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CHARLES AUGUST KRAUS

1875—1967

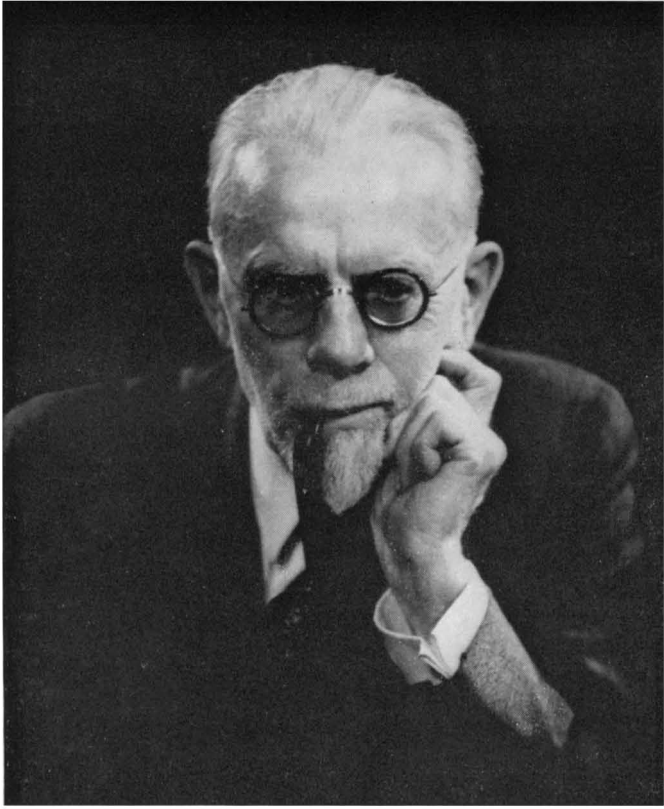
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*A Biographical Memoir by*  
RAYMOND M. FUOSS

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*Biographical Memoir*

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*Charles K. Williams.*

# CHARLES AUGUST KRAUS

*August 15, 1875–June 27, 1967*

BY RAYMOND M. FUOSS

ON APRIL 24, 1857, the *Mississippi* arrived at New York, after a 55-day voyage from Amsterdam. One of the passengers, Johann Heinrich Kraus, was then a boy of seventeen. He, his mother, and his sister were emigrating from Traubach in the Rhineland, because 1856 had been a poor wine year. They had sold their vineyard and put part of the proceeds into transatlantic fares. They went first to Scranton, Pennsylvania, where an uncle was living. Later, John Henry moved further west, to Knightsville, Indiana, a small coal mining town, and started farming nearby. He married Elizabeth Schaefer; on August 15, 1875, their son Charles August Kraus was born.

The early education of young Charles August was in a one-room country schoolhouse, about a mile from the farm; he once said that the school term varied from year to year, ranging from three to eight months, depending on weather, crops, and availability of teachers. By 1890, Kraus was ready to enter high school; the nearest was at Hayes City, about four miles distant. He did the commuting on horseback. In later reminiscences, he credited L. H. Gehman, the principal of the high school, and a graduate of Gettysburg College, for arousing his interest in science in general and in electrical phenomena in particular. He graduated from Hayes City High School in 1893, and decided to go to the University of Kansas to study electrical

engineering. He could meet all the entrance requirements except the one calling for knowledge of French; he was fluent in German, but that was no help in satisfying a French requirement. He studied French during the summer of 1893, and as he put it, "managed to gain admission to the course in scientific French," which he passed "in creditable fashion," after being admitted to the University of Kansas in the fall of 1893.

At the University of Kansas, he entered the course in electrical engineering, which was headed by Lucian Ira Blake, who had received his doctorate in physics at the University of Berlin while Helmholtz, Kirchhoff, and Hertz were there. Probably Blake encouraged Kraus toward fundamental rather than applied science; in any case, Kraus wrote the following about his Kansas years in a brief autobiographical sketch (which unfortunately was never completed): "I became more interested in physics than in engineering, and by the beginning of the Junior year, was spending more time reading literature relating to physics than to engineering. I was familiarizing myself with the work of Van Ard, Crookes, and Hittorf, and, of course, with work on X-rays (discovered by Roentgen in 1895) and radioactivity, which came along a year later. I early became interested in the process whereby electricity was conducted through metals. At that time, little was known about it; the concept of electrons was just in the stage of being developed. Drude, in fact, wrote a book on metallic conductance in which he accounted for a good many properties of metals on the assumption that electrons were small, gas-like particles. The most significant result was the relation between electrical and thermal conductivity. In the spring of 1897, H. P. Cady, then a senior in chemistry in the University, published a paper (*J. Phys. Chem.*, 1:707 [1897]) in which he presented the first measurements on the conductance of electrolytes in liquid ammonia. Among other substances whose conductances he measured was metallic sodium. While the measurements were

rough, they clearly showed that solutions of sodium were much better conductors than solutions of salts. Another most important observation was that the passage of current from solution to electrode is reversible. This paper was published in the spring of 1897; when I ran across it, I understood that light might be thrown on the conductance process of electrons through metal by a study of metals in liquid ammonia."

