

Bringing Statistical Mechanics into Chemistry: The Early Scientific Work of Karl F. Herzfeld

Karen E. Johnson¹

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The physicist Karl F. Herzfeld was instrumental in introducing the techniques of statistical mechanics to physical chemists in the years between 1920 and 1935. Herzfeld's work included an early derivation of the rate constant for a first order reaction. This was similar to and fifteen years earlier than Eyring's calculation of the rate constant. Herzfeld also carried out the first calculation of a relaxation equation for vibrational energy transfer. Herzfeld's success lay in his classical approach to physics, which, it is suggested, made his work accessible to chemists.

KEY WORDS: History of science; statistical mechanics; chemical kinetics; energy distribution; transfer; relaxation.

We all are familiar with the names and work of the so-called pioneers who first applied quantum mechanics to chemical problems, such as Pauling, Urey, Van Vleck, and Mulliken. On the other hand, although statistical mechanics is also now an integral part of physical chemistry, very little attention has been paid to how or when it was introduced into chemistry, or, for that matter, when it became a standard part of physics. I will discuss here the work of Karl Herzfeld (1892–1978), one of the pioneers of this other revolution in chemistry—the revolution of statistical mechanics.

Theoretical chemistry has traditionally concerned itself with two sorts of questions—those of structure, and those of reaction mechanisms and rates. In the early part of the 20th century, most chemists felt that very little could be said about either chemical structure or reaction rates, although thermodynamics could yield useful results about the energetics of chemical reactions. Statistical mechanics in the Gibbs–Boltzmann formulation, however, is well suited to the study of chemical reaction rates. As J. Willard

¹ Department of Physics, St. Lawrence University, Canton, New York 13617.

Gibbs pointed out in 1901 in his *Elementary Principles in Statistical Mechanics*, the fundamental equation of statistical mechanics is one that gives the rate of change in the energy distribution for a system.⁽¹⁾ When it was realized in the late 1920s and 1930s that a description of equilibrium conditions could also be applied to the study of nonequilibrium situations, the application of statistical mechanics was of far more interest to most chemists than the unfamiliar approach of quantum mechanics, and it was only later that quantum mechanics became an important part of the average chemist's repertoire. The chemists' shift from thermodynamics to statistical mechanics took place roughly between 1920 and 1935, the period covered in this study. Most chemists were still thinking in a predominantly classical mode, and were receptive to the introduction of statistical mechanics in classical terms. This paper is a study of the work of a physicist who was particularly important in this process.

Karl F. Herzfeld is not widely known in the fields of chemical physics or physical chemistry today. This is unfortunate because he was an unusual character who led a full and varied life, and who made major contributions to physics and chemistry between 1912 and 1960. He fought in the Austrian army during World War I, writing research papers while in combat duty. He came to the United States during the 1920s, before the general migration of European scientists to America. He was a committed Catholic in an era when very few Catholics went into science, and was instrumental in building up the Catholic University physics department. Herzfeld's research was unusual because, in the 1920s, 1930s, and later he made almost no use of the Schrödinger/Heisenberg formulation of quantum mechanics, although he was a champion of the old quantum theory. Herzfeld was also one of the European scientists who brought the work of Gibbs back to American physicists some 20 years after Gibbs' death. The statistical physicist and chemist Elliott Montroll characterised Herzfeld (in the early 1970s) as the greatest living classical physicist.⁽²⁾ Montroll also has credited Herzfeld with founding the American branch of what he calls the "statistical mechanics tree," descending from Ludwig Boltzmann and Friedrich Hasenöhl, and going on through Herzfeld's student John Wheeler and Wheeler's student Richard Feynman.^{(3),2}

Herzfeld's research covered many areas of physics, and had implications for many more. I will focus here on one aspect of that work—his contributions to the field of physical chemistry in the first half of his career. As a point of departure, I will use a letter written by the members of the chemistry department of the Johns Hopkins University in March 1936,

² According to Herzfeld's recollections, this lineage misrepresents the matter, since he claimed not to have learned statistical mechanics from Hasenöhl, but from Otto Stern.

when Herzfeld announced his decision to leave Hopkins; it was addressed to the president of the University, Isaiah Bowman:

We know of no theoretical physicist who enjoys nearly the reputation of Professor Herzfeld and who has at the same time the thorough knowledge of the science of chemistry and the acquaintance with chemical problems which he possesses. We regret particularly that the absence of Professor Herzfeld will necessarily mean the loss of a very effective and fruitful connecting link between physics and chemistry.⁽⁴⁾

I will examine Herzfeld's life and work in the context of his role as an "effective connecting link" between physics and chemistry.

1. A STUDENT AT THE UNIVERSITY OF VIENNA AND A PRIVATE IN THE AUSTRIAN ARMY

Karl Ferdinand Herzfeld was born in Vienna in 1892. He came from a successful and talented Austrian family. According to family legend, the Herzfelds descended from a member of Napoleon's army who dropped out during the retreat of 1812 and settled in Vienna. The family was Jewish; by Herzfeld's grandfather's generation they were well-assimilated, prosperous members of the Viennese professional class.^{(5),3}

Herzfeld's father was a physician and Associate Professor of Obstetrics and Gynecology at the University of Vienna. He had an extensive practice in Viennese society, including among his patients at least one Balkan princess. Herzfeld's mother was the daughter of a newspaper publisher and sister of a well-known organic chemist, R. O. Herzog. Both of Herzfeld's parents had converted to Catholicism by the time of their marriage (ref. 5, pp. 33 and 44).

From ages 10 to 18 Herzfeld attended the Schottengymnasium, a Benedictine school. He credited it with giving him a rigorous classical education, an extensive background in science and mathematics, and a great appreciation for intellectual activity and mental discipline. It was at the Schottengymnasium that he also developed his religious faith and reconciled it with the rational foundations of science. His strong religious convictions did not come from his parents or home life, but seem to be the product of his own temperament and education.

Herzfeld's interest in science dated from 1900, when Vienna installed electric streetcars. He became fascinated with the phenomenon of electricity, and from that time studied many branches of physical science. He had his own laboratory at home, where he was allowed to carry out

³ Most of the subsequent information about Herzfeld's life, unless otherwise noted, comes from ref. 5.

physics experiments with a vacuum pump and coil, but was forbidden to perform chemistry experiments on the grounds that they were too dangerous.

