Res., 5:112–20.

With D. R. Chang. Thermodynamic relationship at the tricritical point in <sup>3</sup>He-<sup>4</sup>He mixtures. Phys. Rev. A, 5:1419–22.

With D. R. Chang. Some thermodynamic relations at the critical point in liquid-vapor systems. Proc. Natl. Acad. Sci. USA, 69:3436–39.

1973

On the relation between  $\lambda$  lines and phase separations. Proc. Natl. Acad. Sci. USA, 70:1241–45.

Foreword. In: *Theory of Unimolecular Reactions*, by W. Forst. New York: Academic Press.

1974

- With D. R. Chang. Density fluctuations and the specific heat near the critical point. *Physica*, 74:266–76.
- With D. R. Chang. Density fluctuations and the specific heat near the critical point. II. *Physica*, 78:490–99.
- With D. R. Chang. The effect of density-gradient terms in the free energy on density fluctuations near the critical point. *Physica*, 78:500–504.
- Critical Phenomena and Liquid Helium, National Technical Information Service AD Report no. 783381/7GA. Washington, D.C.: National Technical Information Service.

1976

- With D. R. Chang. Thermodynamic properties of fluids near the critical point, as interpreted by a simplified renormalization theory and the self-limitation of fluctuations. *Physica*, 83A: 18–32.
- With D. R. Chang. Effect of the density-gradient term in the free energy expression on critical exponents. *Physica*, 83A:609–14.
- The effect of an impurity on the critical point of a binary liquid system as a surface phenomenon. *J. Chem. Phys.*, 64:4362–67.
- Effect of an impurity on the critical point of a binary liquid system as a surface phenomenon. In: *Colloid and Interface Science*, vol. 5, ed. M. Kerker, pp. 405–9. New York: Academic Press.

1977

- Interfacial tension near the critical point and the density-gradient term in the free energy. *J. Phys. Chem.*, 81:1388–92.
- Interfacial tension near the tricritical point of  $^3\text{He}$ - $^4\text{He}$  solutions. *J. Low Temp. Phys.*, 29:269–73.

1979

- Fluctuations, density gradients, and interfaces near the critical point of one-component fluids. *J. Phys. Chem.*, 83:1859–1863.
- Existence of two characteristic lengths in determining the thickness of an interface near the critical point, and the interface profile. *J. Phys. Chem.*, 83:1863–1865.