Here was the beginning of Kraus as a physical chemist. The record shows that his formal training in chemistry totaled one year of general chemistry and about a week of qualitative analysis. But as time went on, he became one of the outstanding figures in all of chemistry: his work on the reactions of compounds of carbon in liquid ammonia and the synthesis and properties of many metallo-organic compounds places him among the organic chemists; the researches on intermetallic compounds, on the oxides of sodium and potassium, on glasses, on the extraction of gallium and germanium from their ores, puts him among the inorganic chemists; when, as usually was the case, a method for analyzing one of his new compounds was not available, he designed one, thereby contributing to analytical chemistry. Researches on the properties of solutions, especially their conductance in a wide variety of solvents ranging from hydrocarbons to highly polar solvents, contributed to physical chemistry over a period of nearly seventy years. His field of research interest and activity was without question far broader than that of any of his contemporaries, embracing as it did the whole scope of chemistry.

Before leaving physics for chemistry, Kraus began research in spectroscopy as a college junior, with two instructors in the physics department at Kansas. Zeeman had reported in the March 1897 issue of *Philosophical Magazine* that the sodium lines from a source in a magnetic field were "broadened" (later work, of course, showed that they were split; Zeeman received the Nobel Prize in 1902 for this work). Zeeman had

used a concave grating to observe the effect of the field on the spectral lines. About ten years before, Michelson at Case Institute had invented the interferometer. The Kansas physicists saw in the interferometer a more precise tool for studying intensities, and applied it to the magnetic effect with immediate success. Their paper in the *American Journal of Science*, dated April 15, 1897, showed that the percentage broadening was directly proportional to the field strength, as predicted by Lorentz from electromagnetic theory. Soon thereafter, the concept of electrons appeared. This early familiarity with subatomic phenomena was certainly the foundation of Kraus's later recognition of the solvated electron as the charge carrier in solutions of the alkali metals in liquid ammonia.

As Kraus recounted the story, it was Cady's work on solutions in liquid ammonia that catalyzed the transition of Kraus from physicist to chemist. The history of the work on ammonia is intrinsically interesting, and relevant to the subsequent development of the field by Kraus. In an address given by Cady before the Division of Physical and Inorganic Chemistry on April 15, 1936, at a meeting of the American Chemical Society at Kansas City, Cady said that "Professor Ira Remsen of Johns Hopkins started the work, though he never knew it." This start was a statement by Remsen in his *Inorganic Chemistry* that "ammonia forms many compounds with salts corresponding closely to those of water with the same salts." To continue quoting from Cady's address: "When I came to the University of Kansas in '94, I read everything available on water of crystallization and ammonia and its compounds, with special attention to liquid ammonia and the ammonia of crystallization. I made many of the compounds just to see what they looked like. The great similarity in every way of water and ammonia impressed itself more and more strongly upon me. I finally laid my information before Franklin with a suggestion that liquid ammonia might reasonably be expected to be an

ionizing solvent. Franklin was instantly all enthusiasm. He persuaded Professor Bailey to invest a large part of the merger fund available to the chemistry department for research, in a cylinder of liquid ammonia. He made me some vacuum jacketed test tubes. There were no vacuum jacketed vessels on the market anywhere in the world in those days. Most unfortunately for me, Franklin was under contract to go to Central America for a gold mining company and left before the ammonia arrived. It was a heart-trying moment when I drew out some liquid ammonia into one of the vacuum tubes and tested it to see if it was a conductor of electricity. Finding the resistance to be very high, as I expected, I then dropped in a piece of potassium iodide, which Gore had shown to be soluble. I shall never again experience a thrill equal to that which I felt when the solution became a good conductor and electrolysis took place!"

On Franklin's return to Kansas, he and Kraus continued the work started there by Cady, who moved to Cornell to study phase rule problems with Bancroft. The first of a series of papers by Franklin and Kraus was entitled "Liquid Ammonia as a Solvent"; it appeared in 1898 in the *American Chemical Journal*, the immediate ancestor of the *Journal of the American Chemical Society*. In this paper they give the earlier history of ammonia solutions, tracing it back to Faraday, who had prepared liquid ammonia by heating dry "ammoniochloride of calcium" in one leg of a U-tube, condensing the ammonia by its own pressure, and simultaneous refrigeration of the other leg, onto a substance whose solubility was to be investigated. Gore, using this method, reported solubilities of some 350 compounds in 1872. Weyl (1863) and Seeley (1871) described the blue solutions formed by sodium and potassium in ammonia. Joannis (1890) began the study of chemical reactions in ammonia. A second paper with Franklin on the "Determination of the Molecular Rise in the Boiling Point of Liquid Ammonia" also came out in 1898, the year Kraus re-

ceived the degree of Bachelor of Science (Engineering) from the University of Kansas.