In 1910 Herzfeld entered the University of Vienna to study physics. Friedrich Hasenöhrle had succeeded Boltzmann as head of the Theoretical Physics Institute. Hasenöhrle is best known for his work on cavity radiation, and the derivation of a relation for mass-energy equivalence in 1904. His most famous student was Erwin Schrödinger, who completed his degree in 1910. Boltzmann's influence was still very strong at Vienna, and Herzfeld received a thorough training in classical physics. Oddly, although he was attending the single most important school of statistical physics in Europe, Herzfeld later claimed that he did not learn statistical mechanics until he attended the University of Zürich. The faculty at Vienna were interested in other areas of physics when he was there.

Herzfeld spent a year at the University of Zürich in 1912-13. Einstein was there at the time, lecturing on thermodynamics and statistical mechanics, but his research was in general relativity, which did not particularly interest Herzfeld, and he did not find his interactions with Einstein particularly rewarding. In later years it was his association with Otto Stern that he pointed to as the most valuable development of his time in Zürich: "He had an incredibly deep understanding of thermodynamics and statistical mechanics, and it was from him that I really learned to master these fields. He was a bachelor and we spent much time together, however he was completely unathletic" (ref. 5, pp. 60-61). The last statement may sound like a *non sequitur*, but it reflects Herzfeld's changing attitude toward athletics. As a child, he was very sheltered and was not allowed to participate in sports with the other boys at his school. While he was at Zürich, though, he took up fencing. Catholics were forbidden to duel, but Herzfeld apparently felt that it was important that he know that he *could* defend himself, even though he would never violate the church's rule by doing so.⁴ At Zürich, Herzfeld also took up skiing and sailing, joining various groups of physicists in these activities.

In 1914 Herzfeld returned to Vienna to complete his degree. The Radium Institute had opened in 1910, and there Herzfeld met the physical chemists Georg von Hevesy and Fritz Paneth. They had just returned from Manchester, and brought with them the first accounts of the Bohr model of the hydrogen atom. They also exposed Herzfeld for the first time to physical chemistry.

By the time he completed his degree in physics, Herzfeld had

⁴ Herzfeld, according to Paul Meijer, later used the same kind of reasoning to justify the development but not the use of atomic weapons.

published six papers. Several of them were straightforward elaborations of statistical mechanics. One was an attempt to derive a model for the hydrogen atom, published just before Bohr's.⁽⁶⁾ Herzfeld used Planck's technique to quantize energy for a modified Thomson atom, leading to the quantization of electron orbital radii. However, he equated the orbital frequency of the electron with the frequency of the emitted light, and so missed the essential relation that Bohr found. Herzfeld's doctoral dissertation was an application of the principles of statistical mechanics to a gas of free electrons, as a model for metals.⁽⁷⁾ His particular interest was in the temperature dependence of electrical conductivity. In the course of this paper, he derived (6 years before Megh Saha) a simple form of what is now known as the Saha equation for the distribution of an atomic species among its stages of ionization.

Graduating in July 1914, Herzfeld was immediately drafted into the Austrian army, where he entered officer training (under the Teutonic respect for titles) as Private Doktor Herzfeld. His positive recollections of his experience in the army reflect a strong dedication to science coupled with an unusual willingness to make the best of any situation: "I was very lucky in the timing of my army service; I did not lose more time than was absolutely necessary. I did not have to interrupt my studies; I was far enough advanced that I could do independent theoretical research in my free time." (ref. 5, p. 121).

Herzfeld's military experience was rigorous. He first joined an artillery regiment at Pola, on the Adriatic Sea. In 1915 the regiment was transferred to the Galician front, where Herzfeld considered himself fortunate to witness (and survive) a cavalry attack by 3000 Russians. The regiment was sent to the Albanian coast in 1916, and he spent 7 months living in a hut in the mountains, above the treeline. In 1917 Herzfeld was sent back to Vienna to work on ballistics research, but he tolerated that for only 6 months before arranging to be sent back to the front. By the conclusion of the hostilities, he had been promoted to first lieutenant. He finished the war in the Italian Alps, and barely managed to get back to Vienna at the end of the war; most members of his regiment did not survive.

Herzfeld wrote five papers while engaged in combat, between 1914 and 1918. All involved the application of statistical methods to particular cases such as the electron theory of metals and the Bohr model of the hydrogen atom. By the end of the war Herzfeld had established himself as a competent physicist, particularly well versed in the techniques of statistical mechanics, and with a strong interest in the problems of concern to chemists. He was well known and respected by most of the leading figures of the German-speaking physics community. All that he lacked was a job.

2. PRIVATDOCENT AT THE UNIVERSITY OF MUNICH

When Herzfeld returned to Vienna late in 1918, the prospects for academic employment were poor. The economic situation was so bad that the university was in danger of closing. Since conditions in Munich were somewhat better, he decided to go there to study analytic chemistry for the winter term, with the intention of becoming an industrial chemist. He studied with Otto Hönigschmidt for that semester, and spent 2 months of the following summer working as a volunteer chemist for a chemical plant. This was all it took to convince him that he was not cut out to be a chemist. In addition to making it easier for him to choose a possible career, the time Herzfeld spent in Munich was valuable because of the contacts he made. He had the opportunity to attend (and speak in) the theoretical seminar of the physics department, run by Arnold Sommerfeld. The result was that in December 1919 Herzfeld was offered a position as Privatdocent in theoretical physics and physical chemistry and a research assistantship with the physical chemist Kasimir Fajans. His attachment to the chemistry institute was brought about by Richard Willstätter, who wrote in his autobiography of bringing Herzfeld to the physical chemistry institute to "round out my pupils' mathematical training."⁽⁸⁾ Such a cross-department appointment was unusual, but turned out to serve as a good predictor of Herzfeld's subsequent career.

Living conditions in Munich in the early 1920s were not good, a result of the extremely high inflation. Herzfeld recalled salaries being paid every 2–3 days until late 1923, and Willstätter writes of the faculty wives waiting in the halls to collect their husbands' pay, since the time it would take to bring it home was long enough for it to lose much of its value.

Unlike the currency, physics in Munich was increasing in value. Among those who came to study or work with Sommerfeld were Werner Heisenberg, Wolfgang Pauli, Fritz London, Gregor Wentzel, and Alfred Landé. Herzfeld typically taught an advanced course in physics and one in physical chemistry. Sommerfeld was away a great deal, and Herzfeld frequently taught his course for him. Herzfeld's potential influence on Sommerfeld's students, such as Heisenberg, Heitler, and Pauling, was considerable (ref. 3, p. 7).