Kraus stayed at Kansas for a year's postgraduate work with Franklin, which culminated in a 36-page paper presenting conductance data for 25 compounds in liquid ammonia, covering a wide range of concentration. This was the first really broad survey of the field, and also represents a masterpiece of laboratory technique. All the intricate glassware required for quantitative manipulation of solutions at  $-33^{\circ}$  in a closed system had to be made by hand from soda glass. (Kraus liked to tell his students in later days how he used to make Dewar flasks by sealing together two oil-lamp chimneys, and deplored the invention of Pyrex as the ruination of the art of glass blowing.) The work on conductance in liquid ammonia was continued for a year at Johns Hopkins (1899-1900), after which Kraus returned to Kansas for another year. He then moved to California, formally as instructor in physics, but the research papers published by Kraus during that period were also on liquid ammonia. One was a continuation of the work on conductance; 37 more compounds were studied. In addition to metallic salts, groups of organic compounds were investigated. It was found that many amides and nitrocompounds, insulators in the pure form, become electrolytic conductors in solution in liquid ammonia. This was pioneer work on general acid-base systems, antedating by many years the "modern" theory of acids and bases. The experimental results showed that the amides and nitrocompounds generated electrolyte when dissolved in ammonia; the latter acted as a base with respect to the solutes to produce salts. Many of these were as good conductors as ordinary salts such as sodium chloride. The parallel between aqueous and ammoniacal systems was clearly shown: the amide and ammonium ions in ammonia are the analogs of the hydroxyl and hydronium ions in water. During the California stay, pioneering work on conductance near the criti-



cal point in methanol and ethanol was also done. The significant finding was that the conductance showed no discontinuity at the critical point; furthermore, the vapor phase is also an electrolytic conductor.

About the turn of the century, A. A. Noyes founded the first school of physical chemistry in the United States at the Massachusetts Institute of Technology. Kraus joined the group as research assistant in 1904. His all-absorbing interest was research; at the insistence of Noyes, however, he took enough time off from research to pass the formal requirements for the degree of Doctor of Philosophy in 1908. He was then promoted to research associate and in 1912 to assistant professor of physical chemistry. The years at M.I.T. (1904-1914) were highly productive: the series of papers on the properties of solutions of metals in ammonia and in several amines are classical. The first paper, published in 1907 in the *Journal of the American Chemical Society*, is Contribution No. 18 from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. At that time, it was known that sodium and potassium form blue solutions in ammonia, and that lithium and cesium dissolve in methylamine, but little quantitative information was available. Kraus determined the phase diagram for the sodium-ammonia system and defined the ranges of Na-NH<sub>3</sub> ratios where the two liquid phases were in equilibrium: a heavier, more dilute blue solution, and a lighter, concentrated solution, "presenting a characteristic bronze colored metallic appearance." The rate of reaction of sodium with ammonia to form sodamide was determined and the catalytic effect of solid amide was observed. The first clearly defined intermetallic compound, NaPb<sub>2</sub>, was formed in liquid ammonia; electrolysis experiments showed that the lead was in the anion. Tin also was found to form a sodium compound which gave a red solution. In the second paper, it was shown that previously claimed solid compounds containing one atom of alkali metal

and one molecule of ammonia did not exist; calcium, however, forms a hexammoniate which is a metallic conductor. Next, the vapor pressures of solutions of sodium in liquid ammonia were determined; in dilute solution, the molecular weight was found to approach the theoretical value of 23 for sodium, while at higher concentrations the pressure changes were considerably less than predicted by Raoult's law.

Papers IV and V, in 1908 and 1914, of the series "Solutions of Metals in Non-metallic Solvents," give the essential part of the explanation of the behavior of the metal-ammonia systems. For sodium solutions, for example, it was shown that the cation was the same sodium ion which was present in ammonia solutions of salts such as sodium chloride. The anion, however, was something quite new to solution chemistry. Kraus showed that it was "an electron, surrounded by an envelope of solvent molecules." The blue color of the solutions was due to the presence of solvated electrons, which are common to all metallic solutions. The identity of the anion with the electron also explained the perfect reversibility of electrodes in sodium-ammonia solutions: the negative carrier can pass into and out of solution without observable material effects at the interface between solution and insoluble electrodes such as platinum. The continuous transition from electrolytic to metallic conductor could be demonstrated by observations on these solutions. In order to determine the relative speeds of cation and solvated electron, the method of electromotive force of concentration cells was used, first because the Hittorf method could not be applied conveniently to metal-ammonia solutions, and second, because here was a system with perfectly reversible electrodes. These experiments showed that in dilute solutions the solvated electron behaved very much like a conventional anion, albeit a rather speedy one, while at higher concentrations "the negative electrons are free from the ammonia envelope for a fraction of the time, and then move with

a speed comparable with that of the negative electrons in metals." This was the first demonstrated tunnel effect in liquids, about twenty years before the advent of wave mechanics.

A real tour de force of the M.I.T. days was the determination of the potential of the normal sodium electrode against the standard calomel electrode. G. N. Lewis was collecting the standard potentials of the metals as fundamental thermodynamic information concerning reactions; the alkali metals presented a seemingly impossible problem, because they react violently with water. Kraus solved the problem by a two-step process: he determined the potential of a 0.206 percent sodium amalgam against normal sodium ion in water as 2.1525 volts, and then determined the potential of the same amalgam against pure sodium in ethylamine as 0.8456 volt. The sum, 2.9981 volts, gave the desired standard potential of sodium. The design of the experiment and of the apparatus for performing it is characteristic of all of Kraus's researches.

It was also during the M.I.T. period that Kraus first became interested in the general problem of electrolytic behavior. In collaboration with W. C. Bray, conductance data for a wide variety of electrolytes in ammonia, sulfur dioxide, the hydrogen halides, and in many other inorganic and organic solvents were critically reviewed, and analyzed on the basis of the mass action equation. The classical Arrhenius form of the equation was modified empirically to give a form which served to reproduce experimental results by the use of two more parameters. The paper concludes with the prophetic comment: "An explanation of the observed deviations from the mass-action law is to be looked for in the interacting forces due to the presence of charged particles (ions) throughout the body of the solution." Here, in 1912, was a qualitative anticipation of the interionic force theory of Debye and Hückel in 1923.

Preliminary work in another field, which was later to become a major activity for Kraus, also began at M.I.T.: the

synthesis, structure, and properties of metallo-organic compounds, in which metallic atoms are covalently bonded to carbon. The alkyl mercury halides were found to be soluble in liquid ammonia. On electrolysis, the deposit at the cathode was shown to be  $\text{HgCH}_3$ , a completely new type of chemical compound: although it contained a methyl group, its properties were those of a metal!

After ten years at the Massachusetts Institute of Technology, Kraus was invited to Clark University as Professor of Chemistry and Director of the Chemical Laboratory in 1914. Until then, Kraus had had only three collaborators: E. C. Franklin at Kansas, and G. N. Lewis and W. C. Bray at M.I.T. The bulk of his research had been planned by himself, and he did the experimental work himself, with no research assistants or graduate students. During the sixteen years since his graduation as an engineer from the University of Kansas in 1898, Kraus had nevertheless established himself as the outstanding authority on the physical properties of solutions in liquid ammonia, and had already begun pioneering work on chemical reactions in ammonia, especially those involving metal-metal and metal-carbon bonds. At Clark, Kraus began to build a graduate department of chemistry. Progress was slow initially, partly as a consequence of World War I, during which Kraus was an active consultant to the U.S. Chemical Warfare Service and to the U.S. Bureau of Mines. This involved direction and advice on research at the federal laboratories as well as diversion of graduate student work to research applied to war-generated problems. (This pattern, incidentally, was to be repeated again several decades later.) Also graduate work in chemistry at Clark was essentially a new venture; it took time for chemistry students graduating from other colleges to realize that at Clark there was developing a school of research in the broad field of general chemistry, combining in each graduate research project physical chemistry with reaction chemistry in non-aqueous sol-

vents. Kraus gradually built up a group of about a dozen graduate students, large enough to be highly productive and small enough for each member to get the benefit of "the King's" advice and direction daily. The students learned how to plan an experimental approach to a problem, and to design and build apparatus for their experiments. This close contact with his students which began at Clark was maintained throughout Kraus's entire career. A student who did his dissertation research with Kraus graduated as much more than one who had fulfilled the formal requirements for the degree of Ph.D. in Chemistry: he was one who had learned research thinking.

The publication record tells the story: only three papers between 1914 and 1921, one on the design of a mercury vapor pump which required only a water-jet as backing pump, and two on the extrapolation of conductance data. But in the next few years, about thirty papers appeared: some continuing the investigation of solutions of metals in ammonia, some on the chemistry of reactions in ammonia, and others in which the scope of the work on conductance was broadened to include aqueous solutions and a variety of organic solvents. In all, fourteen graduate students are named as co-authors in this series of papers from Clark, and this does not complete the roster of the Clark students, because about a dozen moved with Kraus to Brown in 1924, to complete their dissertation researches there.