Herzfeld also worked with Fajans on several projects, although there were disadvantages in this collaboration, as he described:

[His] method of working was occasionally uncomfortable. I would still be asleep at 8:00 AM, when [I was called] to the telephone. In nightshirt and dressing gown, I would then hasten to the telephone in the hallway, to hear the voice of Professor Fajans: 'Dear Colleague, could you explain the mechanism of dielectric polarization to me?' (at 8 a.m. and over the telephone!) (ref. 5, p. 144).

Herzfeld eventually abandoned this style of research, as being too taxing, and chose to support himself instead as a laboratory instructor in chemistry.

Among the Sommerfeld papers in the collection of the Archive for History of Quantum Physics is part of a letter which was written by Sommerfeld evidently as a recommendation for Herzfeld. He begins by listing areas in which Herzfeld had done research, and continues with Herzfeld's special contributions to chemistry:

... statistical foundations of thermodynamics in the Boltzmann-Gibbs formulation, further physico-chemical problems of solutions, crystal structure, reaction rates, statistics of the electron. Meanwhile he has a firm seat in any questions of modern theory, which he has demonstrated through his original judgements and quick comprehension in seminars and colloquia. He has an unusually kindly and upright character. His lectures are valued and well-attended, by the chemists for whom he keeps the mathematics as elementary as possible, as well as the mathematicians and physicists for whom he holds special lectures on more difficult problems. He is particularly recognized for the regular personal help with mathematical questions that he gives to doctoral students in physical chemistry.⁽⁹⁾

2.1. Chemical Reaction Rates

Herzfeld's research during his years at Munich covered a variety of topics, as reflected in Sommerfeld's evaluation. I will examine one in particular—his work on chemical reaction rates. Lacking a useful theory of chemical kinetics, chemists had shown relatively little interest in the question of reaction rates from 1900 to about 1920. Then attention focused on the question of how the energy for a reaction is supplied to the reacting molecule. This interest was prompted by the introduction, by J. Perrin, M. Trautz, and others, of the radiation hypothesis—the theory that a diatomic molecule gets the energy for dissociation through radiation from the walls of the container. This was proposed as an alternative to the older notion that energy is supplied by collisions between molecules. The ensuing debate over the relative merits of the two models resulted primarily in a much-improved understanding of the role of molecular collisions as the source of energy for any reaction.⁽¹⁰⁾ Herzfeld's contribution to the dispute was to use statistical mechanics to derive the rate at which such collisions should occur, as a way to determine the theoretical reaction rates.

Much of Herzfeld's early work on reaction rates was centered around one specific reaction—the formation of hydrogen bromide from molecular hydrogen and bromine. This reaction received particular attention because it did not behave in any way analogous to the formation of compounds like hydrogen chloride or hydrogen iodide, which could be described with

relatively simple rate equations. The empirical reaction rate law for the formation of HBr, as determined by M. Bodenstein and S. C. Lind in 1907,⁽¹¹⁾ was

$$\frac{d[\text{HBr}]}{dt} = \frac{k_0[\text{H}_2][\text{Br}_2]^{1/2}}{\{m + [\text{HBr}]\}/[\text{Br}_2]}$$

where m is an empirical constant. In 1919, in his first publication after the war, Herzfeld⁽¹²⁾ suggested that one can represent the formation of HBr as a chain of four reactions:



The two key reactions are (2) and (3) involving free atoms of one gas with molecules of the other. The reaction can only proceed if it is initiated by the dissociation of molecular bromine (1); hydrogen molecules do not dissociate so readily. Atomic hydrogen is a product of (2), though, and once produced, it can form HBr by (3). The atomic hydrogen can also inhibit the reaction by decomposing HBr (4), but this releases atomic bromine to promote (2).

Herzfeld then determined theoretical rate constants for each of the individual reactions. One of his results is of particular interest here—his calculation of a general expression for the rate constant of a first-order reaction such as reaction (1) in the forward direction. Expressions for chemical equilibrium constants (or concentration quotients) had been derived previously, but rate constants for chemical reactions were more difficult because it seemed that one would need some knowledge of the specific reaction mechanism. Herzfeld recognized that he could not derive the first-order rate constant directly without more specific knowledge of the quantum laws governing the dissociation of molecules, but he could use the equilibrium expression to indirectly derive a rate constant.

If we consider a first-order reaction $\text{AB} \rightarrow \text{A} + \text{B}$ (molecular dissociation) and the accompanying second-order reaction, $\text{A} + \text{B} \rightarrow \text{AB}$ (molecular formation), then at equilibrium the rate of dissociation is equal to the rate of formation:

$$k_1 C_{\text{AB}} = k_2 C_{\text{A}} C_{\text{B}}$$

where k_1 and k_2 are the rate constants for the first- and second-order reactions, respectively, and C_{A} , C_{B} , and C_{AB} are the concentrations of species

A, B, and AB. The reaction's concentration equilibrium constant K is then defined as

$$\frac{C_A C_B}{C_{AB}} = \frac{k_1}{k_2} \equiv K$$

The equilibrium equation had been worked out by Otto Stern in 1914⁽¹³⁾ from kinetic theory and we can assume that Herzfeld's reasoning followed Stern's in this case. He calculated the ratio of relative probability of atoms A and B existing freely to the probability of their existing in combination, assuming that when atom B enters the shell of atom A, the potential energy of the two decreases by Q/N , and that B does not move freely inside of A, but is bound elastically. The result⁵ is

$$K = \frac{1}{4d^2} \left(\frac{2M_A M_B}{M_A + M_B} \frac{RT}{\pi} \right)^{1/2} \frac{1}{Nh} (1 - e^{-hv/kT}) e^{-Q/RT}$$

where d is the distance between atoms in the molecule; M_A , M_B , and M_{AB} are the masses of A, B, and AB; N is Avogadro's number, ν is the vibrational frequency of the excited molecule; and Q is the heat of reaction for the forward (first-order) reaction.

Herzfeld then calculated k_2 , the rate constant for the formation of molecules. He did this by assuming that the spherical atoms are undergoing collisions, and that every time two atoms approach to within some distance s , they will combine to form a molecule. From kinetic gas theory, he wrote an expression for the rate of collisions Z of A and B per unit volume:

$$Z = 2s^2 N^2 \pi^{1/2} \left(\frac{M_A + M_B}{M_A M_B} 2RT \right)^{1/2} C_A C_B$$

The rate constant k_2 is then

$$k_2 = \frac{Z}{N C_A C_B} = 2s^2 N (\pi)^{1/2} \left(\frac{M_A + M_B}{M_A M_B} 2RT \right)^{1/2}$$

Finally, from this, Herzfeld obtained the first-order rate constant:

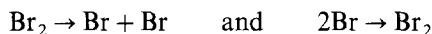
$$k_1 = k_2 K = \frac{s^2}{d^2} RT \frac{1}{NH} (1 - e^{-hv/kT}) e^{-Q/RT}$$

⁵ In Herzfeld's 1919 paper, he has an extra factor of Avogadro's number N in the denominator of this expression, which was apparently a printing error. I thank John Smedley for pointing this out.