The fifth paper on "Solutions of Metals in Non-metallic Solvents" had appeared in 1914, as one of the last of the M.I.T. papers. After arriving at Clark, Kraus continued experimental work on his own; the sixth paper of the series was published in 1921. By comparing the conductance of lithium, sodium, and potassium in liquid ammonia, it became clear that the negatively charged carrier was the same for all three metals. The minimum in equivalent conductance around 0.05 normal marks the transition from electrolytic conductance where the current is carried by metallic cations and by sol-

vated electrons, to metallic conductance where, with increasing concentration of metal, relatively more and more current is carried by the negative carrier which in the more concentrated solutions moves essentially like the free electron in metals. A saturated solution of sodium in ammonia has about half the specific conductivity of mercury at 0°. The conductance of concentrated solutions (from concentrations below that corresponding to the minimum in conductance to saturation) of sodium and potassium was determined by W. W. Lucasse. The temperature coefficients confirmed the transition from electrolytic to electronic conduction, as the concentration passed through the range at the conductance minimum: at dilutions greater than about four liters per atom, the coefficient was about 1.55 percent; with increasing concentration, it goes through a maximum of 3.6 percent at one liter per atom, and then rapidly drops to about 0.07 percent near saturation. The phase diagram for the sodium-ammonia system was determined very precisely. Later, it was found that the temperature coefficient of potassium solutions in liquid ammonia, on the high concentration side of the minimum, was quite similar to that for sodium, an observation which was again confirmation of the hypothesis that the electron was the primary current carrier in the metal-ammonia solutions.

All of the work on the physical chemistry of solutions of the alkali metals in liquid ammonia was to have important consequences for reaction chemistry. The physical work had clearly demonstrated the presence of electrons in these solutions. Now electrons are obviously the most potent reducing substance which can exist, and in liquid ammonia, one has a medium in which the dissolved electrons are stable. (In the presence of certain solid catalytic surfaces, electrons will react slowly with ammonia to form gaseous hydrogen and the amide ion. This reaction is, of course, the analog of the reaction between electrons and water to form hydrogen and hydroxide

ion; the latter is, however, by many orders of magnitude, a much faster reaction.) With George F. White, professor of organic chemistry at Clark, a preliminary study of reduction in ammonia solutions was made. This was a most fruitful research, and represented the beginning of a long series of subsequent chemical investigations. The general pattern of the reactions was an initial step, in which the electronegative constituent or group of an organic compound reacted with the electron to produce the corresponding anion; the residue of the reacting molecule was left as a free radical. Further steps of the reaction then depended on the reactivity and stability of the free radical. For example, triphenylchloromethane reacts first to give chloride ion and triphenylmethyl. The free radical then adds an electron, to give the triphenylmethide ion, so the over-all stoichiometric reaction is  $2\text{Na} + \text{Ph}_3\text{CCl} \rightarrow \text{NaCl} + \text{NaCPh}_3$ . The actual reaction comprises two steps:  $e^- + \text{Ph}_3\text{CCl} \rightarrow \text{Ph}_3\text{C} \cdot + \text{Cl}^-$ ;  $\text{Ph}_3\text{C} \cdot + e^- \rightarrow \text{Ph}_3\text{C}^-$ . The sodium cation takes no part in the reaction. On the other hand, if the electronegative group is accompanied by a group which gives a very reactive radical, ammonolysis occurs. So, for example, propyl iodide gives iodide ion and propyl radical; the latter does not accept an electron to form a propide ion but reacts with solvent ammonia to give propyl amine and propane.

Kraus's earlier interest in intermetallic compounds and organo-metallic compounds continued at Clark. The former included compounds of sodium with tellurium, antimony, and lead; again, liquid ammonia proved to be the unique solvent in which these materials could be prepared and characterized. Vapor pressure measurements showed that Raoult's law was very nearly followed by sodium-tellurium complexes in ammonia, and that two atoms of sodium are present for each complex telluride in solution; the conclusion was that the latter carried two negative charges. The polytellurides thus turned out to be the predictable analogs of the polysulfides previously

known in aqueous systems as polyatomic clusters of fixed valence. At the same time, research began on compounds in which the anion was a metal covalently bonded to carbon, with tin as the first metal to be studied. Trimethylstannane was one of the first of a series of substituted metallic hydrides to be prepared. Sodium in ammonia reacts with trimethylchlorostannane to give the salt sodium trimethylstannide; this in turn reacts with ammonium chloride, the ammonia analog of hydrochloric acid in water, to generate  $\text{Me}_3\text{SnH}$ , plus sodium chloride and ammonia. This parallel, exemplified by the following equations, served as the guiding principle for much of the metallo-organic chemistry developed by Kraus:  $\text{Me}_3\text{Sn}^- + \text{NH}_4^+ \rightarrow \text{Me}_3\text{SnH} + \text{NH}_3$ ;  $\text{X}^- + \text{H}_3\text{O}^+ \rightarrow \text{XH} + \text{H}_2\text{O}$  where  $\text{X}^-$  is a strongly basic anion such as acetate or methoxide. It was shown that trimethylstannyl chloride was practically a nonconductor in the pure state, or in aprotic solvents such as ethers or nitrocompounds; in basic solvents, such as alcohols or amines, however, its conductance resembled that of the hydrogen halides in these solvents. These results suggested that solvolysis produced the conducting species.