He further simplified this expression by assuming that the distance s leading to a reaction is the same as the distance d between atoms in the molecule, and by assuming that the vibrational energy of the excited molecular bond is very high ($h\nu \gg kT$). Then

$$k_1 = \frac{kT}{h} e^{-Q/RT}$$

Herzfeld's use of the heat of reaction Q in this expression stems from the fact that his derivation was carried out specifically in terms of the formation of hydrogen bromide. In general, the first-order reaction $AB \rightarrow A + B$ has an activation energy q_1 ; for the reverse reaction, $A + B \rightarrow AB$, the activation energy is q_2 . The heat of reaction for the forward reaction is $Q = q_2 - q_1$. For the particular case Herzfeld considered, the reactions in question were



In this case $q_1 = 0$ and $q_2 = Q$. He therefore substituted the more easily determined Q for q_2 in his derivation. In 1921 he corrected this to the general form⁽¹⁴⁾

$$k_1 = \frac{kT}{h} e^{-q_0/RT}$$

where q_0 is the activation energy for the forward reaction. If we compare this expression with the basic Arrhenius equation for first-order reactions,

$$k_1 = A e^{-E_0/RT}$$

the factor kT/h corresponds to A , and can be interpreted as a collision frequency, as Herzfeld pointed out. Ten years later, Henry Eyring derived the same expression for the rate constant, using the concept of the activated complex.⁽¹⁵⁾ Eyring's result was derived from very similar reasoning, but used quantum mechanics, while Herzfeld's came out of the old quantum theory. Eyring later referred to Herzfeld's general approach, but never mentioned this specific result. Herzfeld's work is certainly not as general as that of Eyring, nor does it have the same pictorial quality as the activated complex, but it is nonetheless surprising that so little attention was ever paid to this work by physical chemists.⁶

⁶ The one notable exception to this is the physical chemist E. A. Moelwyn-Hughes, who describes Eyring's work as the "examination ... of many reactions ... in light of Herzfeld's equation."⁽¹⁶⁾

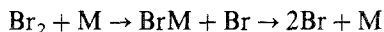
2.2. The Steady-State Assumption

Herzfeld's primary contributions in the determination of the first-order rate constant were the identification of plausible simplifying assumptions about the geometry of atomic collisions and the vibrational energy of the excited molecule. In order to calculate a rate law for the specific case of the formation of hydrogen bromide, he was led to make one more simplifying assumption, one that has proven to be quite enduring. The inherent difficulty with the four-step chain proposed for the formation of hydrogen bromide is that the rates of the individual reactions are dependent on the concentrations of the intermediates, atomic hydrogen and atomic bromine, which cannot be measured. As a way around this problem, Herzfeld assumed that the atomic concentrations rapidly reach a steady-state value, and remain constant thereafter. In determining the reaction rate, then, one can set

$$\frac{d[\text{H}]}{dt} = \frac{d[\text{Br}]}{dt} = 0$$

Using this assumption and calculating values for the rate constants for each of the four constituent reactions, Herzfeld found the derivation of the rate equation to be straightforward. It was the same as that obtained by Bodenstein and Lind from empirical reasoning. At the same time, and independently, Michael Polanyi and Jens Anton Christiansen published similar analyses of the bromine reaction, also introducing what has come to be called the stationary state assumption.⁽¹⁷⁾ This approach has proven to be extremely fruitful in cases where the concentrations of the intermediates in the reaction, in this case atomic hydrogen and atomic bromine, are very low by comparison with the concentrations of the other chemical components.

In 1920 Polanyi identified a difficulty in the scheme just described.⁽¹⁸⁾ Herzfeld had assumed that the energy necessary for the dissociation of molecules in equation (1) above came from collisions with other bromine molecules. Polanyi showed, however, that the rate of collisions in (1) was not sufficient to produce the rate of production of HBr in (2). Where did the energy come from to further dissociate the H₂? Rather than fall back on the radiation hypothesis, Polanyi speculated that there existed some hitherto undetected source of energy from the "aether." Herzfeld's reply to this in 1921 was to point out what had been implicit in his first paper (ref. 12, pp. 1-19). The initiation reaction in the first step (1) actually goes as



where M can be any atom, and could very well be a hydrogen atom, as in step (3). In other words, Br_2 will only dissociate into 2Br in the presence of a third body to provide the dissociation energy.⁽¹⁹⁾ Max Born and James Franck expanded on Herzfeld's theory of three-body collisions in 1925.⁽²⁰⁾ Herzfeld's assumption about three-body collisions was supported experimentally several years later when Bodenstein and H. Lütkemeyer showed that the rate of formation of hydrogen bromide is increased in the presence of light.⁽²¹⁾ In this case, the light quanta were the third bodies in the molecular collisions. Finally, in 1929 G. Jung and W. Jost tested the three-body hypothesis and Herzfeld's calculated rate constants for the formation of hydrogen bromide, and found that his theory was borne out by experiment.^{(22),7}

Although he used kinetic theory to derive an equilibrium constant K in 1919 (above), 2 years later Herzfeld showed that the equilibrium constant could be derived from the (classical) ratio of sums of states in phase space.⁽²⁴⁾ He then went on to show that quantum theory could be applied to the same kind of reasoning to derive a similar expression for K .

Statistical mechanics in the 1920s had not yet worked its way into general usage in either physics or chemistry, and its relation to other branches of physics was still being explored. One common concern was the link between statistical mechanics and thermodynamics. For example, two papers published in 1922, one by C. G. Darwin with R. H. Fowler, and one by R. C. Tolman, examined the relation between statistical mechanics and thermodynamics.⁽²⁵⁾ Although both of these papers mention the possibility of connecting statistical mechanics to quantum theory, neither took that route. In 1920 Herzfeld published "The statistical meaning of thermodynamic functions" in the *Zeitschrift für physikalische Chemie*, in which he investigated the connection between thermodynamics and statistical mechanics from the standpoint of both classical mechanics and quantum theory.⁽²⁶⁾ He then went on to show how this could be applied to an interpretation of chemical potentials. Herzfeld's explicit use of quantum theory, application to chemistry, and publication in a chemistry journal distinguish him from other physicists working in statistical mechanics at the time.

2.3. Kinetische Theorie der Wärme

Herzfeld's other major contributions to physical chemistry during his years at Munich were in the form of a textbook and several handbook

⁷ Jung and Jost, although they clearly credit Herzfeld with originating the three-body collision theory, are often cited as the initiators of the concept in chemistry texts. See N. Semenov, ref. 23.

articles. In 1925 he published *Kinetische Theorie der Wärme* in the Müller-Pouillet series.⁽²⁷⁾ This was the first comprehensive textbook published on the subject of kinetic theory and statistical mechanics. As such, it was tremendously influential in the German-speaking countries, where it was widely used as a textbook. Unfortunately, it is essentially unknown in the United States, except for one section on the behavior of ideal gases, which was translated into English and published in the second edition of Hugh Taylor's *Treatise on Physical Chemistry* in 1931.⁽²⁸⁾ Taylor's decision to publish this chapter in a physical chemistry text demonstrates Herzfeld's appeal for chemists. The book included a systematic presentation of the basis of statistical mechanics and numerous applications of the techniques to chemistry, such as the study of reaction rates. A notable feature of Herzfeld's treatment here is the extensive use he made of complex partition functions. For example, here he again calculates the equilibrium constant for dissociation of a diatomic molecule, but in this case he clearly uses a ratio of partition functions to do so.⁸ Of the classic texts describing the use of partition functions that are generally cited in any physical chemistry text—Tolman (1927), Fowler (1929), and Herzfeld—Herzfeld's is certainly the earliest.⁽²⁹⁾ The value of Herzfeld's book was recognized by one prescient American chemist, who wrote in the *Journal of the American Chemical Society* in 1927, "The trend of modern chemistry in many of its aspects is so obviously toward the kinetic and the statistical that Herzfeld's book, supplemented perhaps by Tolman's *Statistical Mechanics*, will be welcomed by all those who read aright the signs of the times."⁽³⁰⁾

In addition to *Kinetische Theorie der Wärme*, Herzfeld also wrote two articles for the *Handbuch der Physik*, on classical thermodynamics and absorption and dispersion.⁽³¹⁾ According to those who have worked with him, he wrote most of his papers without consulting journals, apparently having an encyclopedic memory of the relevant literature. Between the years 1919 and 1926 he wrote 34 research papers in addition to his textbook and handbook articles, a remarkable achievement by any standards.

3. PROFESSOR OF PHYSICS AT JOHNS HOPKINS UNIVERSITY

In 1926 Herzfeld was offered the first Speyer Visiting Professorship at Johns Hopkins University, which he accepted with alacrity. At the end of the semester of his appointment he was offered a permanent position as a

⁸ Like Planck, Herzfeld referred to these as *Zustandsumme*. The term "partition function" was apparently not introduced until somewhat later and is attributed to R. H. Fowler.

full professor of theoretical physics. Paul Meijer once asked Herzfeld why he left the civilization of Munich to come to the comparative wilderness of Baltimore. Herzfeld's reply was that there were simply no academic jobs in Europe and one did not turn down such an offer.⁽³²⁾ This does not explain, though, why so few other young European physicists chose to come to the United States prior to 1933. Katherine Sopka has shown that the job market was reasonably good for theoretical physicists by 1930, when many physics departments began to realize that they needed some help keeping up with all of the new developments in theory.⁽³³⁾ Herzfeld's decision may also reflect the state of physics in Germany in the 1920s, when many physicists were turning away from the determinism of classical physics. Herzfeld may have found American physicists more receptive to his style of physics.

Herzfeld's life in Baltimore was characteristically modest. For the 10 years he was at Johns Hopkins he lived in a dormitory on campus. He learned American English by going to the movies, particularly westerns. His one indulgence seems to have been his car, which he drove to classes every day, with remarkable punctuality, as well as occasionally venturing further afield.⁽³⁴⁾ While traveling in Canada in 1934, he performed the rather remarkable feat of rolling his car onto its side without appreciable damage to either himself or the car.⁽³⁵⁾

In 1927 Herzfeld was offered an appointment at Princeton, which he declined. Princeton was therefore forced to take as second choice Eugene Wigner. The offer put Herzfeld in the position to bargain with the Hopkins administration, which under President J. S. Ames was sympathetic to the development of strong science departments, and he convinced them to add two new positions to the physics department and to build a new laboratory for the department. He also persuaded the university to offer Erwin Schrödinger a permanent professorship, but Schrödinger was repelled by Prohibition and declined the offer.⁽³⁶⁾

3.1. Vibrational Energy Transfer

While at Hopkins, Herzfeld became a close friend of Frank O. Rice, a chemist, and their friendship led to the single most important collaboration of Herzfeld's years at Hopkins. Recent measurements of the absorption of sound in air had resulted in values that were higher than expected on the basis of the density of air. Rice and Herzfeld, in discussing this, came to the conclusion that the excess absorbed sound energy must be stored in vibrational modes of the air molecules. At the same time R. W. Wood, in the Hopkins physics department, was involved in experiments in ultrasonics, the techniques for which he had picked up in Europe from Paul Langevin

during the war.⁽³⁷⁾ Rice and Herzfeld had the idea that perhaps they could use measurements of sound absorption to determine the rate of energy transfer to the vibrational modes. This resulted in a seminal paper written in 1928 in which they derived the equations relating sound absorption to the time of energy transfer.⁽³⁸⁾

The idea that there is a time delay in thermal equilibration between the external (translational) and internal (vibrational and rotational) modes of a polyatomic molecule was not a new one. In 1881 H. A. Lorentz had suggested just such an effect (see ref. 37). Both Rayleigh and J. Jeans had subsequently related this delay in equilibration to the propagation of sound in gases, but only as a theoretical suggestion. In 1920 Einstein proposed using sound waves in a gas as a way to indirectly determine the rate of simple gas reactions. None of these four, however, suggested any way to actually measure the characteristic time for equilibration.⁹

Herzfeld and Rice's hypothesis was that the velocity of sound propagating through a polyatomic gas should depend upon not only viscosity and heat conduction, as in the classical theory, but also on the rate at which energy in the translational degrees of freedom of the molecules is exchanged with the internal degrees of freedom.¹⁰ They proposed to derive equations for the absorption and dispersion of sound waves in a gas that would lead to a determination of a characteristic relaxation time for this energy transfer. They began by assuming that the energy exchange between the external and internal modes is a first-order rate process and, by analogy with a chemical rate equation, represented the amount of energy per mole which passes from the external to the internal degrees of freedom per unit time as

$$-\alpha R \frac{dT}{dt} = \frac{\alpha R}{\tau} (T - T')$$

where αR is the specific heat of the translational kinetic energy of the gas molecules, T is the temperature of the translational kinetic energy of the

⁹ These measurements require the determination of absorption and dispersion of sound over a frequency range of at least 10^4 – 10^8 Hertz for gases. The ability to generate and measure such waves was dependent on the development of electronic techniques not available until the mid-1920s.