The experience in metallo-organic chemistry led to a most important technological development, the practical synthesis of tetraethyl lead. At the end of an exhaustive systematic search, the Kittering-Midgley research team in 1921 reached this compound as the theoretically ideal antiknock agent for gasoline. But  $\text{PbEt}_4$  was at best a laboratory curiosity: it could be made by the Grignard reaction from lead tetrachloride (which is also a rare specimen) or by reaction between sodium-lead alloy and ethyl iodide, but iodides were too expensive to be considered as raw materials for a gasoline additive. Midgley found that ethyl bromide could replace ethyl iodide, at the price of slower reaction rate, lower yield, and enhanced corrosion problems. Kraus was called in as a consultant in 1922. Knowing that tin and lead are similar in many



ways, and with his broad background of knowledge in the chemistry of tin compounds, Kraus started a group at Clark (Callis, Rosen, and Greer) on a summer research project aimed at an economical synthesis of tetraethyl lead, starting with the relatively inexpensive ethyl chloride as the source of ethyl groups. They discovered that ethyl chloride would react with sodium-lead alloys, and that one alloy in particular, the one which had the equi-atomic composition NaPb, would give very high yields of the desired antiknock agent in a rapid and controllable reaction. This discovery led to the formation of the Ethyl Corporation in 1924 to produce lead tetraethyl in commercial quantities.

As already mentioned, Kraus continued work on conductance of metals in liquid ammonia at Clark. It was during this period that he extended his interest to a wider variety of electrolytic systems. Prompted by the desire to attain high precision in the measurement of electrolytic conductance, he re-examined the fundamental standards, with the result that a discrepancy of nearly half a percent between the relative conductances of 0.1 and 0.01 normal potassium chloride solutions in water, the classical (1898) standards of Kohlrausch, was discovered. This led to a quantitatively precise evaluation of the conductance of standard solutions of potassium chloride, and to the establishment of the Kraus and Parker calibration solutions. These standards were internationally accepted, and remained in general use by research workers for well over a decade, until the introduction of the Jones and Bradshaw demal solutions in 1934. The latter were no more precisely defined than the standard solutions of Kraus and Parker, but had the advantage of being defined in terms of concentration units which, unlike normalities (moles per liter of solution), were independent of temperature. Then, using their standards, Kraus and Parker determined the conductance of iodic acid in water down to a concentration of  $5 \times 10^{-5}$  normal, using a

quartz cell, and water purified to a conductance as low as  $0.1 \times 10^{-6}$ . The work gave a most precise value for the limiting conductance of the hydrogen ion; the value was slightly revised later, after the Debye-Hückel-Onsager and Bjerrum-Fuoss-Kraus theories suggested a somewhat different method of extrapolating to infinite dilution.

A beginning of the later very broad program of investigation of electrolytic conductance was made at Clark, starting with solutions in propanol, amyl alcohol, and phenol. These are all solvents of lower dielectric constant than water. Salts such as iodides, which are normal "strong" electrolytes in water, were found to behave like weak electrolytes in these solvents. Specific differences appeared between salts which gave similar behavior in water: for example, sodium iodide was a much weaker electrolyte in phenol than tetramethylammonium iodide. A minimum in equivalent conductance for  $\text{Me}_4\text{NI}$  in phenol around 0.03 normal was also observed. This early work showed the existence of a whole new field of electrochemical research, that of the specific interactions between ions and ions, and between ions and solvent molecules; this field was to be extensively and intensively worked in the later years at Brown. Another interesting system was explored in a preliminary way at Clark: ordinary soda-lime glass was found to be an electrolytic conductor at temperatures above about  $270^\circ$ . The current was carried mostly by the sodium ions, which could be replaced by other ions such as lithium or silver by electrolysis from amalgams or molten salts.

Based on his many researches on conductance, and his comprehensive knowledge of the literature on the subject, Kraus wrote in 1922 the American Chemical Society Monograph entitled *The Properties of Electrically Conducting Systems*. Modern theory has changed the interpretation of conductance data since 1922 and many more systems have been studied since Kraus wrote the monograph, but even so, it re-

mains the most comprehensive work available on the subject. And it should be added that many of the subsequent advances and expansions in the field of electrolytic conductance originated in the laboratories of Kraus and of his students. Recognition was given Kraus for his outstanding work in non-aqueous solutions by the New York Section of the American Chemical Society with the award of the Nichols Medal in 1923.