¹⁰ Herzfeld and Rice did not distinguish between vibrational and rotational modes as internal degrees of freedom in this paper. It had been shown by Rayleigh in 1904, however, that the rate of equalization for the rotational degrees of freedom would be so short as to be effectively instantaneous. It is common now to treat both translational and rotational energy as being effectively external, that is, as coming into thermal equilibrium instantaneously, and to focus on the exchange of translational and vibrational energy as being the time-dependent process.

gas molecules, T' is the temperature of the internal degrees of freedom, and τ is a reciprocal rate constant, known as the relaxation time, for the energy exchange. They apparently considered the translational energy of the molecules to be the sum of the thermal component and the coherent kinetic energy due to the sound wave. Although assigning a single temperature to this energy is not strictly valid (since the sound energy is not random), it introduces no errors into the calculation. Herzfeld and Rice then combined the equations of motion for a plane wave propagating through a gas with the expression for the rate of exchange of energy between the external and internal modes (above) and derived a dispersion equation for the sound wave. The approximate solution to this equation, to first order in powers of frequency, gave an expression for absorption and one for dispersion, all in terms of the sound frequency, the specific heats of internal and external modes, and the relaxation time. The specific cases treated in this paper were the gases air, carbon dioxide, and hydrogen, for which moderately reliable measurements of absorption and/or dispersion were available. The results for carbon dioxide were in agreement with experiment, and indicated that the contribution of vibrational energy transfer to sound absorption was significant. The results for air did not agree nearly as well; it is now recognized that air cannot be treated with such a simple model. By comparison with experimental data, Herzfeld and Rice calculated relaxation times for these gases on the order of 10^{-8} sec.

This method has been refined considerably since Herzfeld and Rice first introduced it. The general approach now taken is to write a relaxation equation in terms of energy instead of temperature:

$$\frac{-dE'}{dt} = \frac{1}{\tau} [E' - E'(T_{tr})]$$

where E' is the instantaneous value of the vibrational energy and $E'(T_{tr})$ is the value of the vibrational energy in equilibrium with the translational and rotational modes at temperature T_{tr} , where the translational mode includes the kinetic motion due to the sound wave. The energies can then be written in terms of the specific heats of the three energy modes. At a sufficiently high frequency, such that the period of the sound wave is shorter than the relaxation time, the vibrational mode cannot equilibrate with the other two, and the dependence of sound absorption on the vibrational specific heat will drop out. Herzfeld and Rice's initial first-order approximation was extended to higher orders in frequency by A. Rutgers in 1933, who showed that the relaxation equation postulated by Herzfeld and Rice can be derived from quantum considerations.⁽³⁹⁾

Although the initial inspiration for this work came from the problem

of sound absorption in gases, Herzfeld and Rice recognized immediately that their analysis had much broader implications for the study of chemical reaction rates. Molecular energy transfer through collisions in gases is the strongest kind of interaction between molecules that does not involve a rearrangement of chemical bonds. It is frequently a necessary first step in the chemical activation or deactivation of molecules. Chemists recognized that a thorough understanding of vibrational energy transfer was an essential preliminary to a detailed understanding of reaction kinetics. The measurement of sound propagation through a gas leads to just such an understanding. Rice, as a chemist, shared with Herzfeld an interest in the problem of chemical reaction rates, which in turn implied an interest in energy transfer between molecules. This paper was extremely influential in describing a way of using measurements of sound propagation to determine the rate at which molecules transfer energy from translational to vibrational modes through collisions, and represents a second stage in Herzfeld's thinking on the subject of chemical reaction rates.

Herzfeld further developed the theory of vibrational energy transfer in several later works. In 1935 he attempted to explain the unexpectedly high absorption of sound in helium, which, as a monatomic gas, cannot transfer sound energy to any internal modes of the molecules.⁽⁴⁰⁾ Herzfeld assumed that the speed of the process was high enough to account for deviations from the ideal gas law on the part of the helium, but this was not sufficient to account for the excess absorption. In the early 1950s Herzfeld, along with R. Schwartz and Z. Slawsky, reexamined the theory of vibrational energy transfer in light of a much better understanding of the magnitude and range of intermolecular forces.⁽⁴¹⁾ This was one of the few papers in which Herzfeld made use of quantum mechanics. Finally, in 1959, Herzfeld and T. Litovitz wrote *Absorption and Dispersion of Ultrasonic Waves*.⁽⁴²⁾ In spite of its title, this book was not really about ultrasonics, but about the molecular basis for absorption and dispersion. It was a vehicle for analyzing a collection of topics of interest to the authors. Among these topics were relaxation times and reaction rates (for both liquids and gases) as well as a more general theory of liquids (another of Herzfeld's long-term interests) and experimental ultrasonics. As such, the book represents the culmination of Herzfeld's thinking on many of the issues that interested him most in physical chemistry.

3.2. Free-Radical Mechanisms

Herzfeld further pursued the question of reaction rates and chemical kinetics in the second paper he wrote with Rice, dealing with the role of free radicals in the thermal decomposition of organic compounds. In

postulating possible reaction mechanisms for a wide range of chemical reactions, chemists had often considered the possibility of short-lived free radicals as intermediates, but it had proven impossible to conclusively isolate such compounds. Finally in 1929 F. Paneth and W. Hofeditz in Germany succeeded in isolating methyl groups by heating lead tetramethyl in the presence of hydrogen and passing it over metallic surfaces (mirrors), which reacted with the methyl radicals to form products which could be recovered.⁽⁴³⁾ In 1931 Herzfeld and Paneth described a possible mechanism for both the methyl reaction and the analogous reaction for the ethyl radicals, which Paneth and W. Lautsch had isolated in 1930.⁽⁴⁴⁾ In the same year Rice first proposed to describe the pyrolysis of certain organic compounds on the basis of free-radical intermediates.⁽⁴⁵⁾ He postulated chain mechanisms for the decomposition of saturated hydrocarbons that could account quantitatively for the products of various thermal decompositions. Rice proposed chains that were initiated by the splitting of a molecule at its weakest link to produce free radicals, and propagated by the radicals bonding with a hydrogen from the parent compound to form a saturated hydrocarbon and a new free radical. The chain was terminated by the association of the radicals. Rice's theory was controversial because of its obviously speculative nature. Many of the radicals required by his mechanisms had not yet been isolated experimentally. On the other hand, as he pointed out, any other possible mechanisms that could account for the products of these reactions were even more improbable than free radicals.

In 1934 Rice and Herzfeld provided additional support for Rice's theory by showing that not only could it account qualitatively for the products of thermal decomposition, but it could also account for the kinetics of the reactions.⁽⁴⁶⁾ In particular, the authors explained how, in many cases, the sum of a complex series of reaction steps could lead to a first-order rate law, and why the experimental activation energies for decomposition reactions are usually much smaller than the dissociation energy for the carbon-carbon bond. Rice and Herzfeld were able to show that mechanisms could be devised that would lead to an overall first-order rate law and, by the appropriate choice of activation energies, the energy of the total reaction could be made to agree with experiment.

There are a number of fairly obvious parallels between this work and Herzfeld's earlier work on the formation of hydrogen bromide. In both cases he was working with chain reactions for which he could assume that the intermediates (atomic hydrogen and bromine, or free radicals) would arrive at a steady-state concentration after an immeasurably short period of time. The role of the free-radical in three-body collisions is important here and was developed further by Polanyi. Finally, Herzfeld applied the

same techniques here to the calculation of rate constants that he had demonstrated fifteen years earlier in his work on hydrogen bromide.

The response to the so-called Rice-Herzfeld mechanisms was not initially positive. The primary purpose of the paper was to show that free-radical mechanisms could be devised. The assignment of activation energies was purely speculative and the free radicals they discussed had not yet been detected. This left Rice and Herzfeld vulnerable to a great deal of criticism. They were aware of these limitations, as they noted in their conclusion:

Although there is as yet no experimental evidence for the presence of reaction chains in these decompositions and, further, there has been no direct experimental demonstration even of the presence of free radicals below 700° and above a few mm. pressure, nevertheless it should be pointed out that the only way to avoid chain reactions as the explanation of the measured rates would be to increase the heats of activation involved to quite improbable values (ref. 46, p. 289).

As might be expected, many of the activation energies they assigned have been shown to differ considerably from experimentally determined values, and some of the proposed mechanisms have been shown to be invalid. Considering their totally speculative nature, though, the Rice-Herzfeld mechanisms have proven to be surprisingly accurate, and they are now considered to lend a welcome coherence to the data for thermal decomposition.

In considering Herzfeld's contributions to statistical mechanics, we should not neglect the impact of this teaching. When he arrived at Hopkins, the theoretical training, while thorough, was outdated. Herzfeld established a 2-year series of advanced lectures in theoretical physics, modeled on the courses he had experienced in Vienna and Munich. Quantum theory and statistical physics were both a regular part of this series. As early as his first semester at Hopkins, in the spring of 1926, he delivered a series of lectures on statistical mechanics. Herzfeld's student John Wheeler recalled Herzfeld's classes as providing not only a rigorous and clear treatment of the particular topic, but also an unusual overview of how the topic was related to the larger scheme of physics as a whole.⁽⁴⁷⁾ Herzfeld's familiarity with and use of the formulations of Gibbs also helped to introduce these theories to many American physicists for the first time.

Herzfeld also brought to Hopkins the European tradition of a graduate seminar, in which all present were encouraged to participate. Wheeler describes this lively scene with great fondness:

Herzfeld's joint seminar with Maria Goeppert-Mayer on topical issues of quantum mechanics provided an example of the Johns Hopkins tradition at its best. Freed of the traditional regimentation of seats, the students and faculty sat around a long table like board members—interrupting, participating, discussing.

Among the visitors from afar attracted by Herzfeld's deeper interest in issues of principle were Peter Debye and Paul Ehrenfest. One day Herzfeld tried to get Ehrenfest to lead the seminar discussion. Despite much urging, Ehrenfest declined, insisting that Herzfeld himself should take the floor. Herzfeld finally did. He explained why one might hope for a "separation of variables" even in a wave equation that is non-separable by any standard criterion. Look at a given proper function, he proposed, and look where its nodes lie, and pick new coordinates to conform to those nodal surfaces. Then, he suggested, the wave equation might be separable. Ehrenfest smilingly broke in, "My dear Herzfeld, you are completely crazy"; and the liveliest discussion developed between the two friends.⁽⁴⁸⁾

In 1936 Herzfeld left Johns Hopkins and went to Catholic University of America. His reasons for leaving were several: unhappiness with the administration of the university, which under President Isaiah Bowman was alienating most of Hopkins's most talented scholars; a feeling that if someone in the physics department had to be let go as an economic measure, then he was the one to leave since he was the one in the department who had no family to support; and a genuine calling to Catholic University as a religious institution. He felt that he could make significant contributions by making a moribund physics department into an active research center, which he certainly did. It was because of his decision to leave Hopkins and the administration's decision to make no attempt to keep him that the chemistry department wrote the letter referred to at the beginning of this article.

Between 1920 and 1935 Herzfeld was instrumental in introducing the use of statistical mechanics into chemistry through his review articles and book, as well as by example in his own research. Out of this research came the concepts of chemical chain reactions and the stationary-state hypothesis, the three-body collision concept, and relaxation times for vibrational energy transfer. Perhaps more important, though, Herzfeld bridged the two fields of chemistry and physics with his essentially classical approach, which was, I believe, more acceptable to many chemists than the quantum mechanical approach taken by other physicists to chemical questions in this period.

4. STATISTICAL MECHANICS, QUANTUM MECHANICS, AND CHEMISTRY

I have discussed here only a portion of Herzfeld's work. He would probably have been surprised at this appraisal, since he always considered himself to be a physicist and not a chemist. During the period covered here much of his research was in areas that were clearly physics and not chemistry. For example, between 1912 and 1918 he worked on models

of the hydrogen atom, both his own and Bohr's. During the 1920s he published a series of papers on dispersion, at just the time that that phenomenon was leading H. A. Kramers and Heisenberg toward quantum mechanics. None of this, however, had the kind of influence that Herzfeld's chemical work did, and it is primarily for this reason that I think that it is reasonable to focus on his contributions to chemistry.