The following year (1924), Kraus was invited to Brown University as Professor of Chemistry and Director of Chemical Research. He was to remain at Brown for many years: he became Emeritus Professor in 1946 at the age of seventy-one, but continued active direction of research until his middle eighties, when failing vision began to confine him to his home. His research activity started in the Newport Rogers Laboratory, the second floor of a wood and brick building on the Brown campus. This served for thirteen years; in 1938 the research group moved to the then new Metcalf Research Laboratory, which in layout and in many functional details was designed by Kraus. Research at Newport Rogers and at Metcalf was concentrated in the three fields in which Kraus had previously done pioneer work at Massachusetts Institute of Technology and at Clark: physical chemistry of liquid ammonia systems, the chemistry of metallo-organic compounds (especially those containing silicon, germanium, tin, boron, aluminum, and gallium), and conductance in non-aqueous solvents.

The liquid ammonia work included further studies on metal-ammonia systems, and the conductance of a variety of salts which could only exist in ammonia. They included the amides of sodium and potassium, sodium salts of the pattern  $\text{NaMPh}_3$  where M is carbon, tin and germanium, sodium trimethylstannide, salts of phenols and thiophenols, and metal ketyls. All of these react violently with air or water, so it was necessary to design apparatus and techniques by which quanti-

tative measurements of high precision could be made in completely closed systems. Thermochemistry in liquid ammonia called for the design of a precision calorimeter which would function at  $-33^{\circ}$ ; this was achieved by measuring quantitatively the amount of ammonia evaporated by exothermic reactions occurring at the boiling point of ammonia. It was found that the heats of solution of inorganic salts were in general positive, while that of metallic sodium was negative. Heats accompanying a variety of reactions were determined, including some of those involving intermetallic compounds. Precision in conductance equaling that obtained in aqueous solutions was achieved by Hnizda (1949), who measured four alkali halides over a wide range of concentration.

The chemistry of compounds in which a bond is formed between carbon and a metallic atom is an especially interesting field. Kraus contributed about forty research publications to the subject after coming to Brown. Silicon, germanium, tin, and lead are all analogs of carbon, in that they are tetravalent. The series carbon to lead represents a transition from nonmetal to metal. Germanium, halfway through the series, was investigated in depth. It had been a relatively rare element until Kraus devised a method for extracting it from an ore (germanite) discovered in Tsumeb, South West Africa, by Schneiderhöhn in 1920. The method depended on the reduction of germanic sulfide to germanous sulfide by ammonia at  $825^{\circ}$ , and sublimation of the latter. This dry process gave almost quantitative recovery, and was far superior to the previous methods based on solvent extraction. With an adequate supply of starting material thereby made available, a wide variety of alkyl and aryl derivatives of germanium were made. Germanium was found to form a normal hydride  $\text{GeH}_4$ , which gives a sodium salt in liquid ammonia; that salt slowly decomposes to produce sodium germanide,  $\text{NaGe}$ . This, in turn, reacts with ammonium bromide to form a polymeric material in which the ratio of

germanium to hydrogen is one-to-one. The ore from which the germanium was obtained also contains appreciable quantities of another rare element, gallium, which is the next higher analog of boron and aluminum. A method of extracting gallium from the ore residue after recovery of the germanium was developed, and the product was used as the starting material for an extensive study of the compounds of gallium. Metallo-organic compounds of aluminum and tin were also investigated: the alkylaluminum halides later found application in combination with titanium chloride as initiators for ethylene polymerization. Kraus showed that carbon was not unique in its ability to form chains by the synthesis of a compound in which five tin atoms were linked together. Much of our knowledge of the elements of the third and fourth groups of the periodic table had its origin in Kraus's laboratory at Brown. Summaries of this work were published in 1927 and 1928 in Volumes I and II of *Survey of American Chemistry*.

The third major research field was the properties of electrolytic solutions (especially their conductance) in non-aqueous solvents; over seventy papers on this subject were presented. In fact, from the early 1930s, electrolytes became more and more the dominant theme of the researches directed by Kraus. He had pointed out quite early the fact that the traditional physical chemistry of solutions was largely based on observations on solutions in water, which in many ways is an exceptional solvent. Kraus correctly insisted that a general theory of electrolytes must be based on information on a wide variety of solvents, ranging from non-polar to polar, and including aprotic as well as hydrogen bonding solvents. Prior to his sojourn at Brown, he had investigated conductance in liquid ammonia and several of the alcohols. The attack on the general problem began in 1930 with a study by Fuoss of mixtures of dioxane and water, and of benzene and ethylene dichloride. With the first mixtures, the range of dielectric constants from about 80