We can better understand the significance of those contributions if we understand the nature of chemistry as a discipline distinct from physics in the 1920s and early 1930s. Although there was clearly a great deal of overlap between physics and chemistry, and a number of individuals worked in both fields, the concerns of chemists were not necessarily the same as those of physicists, and to whatever extent theoretical chemists used physics, most of them used classical physics. William Scott has recounted an example of this separation of disciplines in his discussion of the scientific career of the physical chemist Michael Polanyi. Scott describes how, in 1921, when Polanyi presented his theory of adsorption (based on thermodynamics) to his colleagues at the University of Berlin,

Nernst and Einstein objected that the then-prevalent Bohr theory had no place in it for such long-range forces, so that Polanyi was undoubtedly wrong... . Hermann Mark, who was there at the same time, remarked that these objections were not important to the chemists, because the adsorption theory seemed to represent the chemical situation well while the Bohr theory was rather remote from their consideration (ref. 19, p. 284).

Polanyi was one of the first physical chemists to make extensive use of both statistical mechanics and quantum mechanics. He had no formal training in either, and was only "aware of statistical ideas" because he had also studied physics when he began his research in the early 1920s. In the United States the two sciences were even more divided. A survey of the *Journal of the American Chemical Society* for the decade of the 1920s finds almost no mention of quantum theory, with the exception of book reviews. There are rare references to statistical mechanics, although the topic of reaction velocities is popular. The *Journal of Physical Chemistry*, which we would expect to have more references to both, shows the same pattern.¹¹ The fact that statistical mechanics was not commonly used by chemists until the 1930s is well illustrated by Joseph Mayer's recollections of his graduate education at Berkeley from 1927 through 1929.⁽⁵⁰⁾ Mayer, who later became known for his application of quantum statistical mechanics in chemistry, was G. N. Lewis's student. He recalled that statistical mechanics was not taught in chemistry at Berkeley when he was a student, and that

¹¹ This can be attributed in part to the unique interests of the editor, Wilder D. Bancroft. See ref. 49.

physical chemistry was done entirely in terms of thermodynamics. In fact, Mayer and Lewis taught themselves statistical mechanics from Tolman's and Fowler's books. For even the progressive chemistry departments, such as Columbia and Harvard, quantum mechanics did not become a standard part of the curriculum until the late 1930s, and then the chemists often found it uncomfortable.^{(51),12}

At the same time, statistical mechanics was not a required part of most physics curricula. The majority of physicists in the 1920s were only just beginning to recognize the power of the statistical approach. Herzfeld suggested that this delay was the result of Planck's use of statistical mechanics to derive the quantum of action: to the classical physicist who resisted the introduction of quantum concepts, this was proof of the wrong-headedness of using statistical mechanics.⁽⁵²⁾ For whatever reason, statistical mechanics was still a new tool in the 1920s. Again, in the United States this was even more noticeable. The author's informal survey of the American Institute of Physics Niels Bohr Library's course lists for graduate physics departments in the 1920s revealed only three courses with "statistical mechanics" in the title. These were J. H. Van Vleck's at Minnesota, one summer session at the University of Michigan, and Herzfeld's course at Johns Hopkins.

5. CONCLUSION

Montroll's categorization of Herzfeld as the greatest living classical physicist is perhaps a bit of an exaggeration, given Herzfeld's willing acceptance of quantum theory, but it does capture the essence of Herzfeld's approach to science. He was, of course, well aware of the development of quantum mechanics, and even tried to teach it at Hopkins,¹³ but he remained firmly classical (in the sense of Einstein and Planck) in his interpretation of the results of quantum mechanics. In an article on the quantum theory of matter written in 1936 for the Catholic journal *Thought*, Herzfeld divided physicists into two groups on the basis of their interpretation of causality. The first group, he says, believe that it is possible to maintain that in reality the true laws of physics satisfy the demands of causality within a probabilistic sense, and that it should be possible to calculate

¹² One of several reasons mentioned for not renewing Joseph Mayer's contract at Hopkins in 1938 was that students and fellow faculty members thought he was demanding too much in his courses by requiring that chemistry students learn both quantum and statistical mechanics.

¹³ This was, perhaps, the only case where Herzfeld's teaching was less than exemplary. Maria Goeppert Mayer was pleased to be asked for help with quantum mechanics by Herzfeld's students, who found his presentation incomprehensible.⁵³

further behavior if only we could know exactly what the present state is. The second group believes that if it is impossible to know a certain thing because of a fundamental principle of nature, then it is futile to assert that such a thing happens "in reality."⁽⁵⁴⁾ Herzfeld, who described himself as a "critical realist," clearly located himself in the first group.⁽⁵⁵⁾

Herzfeld's career did not end when he left Johns Hopkins, but it did change direction. He pursued his interest in the nature of liquids, and extended the concept of vibrational energy transfer to the liquid state. He was instrumental in setting up a research program in ultrasonics at Catholic University, for which that department is still known today. During the Second World War, Herzfeld directed research at Catholic University on underwater explosives as an outgrowth of this program. This grew further into the Navy underwater sound program after the war. He was responsible for designing a graduate program that enabled many employees of government laboratories to pursue graduate degrees in physics part-time. During his years in Baltimore and then Washington, he became known as the most eminent and helpful theorist in the region; as Elliot Montroll wrote, "For many years he was the capital area's wise theoretical physicist to whom local researchers went with their problems, which he generally clarified and frequently resolved" (ref. 3, p. 7).

If, as I have stated, Herzfeld made serious contributions to the field of physical chemistry, then why is his name so little known by the chemists who regularly profit from his legacy? He frequently appears in physical chemistry texts as a reference for the stationary-state hypothesis and/or the theory of free radical mechanisms, but these are isolated references among hundreds of other such references. Taken alone, neither of these could make a reputation. One explanation for his relative obscurity in the United States is that some of his most important early work was published in German, which many American chemists did not read. This problem is particularly glaring in the case of Herzfeld's article on the statistical meaning of thermodynamic functions, published in 1920.⁽²⁶⁾ In *Chemical Abstracts* the title is translated "The static meaning of thermodynamic functions." It is not surprising that chemists would not have found it of possible interest. A more important factor, though, may be the emphasis physicists and chemists have tended to place on quantum mechanics. In the 20th century, physics has made two major contributions to chemistry—quantum mechanics and statistical mechanics. Historians of the physical sciences have often seemed to assume that quantum mechanics had an immediate impact in chemistry and that it was the one really important development in the discipline in the 1920s and 1930s. Statistical mechanics has received a great deal less attention from scientists and historians.

When the stationary-state hypothesis and free-radical mechanisms,

along with vibrational energy transfer, are seen as an ongoing attempt to understand chemical reaction mechanisms via the approach of statistical mechanics, then Herzfeld's work has a coherence it might otherwise appear to lack. It was this consistent theme, coupled with Herzfeld's ability to talk with chemists on their own terms, that helped to make statistical mechanics an essential part of physical chemistry today.

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