down to 2.2 in protoic solvents is accessible, and with the second, the range from 10.2 to 2.3 can be covered in media which contain no bonding hydrogen atoms. The fundamental significance of dielectric constant was quantitatively demonstrated, and the primary control of ion pair formation through dielectric constant was established. By combining the Debye-Hückel theory of long-range ionic interaction with the Bjerrum hypothesis of ion pair formation, Fuoss and Kraus presented the first general and comprehensive treatment of electrolytic solutions. This theory, modified and improved as time went on, was the guiding principle for a long series of conductance studies, in which molecular structure of solute and solvent was correlated with the macroscopically observed properties of the solutions. The formation of triple ion clusters was shown to be the cause of the minima observed in conductance curves; dependence of the location of the minima on dielectric constant was theoretically established. Quadrupole clusters were shown to exist by precise measurements of freezing points in benzene and in dioxane. Direct physical evidence for the existence of stable ion pairs was given by dielectric constant measurements in benzene solutions of quaternary salts: dipole moments of the order of 15-25 Debyes were observed. Solvents used in the conductance work included dioxane, benzene, ethylene chloride, ethylene bromide, anisol, nitrobenzene, pyridine, acetone, methyl bromide, methylene chloride, and bromine. The problem of determining single ion conductances in non-aqueous solvents was solved by Fowler and Kraus by the synthesis of tetrabutylammonium triphenylborofluoride. The ions of this salt have practically equal volumes, and therefore the single ion conductance of each is given by half the limiting conductance of the salt. Given the conductance of one anion (or cation), the conductances of other single ions are of course determined by Kohlrausch's law of independent mobilities at infinite dilution. Among the most important of Kraus's publi-

cations on electrolytes are the reviews which he wrote at about five-year intervals; these served as supplements which kept the 1922 monograph on conductance up to date.

Kraus's eminence in research was recognized by a number of awards, beginning with the Nichols Medal in 1923. In 1935 he received the Willard Gibbs Medal, with the citation: "Substituting ammonia for the common solvent water, Dr. Kraus has been able to arrive at conclusions which have added immensely to a better understanding of the behavior of chemical substances in any solutions." The Theodore William Richards Medal was awarded in 1936, "for conspicuous achievements in the chemistry of liquid ammonia and electrolytes." In 1938 he received the Franklin Medal, which is "awarded annually to those workers in physical science or technology, without regard to country, whose efforts have done most to advance a knowledge of physical science or its applications." The citation read: "To Dr. Kraus, in recognition of his numerous researches in chemistry and electrochemistry, particularly his valuable contributions to the knowledge of reactions in liquid ammonia, of the chemical behavior of metals, and of the properties of electrolytic solutions." He was President of the American Chemical Society in 1939. The Naval Distinguished Public Service Award, the Navy's highest civilian award, was given to Kraus in 1948 for direction of naval research at the Metcalf Laboratory during the war. The American Chemical Society honored Kraus in 1950 with its most outstanding mark of recognition, the Priestley Medal. Honorary doctorates were conferred by Brown University, Clark University, Kalamazoo College, Colgate University, and Indiana University.

Kraus was a member of many professional and honorary societies. These included the National Academy of Sciences, American Academy of Sciences, American Philosophical Society, American Chemical Society, American Physical Society, American Association of University Professors, American

Association for the Advancement of Science, Faraday Society, Washington Academy of Sciences, Phi Beta Kappa, Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma. He was an Honorary Fellow of the Franklin Institute.

Kraus was elected to membership in the National Academy of Sciences in 1925. He was a member of the Council of the Academy for 1939-1942, a member of the Executive Committee of the Council of the Academy during 1940-1942, chairman of the Section of Chemistry for 1935-1938, and a member of the Board of Directors of the Wolcott Gibbs Fund for 1938-1960. He was chairman of the Division of Chemistry and Chemical Technology of the National Research Council in 1932-1933 and Field Secretary of the Fellowship Board in Physics, Chemistry, and Mathematics of the National Research Council in 1934-1935.

Kraus died June 27, 1967, at Providence, Rhode Island. His wife, Frederica Feitshans Kraus, predeceased him in 1963. He is survived by three sons, C. Newton Kraus, Philip B. Kraus, and Douglas L. Kraus, one daughter, Mrs. H. K. Hartline, thirteen grandchildren, and several great-grandchildren.



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## KEY TO ABBREVIATIONS

- Am. Chem. J. = American Chemical Journal  
Chem. Eng. News = Chemical and Engineering News  
Chem. Rev. = Chemical Reviews  
J. Am. Chem. Soc. = Journal of the American Chemical Society  
J. Chem. Educ. = Journal of Chemical Education  
J. Chem. Phys. = Journal of Chemical Physics  
J. Franklin Inst. = Journal of the Franklin Institute  
J. Phys. Chem. = Journal of Physical Chemistry  
Phys. Rev. = Physical Review  
Proc. Nat. Acad. Sci. = Proceedings of the National Academy of Sciences  
Surv. Am. Chem. = Survey of American Chemistry  
Trans. Am. Electrochem. Soc. = Transactions of the American Electrochemical Society (later, Transactions of the Electrochemical Society)  
Trans. Faraday Soc. = Transactions of the Faraday Society

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